

Invited Lecture

## Transition Metal Cation Salts in Organic Synthesis

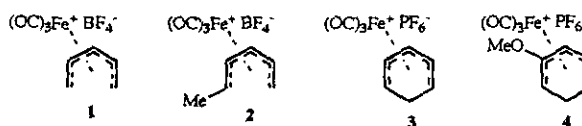
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Reaction of lithium diisopropylamide (LDA) with  $(\eta^4\text{-1,3-cyclohexadiene})\text{Fe}(\text{CO})_3$  complexes bearing functionalized side chains at C-5, under an atmosphere of carbon monoxide, gives bridged bicyclo[3.2.1]octene and bicyclo[3.3.1]nonene systems after electrophilic quenching. Under the same reaction conditions, intramolecular cyclization of acyclic  $(\eta^4\text{-1,3-butadiene})\text{Fe}(\text{CO})_3$  complexes with functionalized side chains at the terminal position of the diene ligands furnishes fused bicyclo[3.3.0]octanone and bicyclo[4.3.0]nonanone derivatives after acid quenching. The addition of a variety of the highly functionalized zinc-copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  to the  $(\eta^7\text{-cycloheptatrienyl})\text{Cr}(\text{CO})_3$  gives  $(\eta^6\text{-cyclohepta-1,3,5-triene})\text{Cr}(\text{CO})_3$  complexes with a functionalized side-chain at the C-7 position of the ring. Intramolecular cyclization of ester-substituted adducts using lithium diisopropylamide generates fused bicyclo[5.3.0]decane and bicyclo[5.4.0]undecane derivatives. The addition of a variety of the highly functionalized zinc-copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  to the  $(\eta^4\text{-cyclohexa-1,3-diene})\text{Mo}(\text{CO})_2(\text{Cp})$  at the terminus of the coordinated diene ligand gives  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2(\text{Cp})](\text{Cp} = \text{cyclopentadienyl})$  complexes with the functionalized side-chain at the C-4 position of the ring. Intramolecular cyclization of the  $(\pi\text{-allyl})\text{molybdenum}$  complex containing a pendant propanoic acid unit generates the  $\delta$ -lactone derivative.

## INTRODUCTION

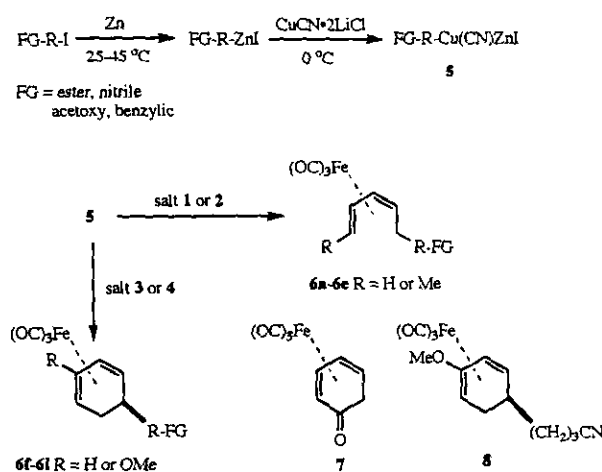
Transition metal cation salts are versatile organic substrates towards nucleophilic additions. Due to the highly electron-deficient character and the high stereo- and regio-chemical control, transition metal cations promoted carbon-carbon bonds formation has attracted much attention. Several transition metal cation salts are known to undergo nucleophilic attack and are used in the synthesis of complex molecules. These cations include  $(\eta^2\text{-alkene})\text{Fe}(\text{CO})_2\text{Cp}$  ( $\text{Cp} = \text{cyclopentadienyl}$ ),<sup>1</sup>  $(\eta^3\text{-allyl})\text{Fe}(\text{CO})_4$ ,<sup>2</sup>  $(\eta^4\text{-butadiene})\text{Mo}(\text{CO})_2\text{Cp}$ ,<sup>3</sup>  $(\eta^4\text{-cyclohexadiene})\text{Mo}(\text{CO})_2\text{Cp}$ ,<sup>4</sup>  $(\eta^5\text{-pentadienyl})\text{Fe}(\text{CO})_3$ ,<sup>5</sup>  $(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3$ ,<sup>4,6</sup>  $(\eta^6\text{-arene})\text{Mn}(\text{CO})_3$ ,<sup>7</sup> and  $(\eta^7\text{-cycloheptatrienyl})\text{Cr}(\text{CO})_3$  cation salts. Among  $\eta^5$ -metal cation species, cyclohexadienyl tricarbonyl cation salts, generating from hydride abstraction of neutral  $\eta^4$ -(cyclohexa-1,3-diene) $\text{Fe}(\text{CO})_3$  complexes with triphenylcarbenium hexafluorophosphate, have been most extensively studied and used in organic synthesis. Since substituted cyclohexadienes are readily available by Birch reduction of substituted aromatics, a variety of diene substrates is readily available. These cationic cyclohexadienyl complexes are general reactive toward a wide range of nucleophiles, including organolithium, -copper, -cadmium, and -zinc reagents, ketone enolates, nitroalkyl anions, amines, phthalimide, and even nucleophilic aromatic compounds such as indole and trimethoxybenzene.<sup>9</sup> Nucleophilic addition occurs exclusively from the face opposite the

metal carbonyl moieties, and exclusively at a terminal position of the dienyl ligand, regenerating an  $\eta^4$ -diene iron tricarbonyl complex. Decomplexation of neutral complexes by oxidation with amine oxides liberates the organic ligand. Manipulation of the organic substance to the synthesis of natural products has been extensively used by Pearson.<sup>10</sup> However, the sequential addition of nucleophiles to transition metal cation salts will be an excellent strategy for construction of cyclic products in highly diastereomeric fashion, if the initial nucleophile bears functional groups. A functional group on the side chain of a neutral  $\eta^4$ -diene iron tricarbonyl complex will allow intramolecular cyclization occur by simply treating the  $\eta^4$ -diene iron tricarbonyl complex with LDA (lithium diisopropylamide). Therefore, a molecule having two nucleophilic sites will be suitable for the sequential addition. Recently Knochel has found that polyfunctionalized zinc-copper reagents (also known as the Knochel reagents) can be generated by transmetalation of the corresponding functionalized zinc compounds with  $\text{CuCN}\cdot 2\text{LiCl}$  in THF.<sup>11</sup> Prior to our study, several classes of stabilized lithium nucleophiles such as enolates, as well as nonstabilized lithium, magnesium, cadmium, and zinc organometallics have been shown to add to the cations 1-4.



However, there are some disadvantages among these alkylating reagents. Reaction of the cation **1** with lithium reagents occurred at both C-2 and C-1 positions of the  $\pi$ -system, generating a mixture of  $\sigma, \eta^3$ -iron complexes and  $\eta^4$ -diene complexes.<sup>6a</sup> Reaction of the cation **2** with dimethyl sodiomalonate proceeded by attacking at both C-1 and C-5 termini (C-1/C-5 = 1/1.8) in only 51% yield.<sup>12</sup> Reaction of Grignard reagents with the cation **3** has been shown to lead by reductive coupling to the bis [5,5'-( $\eta^4$ -cyclohexa-1,3-diene)tricarbonyliron(0)] complex or to decomposition.<sup>6a</sup> Organo-cadmium and -zinc reagents (prepared in ether or THF by reaction of the appropriate Grignard reagents with cadmium and zinc chloride) reacted with cations **3** or **4** to give adducts only in satisfactory yields.<sup>6c</sup> Moreover, the alkylation is unsuccessful with dimethylzinc and dimethylcadmium. Surprisingly, the reports on the addition of organocuprates to cations **1-4** are rare.<sup>6d,n,o</sup> Furthermore, organocuprates obtained from the corresponding lithium reagents and copper salts do not bear functional groups. We now report the reaction of functionalized copper reagents with cations **1-4** (Scheme I).<sup>13</sup> The reactions are performed in the expectation that further manipulation of the molecules will then be possible after the initial additions.

Scheme I



Excess functionalized copper reagents (1.6 molar equiv) is added at 5 °C under nitrogen to a stirred suspension of the cations **1-4** in dry THF. The reaction mixture is stirred at 28 °C for 2 h. The yields of the addition are generally high (60-98%, Table 1) after chromatography on silica gel. The highly reactive benzylic copper reagent **5d** adds smoothly under our reaction conditions to give complexes **6d**, **6i**, and **6k** (see Entries 4, 9, and 11, Table 1) with higher yields than the benzylic zinc compound.<sup>14</sup> However, with the less reactive cation **4**,<sup>15</sup> the reaction became very slug-

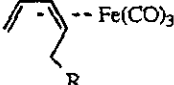
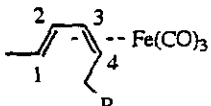
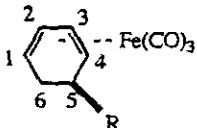
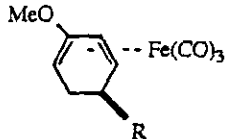
gish with copper reagents **5a** and **5b**. Addition of the copper reagent **5b** to the cation **4** did not give the desired adduct. Instead, ( $\eta^4$ -cyclohexa-2,4-dien-1-one)tricarbonyliron(0) complex **7** was isolated in 70% yield after hydrolysis of the reaction mixture.<sup>16</sup> While the addition of the copper reagent **5a** to the cation **4** gave the desired adduct **8** in only 45% yield together with a significant amount of complex **7**. The addition is highly regioselective (C-5 attack) with cations **2** and **4**. Normally less than 5% of C-1 adducts can be detected in the crude reaction mixture by 200 MHz <sup>1</sup>H NMR spectroscopy. The results are consistent with organocuprates attacking at less sterically hindered sites.<sup>6d,6n,6o</sup> The stereochemistry assignment for diene complexes **6a**, **6b**, **6c** (Z), and **6d**, **6e** (E,Z) is based on the coupling constants of the adjacent protons. For instance, the <sup>1</sup>H NMR spectroscopic data of complex **6e** exhibits a signal at  $\delta$  5.22 (dd,  $J = 5.0, 9.0$  Hz) for H-2 and a signal at  $\delta$  5.09 (dd,  $J = 5.0, 7.0$  Hz) for H-3 (see Entry 5, Table 1).<sup>6n</sup> The easy availability of the ( $\eta^4$ -1,3-diene)tricarbonyliron(0) derivative took 5 steps starting with dimethyl potassiummalonate and the cations in 29% overall yield.<sup>16</sup> While under our reaction conditions, complex **6g** is obtained in only one step and 78% yield.

### Intramolecular Nucleophile Additions

Our cyclization study began with complex **6h**. Treatment of **6h** with 1.5 molar equiv of LDA at -78 °C under nitrogen produced a major product in 50% yield, identified as bicyclo[3.3.1]nonenecarboxylic acid derivative **9** with an incorporated CO at the C-9 position. Thus, the addition was performed under an atmosphere of CO (14 psi), which increased the yield of cycloadduct **9** to 82% after purification by flash column chromatography and distillation under reduced pressure. It is important to note that three new stereogenic centers of compound **9** are created, however, only the single diastereomer shown was isolated.

NMR studies provided the initial evidence for support of the structural assignments. The <sup>1</sup>H NMR spectrum of compound **9** exhibited a broad singlet at  $\delta$  9.59 assigned to the formyl H at C-10; a doublet of triplets, centered at  $\delta$  5.94, assigned to the vinyl H at C-7; a broad doublet of doublets, centered at  $\delta$  5.67, assigned to the vinyl H at C-8; two narrow quartets, centered at  $\delta$  4.15, assigned to the two diastereotopic methylene protons at C-12; and a triplet, centered at  $\delta$  1.28, assigned to the methyl group at C-13. The <sup>13</sup>C NMR spectrum exhibited a signal at  $\delta$  203.3 assigned to C-10 (formyl), a signal at  $\delta$  173.8 assigned to C-11 (carbonyl of the ester functionality), and two signals at  $\delta$  133.1 and 124.5 assigned to two vinyl carbons (C-7 and C-8). Attempts to confirm the relative stereochemistry of bicyclo[3.3.1] compound **9** using NOESY (nuclear Overhauser

Table 1. ( $\eta^4$ -Diene)tricarbonyliron(0) Complexes (6a-6l) Obtained by the Functionalized Copper Reagents (5a-5d) to the Cationic Salts (1-4)

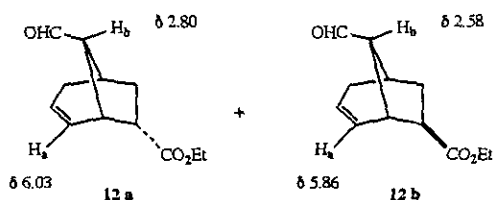
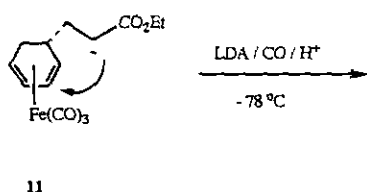
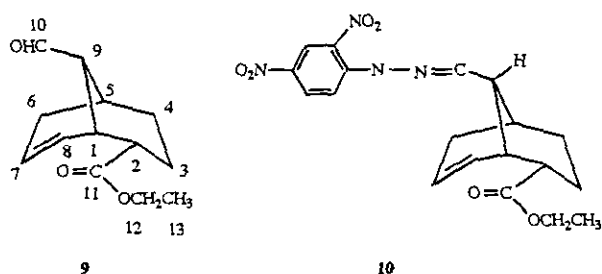
Entry	FG-RCu(CN)ZnI	Cationic Salt	Product	Yield(%) <sup>a</sup>
1	NC(CH <sub>2</sub> ) <sub>3</sub> Cu(CN)ZnI 5a	1		6a: R = NC(CH <sub>2</sub> ) <sub>3</sub> - 90
2	NC(CH <sub>2</sub> ) <sub>2</sub> Cu(CN)ZnI 5b	1	6b: R = NC(CH <sub>2</sub> ) <sub>2</sub> - 84	
3	EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> Cu(CN)ZnI 5c	1	6c: R = EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> - 97	
4	PhCH <sub>2</sub> Cu(CN)ZnBr 5d	2		6d: R = Ph <sub>2</sub> CH <sub>2</sub> - 96
5	5a	2	6e: R = NC(CH <sub>2</sub> ) <sub>3</sub> - 98	
6	5a	3		6f: R = NC(CH <sub>2</sub> ) <sub>3</sub> - 75
7	5b	3	6g: R = NC(CH <sub>2</sub> ) <sub>2</sub> - 78	
8	5c	3	6h: R = EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> - 83	
9	5d	3	6i: R = Ph <sub>2</sub> CH <sub>2</sub> - 81	
10	AcO(CH <sub>2</sub> ) <sub>4</sub> Cu(CN)ZnI 5e	3	6j: R = AcO(CH <sub>2</sub> ) <sub>4</sub> - 60	
11	5d	4		6k: R = Ph <sub>2</sub> CH <sub>2</sub> - 92
12	5c	4	6l: R = EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> - 76	

<sup>a</sup> All products described in this table are purified and exhibit spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, Mass) and analytical (HRMS) data consistent with the assigned structures.

enhancement spectroscopy) measurements were unsuccessful. Rigorous proof of the structure of **9** was finally accomplished by X-ray diffraction analysis of the (2,4-dinitrophenyl)hydrazone derivative **10**.<sup>17</sup> The X-ray diffraction analysis clearly shows that both bulky ester and hydrazone groups occupy equatorial positions on the six-membered ring.<sup>18</sup> Under the same reaction conditions, however, cyclization of the starting complex **11** gave a mixture of diastereomeric products **12a** and **12b** in a 2:1 ratio in 37% total yield.

The structures for **12a** and **12b** were established by comparison of their <sup>1</sup>H and <sup>13</sup>C NMR spectral data with the

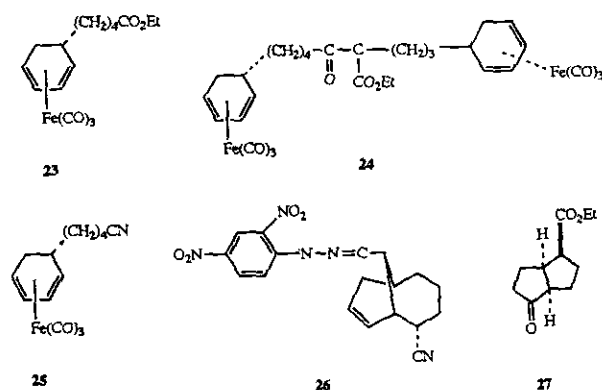
corresponding data of **9**. The stereochemistry assignment for **12a** as an endo isomer was based on the downfield shift of H<sub>a</sub> (δ 6.03), due to the deshielding effect of the carbonyl of the endo ester group, and the assignment for **12b** as the exo isomer was deduced from the upfield shift of H<sub>b</sub> (δ 2.58), owing to the shielding effect of the carbonyl of the exo ester group. The reason for the formation of two diastereomeric products of the bicyclo[3.2.1]octenecarboxylic acid derivatives **12a**, **12b** and a single isomer of the bicyclo[3.3.1]nonene carboxylic acid derivative **9** was not clear. It was suggested, that for complex **6h**, only one of the diastereotopic protons at the α-carbon of the ester group was re-



moved by LDA under the kinetically controlled reaction conditions. Thus, only one diastereomer was isolated. However, with only two carbon atoms on the side chain, for example complex **11**, deprotonation would be affected by both the ester group and the cyclohexadiene ring. Therefore, the selectivity for the removal of the diastereotopic protons at the  $\alpha$ -carbon was poor, and the cyclization gave both diastereomers. The same reaction mixture could be coupled with carbon electrophiles such as iodomethane or benzyl bromide to give methyl and benzyl ketone, respectively, in moderate yields.<sup>19</sup> Results of cycloaddition/quenching processes are summarized in Table 2.

Several entries in Table 2 deserve special mention. Intramolecular cyclization of **6f** produced a mixture of endo (**14a**) and exo (**14b**) isomers in a ratio of 1:2 (entry 4, Table 2). Unlike an ester group, a cyano group is rather small. Thus, either one of the two  $\alpha$ -protons is possibly removed by LDA. Furthermore, cycloaddition of the starting complexes with a methoxy group at C-2 of the diene ligand gave bicyclo[3.3.1]nonanone derivatives without incorporation of a carbon monoxide molecule (entries 10 and 11, Table 2). Nonetheless, the product distributions of the reactions were consistent with the previous results. Cyclization of complexes with three carbon atoms and an ester group on the side chain of the starting complex, for example, cyclization of complex **61**, gave only one isomer (**20**, entry 10, Table 2).

Attempted intramolecular cyclization using tethers longer than three methylene groups, for example complex **23**, gave only Claisen-condensation product **24**. However, we were able to isolate bicyclo[4.3.1]decene derivative **26** by cyclization of starting complex **25** followed by conversion of the resulting aldehyde to hydrazone derivative **26** in 5% overall yield. The difficulty in forming bicyclo[4.3.1]decene systems might be attributed to unfavorable formation of seven-membered rings.



Using the same methodology, we are able to construct fused bicyclo[3.3.0]octanone and bicyclo[4.3.0]nonanone derivatives via intramolecular cyclization of acyclic ( $\eta^4$ -1,3-diene)Fe(CO)<sub>3</sub> complexes with functionalized side chains at the terminal positions of the diene ligands. Treatment of **28** with LDA under an atmosphere of CO at -78 and 25 °C for 2 h, respectively, followed by quenching the reaction mixture with CF<sub>3</sub>COOH at -78 °C, gave bicyclo[3.3.0]octanone **29** as the only diastereomeric product in 55% yield after purification via flash column chromatography and short-path distillation of the residue. None of the endo isomer **27** was obtained.

The relative stereochemistry at the ring juncture in **29** was fixed by more stable cis fusion, and <sup>1</sup>H NMR studies provided the initial evidence for support of the structure assignments. The proton at  $\delta$  2.69 as a dt,  $J = 9.5, 4.9$  Hz, was assigned to H<sub>b</sub>. The coupling constant of H<sub>a</sub>-H<sub>b</sub> ( $J_{ab}$ ) of 9.5 Hz agrees with the 9-10.5 Hz coupling constant for similarly disposed trans hydrogens compared to the 7-8 Hz observed when these protons are cis.<sup>20</sup> The excellent diastereoselectivity can also be explained by the kinetically controlled reaction conditions and is consistent with complexes **6h** and **61** having a long side chain and an ester functionality. Several examples of cyclization of acyclic diene-iron complexes are summarized in Table 3.

Substrates with an additional methyl group at the diene ligand, **30** and **32** (entries 2 and 3, Table 3), also underwent intramolecular cyclization to produce bicyclo-

Table 2. Intramolecular Cyclization and Electrophilic Quenching of Complexes

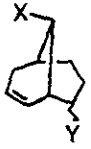
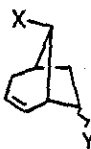
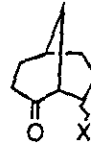
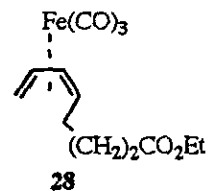
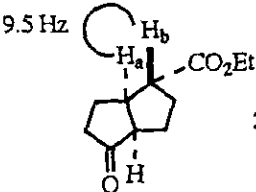
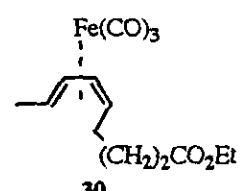
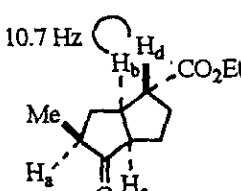
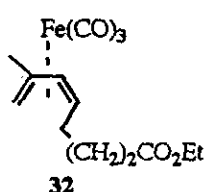
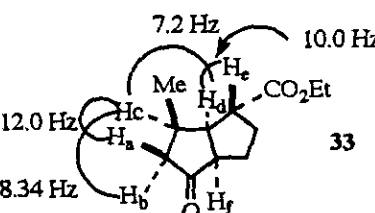
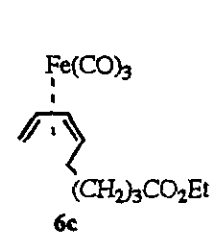
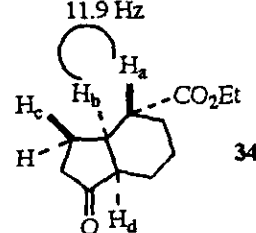
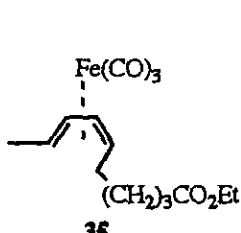
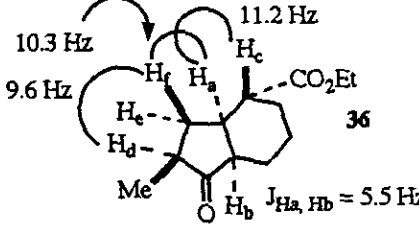
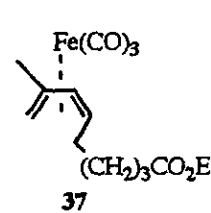
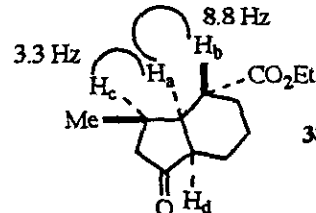
Entry	Starting Complex	Electrophile	Product	Yield (%)
1	6h	CF <sub>3</sub> COOH	9	82 %
2	11	CF <sub>3</sub> COOH	12 a + 12 b 2 : 1	37 %
3	6h	MeI	 13 X = MeCO Y = endo CO <sub>2</sub> Et	40 %
4	6f	CF <sub>3</sub> COOH	14a + 14b X = CHO Y = endo CN 1 : 2	79 %
5	6f	MeI	15a + 15b X = MeCO Y = endo CN 1 : 2	42 %
6	6f	PhCH <sub>2</sub> Br	16a + 16b X = PhCH <sub>2</sub> CO Y = endo CN 1 : 2	49 %
7	6g	CF <sub>3</sub> COOH	 17a + 17b X = CHO Y = endo CN 7 : 4	45 %
8	6g	MeI	18a + 18b X = MeCO Y = endo CN	15 %
9	6g	PhCH <sub>2</sub> Br	19a + 19b X = PhCH <sub>2</sub> CO Y = endo CN	14 %
10	6l	CF <sub>3</sub> COOH	 20 X = endo CO <sub>2</sub> Et	74 %
11	21	CF <sub>3</sub> COOH	22a + 22b X = endo CN X = exo CN	42 %

Table 3. Intramolecular Cyclization of Complexes

Entry	Starting Complex	Product	Yield %
1	 <p>28</p>	 <p>29</p>	55
2	 <p>30</p>	 <p>31</p>	34
3	 <p>32</p>	 <p>33</p>	30
4	 <p>6c</p>	 <p>34</p>	54
5	 <p>35</p>	 <p>36</p>	25
6	 <p>37</p>	 <p>38</p>	28

[3.3.0]octanones **31** and **33**, respectively, as the only diastereomeric product in each case. It is worth noting that three carbon-carbon bonds and four stereogenic centers are created in a single step, and only one diastereomer is isolated.

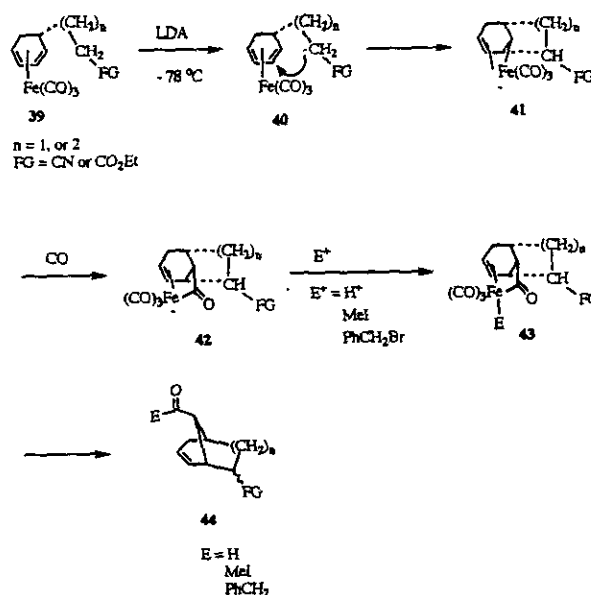
The relative stereochemistry of products **31** and **33** was determined by  $^1\text{H}$  NMR spectroscopy, with assignments deriving from decoupling experiments. For example, coupling constants of 7.2 and 10.0 Hz for  $\text{H}_c\text{-H}_d$  and  $\text{H}_d\text{-H}_c$  of **33**, re-

spectively, indicated a *cis* relationship between  $H_c$  and  $H_d$  and a *trans* relationship between  $H_d$  and  $H_e$ . A coupling constant of 10.7 Hz for  $H_b$ - $H_d$  of **31** suggested a *trans* relationship between  $H_b$  and  $H_d$ . A cross peak for  $H_a$  and  $H_b$  in the NOESY spectrum of **31** showed the *cis* relationship between  $H_a$  and  $H_b$ .

Increasing the tether length by one with complex **6c** (entry 4, Table 3) led to a 54% yield of bicyclo[4.3.0]nonanone derivative **34** as the only diastereomeric product isolated. The stereochemistry of the ring juncture was assigned as *cis* on the basis of  $^{13}\text{C}$  NMR spectral data, which was close to that of the parent *cis*-1-hexahydroindanone reported in the literature.<sup>21</sup> A coupling constant of 11.9 Hz for  $H_a$ - $H_b$  indicated a *trans* relationship between  $H_a$  and  $H_b$ . Additional support for this assignment came from a cross peak for  $H_a$  and  $H_c$  in the NOESY spectrum of **34**. With an additional methyl group at the C-1 position of the starting complex, for example, cyclization of complex **35** (entry 5, Table 3) gave bicyclo[4.3.0]nonanone derivative **36** as the major product under conditions identical with those used above. A small amount (< 7%) of the other diastereomer was also isolated, presumably derived from epimerization at the  $\alpha$ -carbon (C-8) of the keto group during acid quenching and aqueous workup. The relative stereochemistry of compound **36** was determined by  $^1\text{H}$  NMR spectroscopy, with assignments deriving from decoupling experiments. Coupling constants of 5.5 and 11.2 Hz for  $H_a$ - $H_b$  and  $H_a$ - $H_c$ , respectively, in **36**, indicated a *cis* ring juncture and a *trans*  $H_a$ - $H_c$  relationship. The methyl group at C-8, assigned to be on the endo face, was determined by the peak patterns and coupling constants of  $H_d$ - $H_e$ , and  $H_d$ - $H_f$ . Coupling constants of 9.6 and 1.0 Hz for  $H_d$ - $H_f$  and  $H_d$ - $H_e$ , respectively, suggested that  $H_d$  and  $H_f$  would likely be *trans*. This assignment was also confirmed by the large coupling constant of  $H_f$ - $H_a$  (10.3 Hz, *trans* relationship). Cyclization of complexes with a methyl group at the C-2 position of the diene ligand, for example, cyclization of complex **37** (entry 6, Table 3), gave bicyclo[4.3.0]nonanone derivative **38** in 28% yield, and only the diastereomer shown was isolated. The relative stereochemistry of compound **38** was assigned on the basis of decoupling experiments. A coupling constant of 8.8 Hz for  $H_a$ - $H_b$  suggested a *trans* relationship between  $H_a$  and  $H_b$ . A coupling constant of 3.3 Hz for  $H_a$ - $H_c$  suggests a *cis* relationship between  $H_a$  and  $H_c$ . The stereochemistry of the ring juncture was assigned as *cis* on the basis of its  $^{13}\text{C}$  NMR spectral data, which was close to that of compound **34**. The high diastereoselectivity of these fused bicyclic compounds may be due to the formation of kinetic enolates and is consistent with cyclic precursors having a long side chain and an ester functionality, for example, complexes **6h** and **6l**.

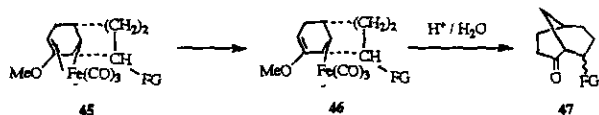
The formation of bicyclo[3.3.1] and -[3.2.1] skeletons agrees closely with the mechanism proposed for the intermolecular addition of nucleophiles to  $(\eta^4\text{-}1,3\text{-cyclohexadiene})\text{Fe}(\text{CO})_3$  complex.<sup>22a,c</sup> Deprotonation of **39** using LDA at  $-78^\circ\text{C}$  gave anion **40** (Scheme II). The stabilized secondary carbanion underwent kinetically controlled anti addition at C-3 of the diene ligand to give the putative homoallyl anion intermediate **41**. It is important to mention that secondary carbanions such as 2-lithiopropionitrile and *tert*-butyl 2-lithiopropionate do not add efficiently to  $(\eta^4\text{-}1,3\text{-cyclohexadiene})\text{Fe}(\text{CO})_3$  complexes intermolecularly.<sup>22a</sup> Moreover, the intramolecular addition occurred exclusively at the C-3 position of the diene ligand, and none of the addition at C-2 was found. Carbonyl insertion was then enhanced by an external CO (14-18 psi) to generate acyliron anion intermediate **42**. Electrophilic quenching of **42** with trifluoroacetic acid or carbon electrophiles (iodomethane or benzyl bromide) produced **43**, which underwent reductive elimination to form bicyclo[3.3.1] and bicyclo[3.2.1] compounds **44**. In general, two diastereomeric products were generated from intramolecular nucleophile additions, whereas in the cases of **6h** and **6l**, only one isomer was isolated. It is presumed that the relative stereochemistry of bridgehead carbons and the  $\alpha$ -carbon of the formyl group was fixed according to the mechanism proposed above. With a long side chain (three carbon atoms away from the cyclohexadiene ring and the iron-carbonyl moiety) and an ester functionality, only one of the diastereotopic protons was removed under the kinetically controlled reaction conditions. It is important to mention that trifluoroacetic acid is the most efficient quenching

Scheme II



reagent for acyliron anion **42**. Iodomethane and benzyl bromide were able to couple with **42**, however, only in less than 50% isolated yields. Unlike the previous results, cyclization of complexes with a methoxy group at C-2 of the diene ligand, for example complexes **61** and **21** (entries 10, 11, Table 2), gave the bicyclo[3.3.1] skeletons without an incorporated CO. The reason for this difference is not clear. It is suggested that the homoallyl anionic intermediate **45** was formed initially (Scheme III). Detachment of the alkene ligand (due to the electronic effect of the methoxy group at C-2) generates **46**.<sup>22d</sup> Reaction of anion **46** with strong acid gave bicyclo[3.3.1]nonanone derivative **47** after hydrolysis of the methyl vinyl ether during aqueous workup.

### Scheme III

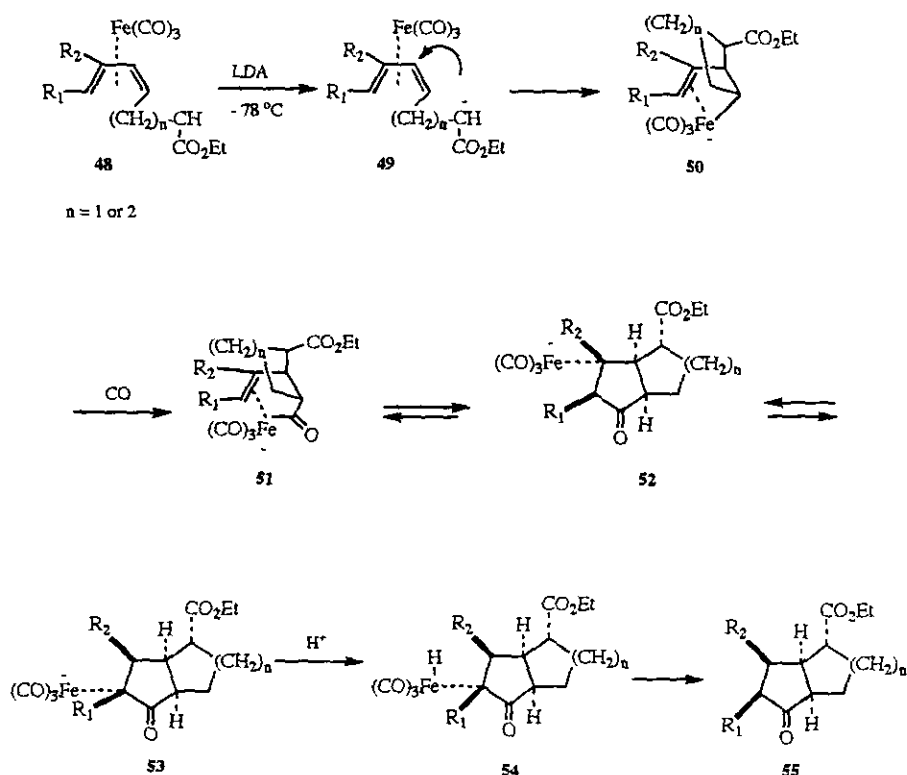


Under the same reaction conditions, intramolecular cyclizations of acyclic substrates **28**, **30**, **32**, **6c**, **35**, and **37** led to 25–55% yields of bicyclo[3.3.0]octanones **29**, **31**, **33**, and bicyclo[4.3.0]nonanones **34**, **36**, **38** as the only diastereomeric product in each case. The highly stereocon-

trolled outcome is consistent with the formation of cyclopentanone derivatives by intermolecular addition of nucleophiles to acyclic diene-iron complexes under an atmosphere of carbon monoxide.<sup>22b,e</sup> Under kinetically controlled reaction conditions ( $-78^\circ\text{C}$ ), the kinetic ester enolate **49** (Scheme IV) could add at the internal C-3 of the diene ligand to produce the homoallyl anion intermediate **50**, followed by carbonyl insertion (to give **51**) and intramolecular alkene insertion (to give **52**). The postulated initial bicyclic intermediate **52** could rearrange rapidly to the enolate-iron derivative **53**. The rearrangement involves a stereospecific hydrogen transfer, presumably via  $\beta$ -hydride elimination/readdition. Protonation of **53** generates bicyclic compound **55**. It is important to mention that the *endo* stereochemistry of the methyl groups of **31** and **33** and of **36** and **38** as well as only *cis* ring fusion found for bicyclo[4.3.0]nonanones **34–38** is consistent with the reaction pathway proposed above. However, bicyclo[3.3.0]octanone derivative **31** and bicyclo[4.3.0]nonanone derivative **36** could epimerize at C-7 and C-8, respectively, to give the more stable *exo* form (methyl group) when the reaction mixture stirred in trifluoroacetic acid for 12 h.

The reactions outlined herein demonstrate that the intramolecular iron-mediated cycloaddition can be an effective method for the formation of bridged and fused bicyclic

### Scheme IV





compounds. The ability to achieve exclusive *cis* ring juncture and excellent stereocontrol of four stereogenic centers in fused bicyclic compounds in a simple reaction may have further applications. Specifically, the preparation of more highly substituted systems for natural product synthesis would be expected to demonstrate still higher levels of stereocontrol, as is often the case for the intramolecular Diels-Alder reaction.<sup>23</sup>

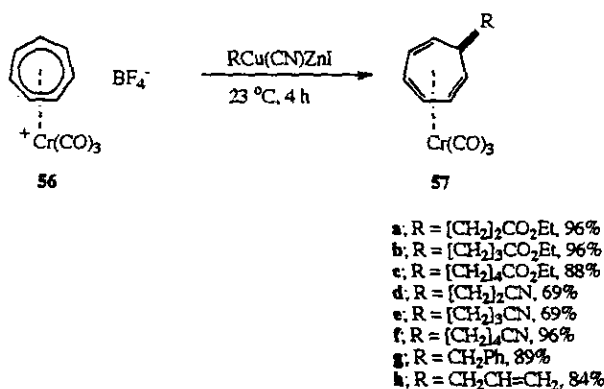
### Construction of Fused Bicyclo[5.3.0]decane and Bicyclo[5.4.0]undecane Ring Skeletons Mediated by Chromi-umtricarboxyls

Seven-membered carbocycles are often used in construction of complicated natural products.<sup>44,24</sup> Specially, the perhydroazulene or bicyclo[5.3.0]decane ring system is the most commonly encountered of the cycloheptane derived structure in natural occurring biological active compounds.<sup>25</sup> Recently, tropone has been shown to be a versatile building block for the synthesis of a variety of sesquiterpenes with the bicyclo[5.3.0]decane ring skeleton.<sup>26</sup> Normally, several steps starting from 1,8-addition of a protected functionalized three-carbon chain to tropone are needed to construct the bicyclo[5.3.0]decane ring skeleton. However, bicyclo[5.3.0]decane and bicyclo[5.4.0]undecane derivatives may be easily available via sequential additions of nucleophiles to [(tropylium)Cr(CO)<sub>3</sub>] cation **56**. This method allows the formation of 5,7- and 6,7-*cis*-fused bicyclic systems which can not be generated by sequential additions of nucleophiles to (η<sup>5</sup>-pentadienyl)Fe(CO)<sub>3</sub>.<sup>27</sup> Prior to our investigation, several classes of nucleophiles, such as hydrides, methoxides, and hydrogen sulphides have been shown to add to cation **56** to produce 7-*exo*-substituted (η<sup>6</sup>-cyclohepta-1,3,5-triene)Cr(CO)<sub>3</sub> complexes.<sup>8a</sup> However, the addition of an excess of sodium diethylmalonate or lithium cyclopentadienide to **56** provided the ring construction product [C<sub>8</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>]<sup>8b</sup> and the reaction of cyanide with **56** led by reductive coupling to a mixture of bi(cycloheptadienyl)Cr<sub>2</sub>(CO)<sub>6</sub> and bi(cycloheptadienyl)Cr(CO)<sub>3</sub>.<sup>8c</sup> Moreover, phenyl lithium failed to react with **56**. Surprisingly, reports on the addition of organocopper derivatives to cation **56** are lacking. We now report that the highly functionalized zinc-copper reagents [RCu(CN)ZnI]<sup>11</sup> add efficiently to **56** to afford (η<sup>6</sup>-cyclohepta-1,3,5-triene)Cr(CO)<sub>3</sub> complexes **57a-h** with a functionalized side-chain at the C-7 position of the ring. The reactions are performed in the expectation that further manipulation of the resulting complexes will then be possible after the initial additions.

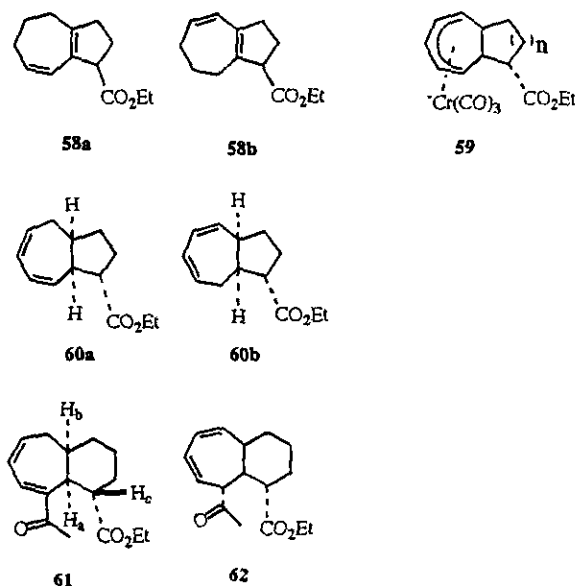
Cation **56** was prepared in two steps from cyclohepta-1,3,5-triene and Cr(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> (85% overall yield) following the literature procedures.<sup>28</sup> Finally, our synthesis of

C-7-substituted (η<sup>6</sup>-cyclohepta-1,3,5-triene)Cr(CO)<sub>3</sub> complexes **57** involved the slow addition of a tetrahydrofuran (THF) solution of the highly functionalized zinc-copper reagents RCu(CN)ZnI (1.2 mol. equiv.) to a stirred suspension of cation **56** in THF at 0 °C under nitrogen. The addition was carried out for 5 h at 23 °C followed by workup with saturated aqueous ammonium chloride and ether extraction. After purification by flash column chromatography on silica gel, complexes **57a-h** were obtained as the major products and in good yields (69-96%, Scheme V). The *trans* relationship between the nucleophile and the metal moiety of complexes **57** was assigned based upon comparison of their <sup>1</sup>H NMR spectra with the spectra of 7-*exo*-(η<sup>6</sup>-cyclohepta-1,3,5-triene)Cr(CO)<sub>3</sub> complexes reported in the literatures.<sup>29</sup> Further manipulation of the resulting complexes **57** was demonstrated as follows. Treatment of **57b** with lithium diisopropylamide (LDA, 1.2 mol. equiv.) in THF and hexamethylphosphoramide (HMPA, THF/HMPA = 3/1) at -78 °C for 1 h followed by quenching of the reaction mixture with trifluoroacetic acid (10 mol. equiv.) produced a mixture of perhydroazulene derivatives **58a** and **58b** in a 1:1 ratio in 77% total yield. The formation of bicyclo[5.3.0] compounds **58a** and **58b** agrees closely with the mechanism proposed for the intermolecular addition of nucleophiles to (η<sup>6</sup>-arene)Cr(CO)<sub>3</sub>.<sup>30</sup> Deprotonation of **57b** using LDA at -78 °C in THF/HMPA would result in the formation of the kinetic ester enolate.<sup>27,31</sup> Anti addition of the ester enolate to the terminal position of the triene ligand gave (η<sup>5</sup>-cycloheptadienyl)Cr(CO)<sub>3</sub> anion complex **59** (n = 1). Electrophilic quenching of **59** with trifluoroacetic acid afforded bicyclo[5.3.0]decane derivatives **60a** and **60b**. However, diene migration occurred and produced thermally more stable isomers **58a** and **58b** under the reaction conditions. Treatment of **57c** with LDA (1.2 mol. equiv.) in THF/HMPA (3/1) under an atmosphere of CO at -78 °C for 1 h followed by quenching of the reaction mixture with iodomethane (5 mol.

Scheme V



equiv.; CO; 25 °C; 2 h), and then iodine (4 mol. equiv.; 25 °C; 4 h) generates bicyclo[5.4.0]undecane derivative **61** as the major product in 63% yield. Reaction of **59** ( $n = 2$ ) with iodomethane under an atmosphere of CO would give the bicyclo[5.4.0]undecane derivative **62**<sup>32</sup> which isomerized to provide the highly conjugate dienone **61**. The *cis* stereochemistry at the ring juncture of **61** is fixed by anti addition of the ester enolate to the terminal position of the triene ligand (to give **59**,  $n = 2$ ), and the ester group assigned as *exo* was resulted from the formation of the kinetic ester enolate under the kinetically controlled reaction conditions.<sup>27</sup> <sup>1</sup>H NMR studies provided the initial evidence for support of the structural assignments. The <sup>1</sup>H NMR spectrum of compound **61** exhibited a doublet of doublets, centered at  $\delta$  3.2,  $J = 12.0, 2.8$  Hz, assigned to  $H_a$ . The coupling constant of  $H_a-H_b$  ( $J_{ab}$ ) of 12.0 Hz agrees with the 12.7 Hz coupling constant observed for the similarly *cis* fused bicyclo[5.4.0]undecanone and the coupling constant of  $H_a-H_c$  ( $J_{ac}$ ) of 2.8 Hz agrees with the 3.2 Hz coupling constant observed for the similarly disposed *trans* hydrogens.<sup>33</sup>



We have demonstrated that the addition of the highly functionalized zinc-copper reagents  $RCu(CN)ZnI$  to the [(tropylium)Cr(CO)<sub>3</sub>] cation **56** gave [( $\eta^6$ -cyclohepta-1,3,5-triene)Cr(CO)<sub>3</sub>] complexes **57** in good yields. Intramolecular cyclisation of ester-substituted complexes **57b** and **57c** using LDA furnished bicyclo[5.3.0]decane and bicyclo[5.4.0]undecane derivatives, respectively.

### Synthesis of Bicyclic $\delta$ -Lactone Mediated by Molybdenum Carbonyl

The addition of various nucleophiles at the terminal

position of the  $[Mo(\eta^4$ -cyclohexa-1,3-diene)(CO)<sub>2</sub>(Cp)]<sup>+</sup> cation **63** offers an easy access to a variety of  $[Mo(\pi$ -allyl)(CO)<sub>2</sub>(Cp)] complexes (Cp = cyclopentadienyl).<sup>4b,c,d</sup> Detachment of the metal moiety can be performed efficiently by using iodolactonisation-ozonisation procedures to give useful organic intermediates.<sup>4e,f</sup> Alternatively, the resulting ( $\pi$ -allyl)molybdenum complexes can be further activated towards nucleophilic additions by hydride abstraction on treatment with triphenylcarbenium hexafluorophosphate (Ph<sub>3</sub>CPF<sub>6</sub>) to form a new cationic salt. A second nucleophile can then add to the new cation at the less hindered terminus of the coordinated diene ligand to establish 1,3-stereocontrol in the six-membered ring.<sup>34</sup> Several classes of stabilized lithium enolates as well as nonstabilized enolates of simple esters, keto imines, hydrides, Grignard reagents and the cyano anion have been shown to add to cation **63**.<sup>4b,c,d</sup> Among these, the stabilized enolates add most efficiently to the cation. However, the reactions can only introduce a two carbon atom side chain at the C-4 position of the  $[Mo(\pi$ -allyl)(CO)<sub>2</sub>(Cp)] complexes. Surprisingly, reports on the addition of organocopper derivatives to cation **63** are rare<sup>35</sup> and the reactions proceed in low yields (*ca.* 35%),<sup>35</sup> this has been confirmed in our preliminary investigations (Table 4, entry 9). Furthermore, organocuprates obtained from the corresponding lithium reagents and copper salts do not bear functional groups. Recently Knochel has found that polyfunctional copper reagents can be generated by transmetalation of the corresponding functionalized zinc organometallic compounds with  $CuCN \cdot 2LiCl$  in tetrahydrofuran (THF). We now report that the highly functionalized copper reagents **64a-h** add efficiently at the terminal position of the coordinated diene ligand of cation **63** to generate  $[Mo(\pi$ -allyl)(CO)<sub>2</sub>(Cp)] complexes **65a-h** with a function-

Table 4. Reaction of Cation **63** with the Highly Functionalized  $RCu(CN)ZnI$

Entry	$RCu(CN)ZnI$ <b>64</b>	Product <b>65</b> <sup>a</sup>	Yield (%)
1	<b>a</b> ; R = [CH <sub>2</sub> ] <sub>2</sub> CO <sub>2</sub> Et	<b>65a</b>	90
2	<b>b</b> ; R = [CH <sub>2</sub> ] <sub>3</sub> CO <sub>2</sub> Et	<b>65b</b>	90
3	<b>c</b> ; R = [CH <sub>2</sub> ] <sub>2</sub> CO <sub>2</sub> Et	<b>65c</b>	33
4	<b>d</b> ; R = [CH <sub>2</sub> ] <sub>4</sub> CN	<b>65d</b>	58
5	<b>e</b> ; R = [CH <sub>2</sub> ] <sub>3</sub> CN	<b>65e</b>	41
6	<b>f</b> ; R = [CH <sub>2</sub> ] <sub>4</sub> OAc	<b>65f</b>	51
7	<b>g</b> ; R = [CH <sub>2</sub> ] <sub>4</sub> OCOPh	<b>65g</b>	57
8	<b>h</b> ; R = CH <sub>2</sub> Ph	<b>65h</b>	57
9	<b>i</b> ; Bu <sub>2</sub> CuLi	<b>65i</b>	18

<sup>a</sup> All products were purified by flash column chromatography on silica gel and have been fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, mass, and high resolution mass spectra.

alized side-chain at the C-4 position. The reaction of **64i** led to a lower yield. The reactions are performed in the expectation that further manipulation of the resulting complexes will then be possible after the initial additions.

Cation **63** was prepared in five steps from cyclohexene (62% overall yield) following the literature procedures.<sup>4b,c,d</sup> Slow addition of a THF solution of the highly functionalized copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$  (1.2 mol. equiv.) to a stirred suspension of cation **63** in THF at 0 °C for 5 h under nitrogen, followed by work-up with saturated aqueous ammonium chloride, ether extraction and flash column chromatography on silica yielded the  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2\text{Cp}]$  complexes **65a-h** in fair to good yields (33-90%). In general, the additions proceeded smoothly under our reaction conditions. However, the zinc-copper homoenolate of ethyl propionate **64c** appeared to be less reactive even in the presence of hexamethylphosphoramide (HMPA).<sup>36</sup> The *trans* relationship between the nucleophile and the metal moiety of complex **65** was assigned based upon comparison of their <sup>1</sup>H NMR spectra with the spectra of  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2(\text{Cp})]$  complexes made by Faller and Pearson. Further manipulation of the resulting complexes **65** was demonstrated as follows. Hydrolysis of the ester **65c** using KOH in MeOH-THF-H<sub>2</sub>O at 23 °C gave the corresponding acid **66** in 90% yield (Scheme VI). The carboxylic acid **66** was converted to cation **67** by ligand exchange ( $\text{NOBF}_4$ ), followed by addition of triethylamine to produce the  $\delta$ -lactone **68**

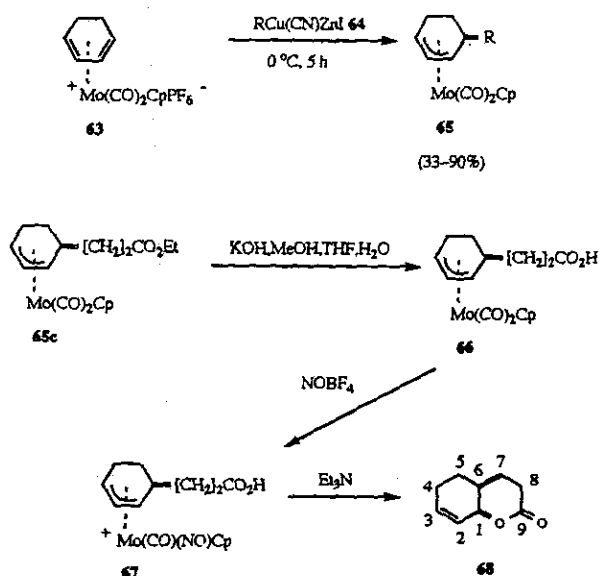
(35%, two steps).<sup>37</sup> The  $\delta$ -lactone **68** was previously not accessible since the addition of lithium enolates to the cation could only introduce a two carbon atom side chain onto the six-membered ring. Alternatively, iodolactonisation of complex **67** ( $\text{I}_2$ ; MeCN; 23 °C) also gave the  $\delta$ -lactone **68** in 27% yield. The *cis*-stereochemistry of the  $\delta$ -lactone **68** was assigned based upon the coupling constant (5.0 Hz) of the adjacent 1-H and 6-H. This assignment is consistent with that for the *cis*- $\gamma$ -lactones reported by Pearson.<sup>38</sup>

In conclusion, we have demonstrated that the addition of the highly functionalized zinc-copper reagents  $\text{RC}(\text{CN})\text{ZnI}$  to the  $[\text{Mo}(\eta^4\text{-cyclohexa-1,3-diene})(\text{CO})_2(\text{Cp})]$  cation **63** occurred at the terminus of the diene system to furnish polyfunctionalized  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2\text{Cp}]$  complexes. Further activation of the resulting  $(\pi\text{-allyl})\text{molybdenum}$  complexes to the new cations can be accomplished by ligand exchange using  $\text{NOBF}_4$  or by hydride abstraction adding  $\text{Ph}_3\text{CPF}_6$ .

## EXPERIMENTAL SECTION

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Methylene chloride was distilled from calcium chloride. Copper cyanide ( $\text{CuCN}$ ), 1,3-cyclohexadiene, 1-methoxy-1,4-cyclohexadiene, triphenylcarbenium hexafluorophosphate, (2,4-dinitrophenyl)hydrazine, *trans,trans*-2,4-hexadien-1-ol, fluoroboric acid (48% in water), and hexafluorophosphoric acid (60% in water) were purchased from Aldrich Chemical Co. and used as received. Zinc particles (purity > 99.9%), ethyl 4-chlorobutyrate, 4-chlorobutyronitrile, 3-chloropropionitrile, and ethyl 3-chloropropionate were purchased from Merck Co. and used without further purification.  $(\eta^4\text{-1,3-Diene})\text{Fe}(\text{CO})_3$  complexes **2a** and **5** were obtained by treatment of the corresponding free dienes with diiron nonacarbonyl in refluxing ether for 12 h. Complex **2b** was obtained in three steps from 2-cyclohexen-1-one according to the literature procedure.<sup>19</sup> Diiron nonacarbonyl was obtained by photolysis of iron pentacarbonyl in benzene and acetic acid according to the literature procedure.<sup>39</sup> Flash column chromatography, following the method of Still,<sup>40</sup> was carried out with E. Merck silica gel (Kieselgel 60, 230-400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F<sub>254</sub> plastic plates of 0.2-mm thickness from E. Merck. The term

**Scheme VI** Formation of functionalized  $[\text{Mo}(\pi\text{-allyl})(\text{CO})_2(\text{Cp})]$  complexes **65** and the  $\delta$ -lactone **68**. R may contain an ester, a nitrile, an acetoxy, a benzoyloxy or a benzyl group



"concentration" refers to the removal of solvent with an aspirator pump (Yamato Instrument Company Model WP-15) with a Buchi Rotovapor-R. The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. The term "flash distillation" refers to a vacuum distillation at 25 °C with a receiver at -78 °C. The term "short-path distillation" refers to the process in which the entire distillation apparatus (a tube closed at one end, held horizontally) with the exception of the collection bulb was slowly heated in an air bath from 25 to 150 °C under vacuum; the distillate was collected at -78 °C, and boiling points for fractions refers to the bath temperature range. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz), Bruker AC-300 (300 MHz), and Bruker AC-200 (200 MHz) spectrometers. Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl<sub>3</sub> (7.26 ppm) as internal standards. <sup>13</sup>C NMR spectra were recorded with JEOL-EX 400 (100.4 ppm) and Bruker AC-200 (50.2 ppm) spectrometers with CDCl<sub>3</sub> (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a IEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/z* with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer in the Department of Chemistry, Northern Instrument Center, Hsin Chu.

#### General Procedure for the Formation of Cation 3<sup>6a,41</sup>

To a solution of triphenylcarbenium hexafluorophosphate (Ph<sub>3</sub>CPF<sub>6</sub>, 8.5 g, 22 mmol) in 60 mL of dry dichloromethane under nitrogen was added rapidly a solution of complex 2 (16.2 mmol). The reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was diluted with 100 mL of cold ether, and the precipitate was filtered. The yellow solid was washed four times with ether and dried under vacuum to give cation 3 (**3a** 99%, **3b** 92%) as a pale yellow powder.

#### General Procedure for the Formation of Functionalized Zinc-Copper Reagents<sup>11a</sup>

To a solution of sodium iodide (30 g, 0.2 mol) in 90 mL of anhydrous acetone were added functionalized alkyl chlorides (0.1 mol). The reaction mixture was stirred under reflux for 16 h. After a regular aqueous process, the residue was distilled under vacuum to give the corresponding functionalized alkyl iodides (60-90%). Zinc (1.8 g, 28 mmol)

was added in a dried three-neck round-bottom flask equipped with a dropping funnel, a thermometer, and a nitrogen outlet. To the reaction were added 2.5 mL of THF and 0.2 mL of 1,2-dibromoethane. The reaction mixture was heated with a heat gun for 30 s and allowed to cool to room temperature. The process was repeated two times before 0.2 mL of chlorotrimethylsilane was added via syringe. The mixture was stirred for 30 min before a THF (4 mL) solution of functionalized alkyl iodides (14 mmol) [I(CH<sub>2</sub>)<sub>n</sub>FG, FG = CO<sub>2</sub>Et or CN] was added via the dropping funnel. Normally, the reaction was stirred at 40-50 °C for 14 h. In the case of ethyl iodopropionate and iodopropionitrile, the insertion was complete at 25 °C for 8 h. Copper cyanide (0.98 g, 10.95 mmol) was added to predried LiCl (150 °C, 3 h under vacuum, 0.93 g, 22 mmol) in a Schlenk flask under nitrogen. The reaction mixture was cooled to 0 °C before 10 mL of THF was added via syringe. The reaction mixture was stirred at 25 °C until the solid was dissolved. The above solution was cooled to -78 °C, and the functionalized alkylzinc iodide was added dropwise to the reaction mixture. The resulting light green solution was stirred at 0 °C for 30 min, and the functionalized zinc-copper reagent was ready to use.

#### General Procedure for Addition of Functionalized Zinc-Copper Reagents RCu(Zn)CN to (η<sup>5</sup>-Cyclohexadienyl)- and (η<sup>5</sup>-Pentadienyl)Fe(CO)<sub>3</sub> Cation Salts

A solution of functionalized zinc-copper reagents (2.0 molar equiv) in 5 mL of THF was added to a stirred suspension of a cation salt (3 or 6) in 5 mL of THF at 5 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with 100 mL of 50% ethyl acetate/hexanes. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography to give pure compound. Spectral data of these compounds are listed in Table 5.

#### General Procedure for Intramolecular Cyclization of (η<sup>4</sup>-Diene)Fe(CO)<sub>3</sub> Complexes Bearing Functionalized Side Chains

In a typical procedure, to a solution of diisopropylamine (0.64 mL, 4.5 mmol) in 4 mL of THF under nitrogen at -78 °C was added rapidly, neat, via syringe, a solution of *n*-butyllithium (2.8 mL, 4.5 mmol, 1.6 M) in hexane followed by addition of 0.8 mL of hexamethylphosphoramide.

Table 5. Spectral Data for Compounds 6c, 6f-h, 6l, 11, 21, 25, 28, 30, 32, 35, 37

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
6c	266 (M-2CO)	266.0605 (266.0609) (M-2CO)	3051, 2988, 2935, 2860, 2046, 1973, 1728, 1658, 1448, 1375, 1275, 1182, 1141, 927	211.3, 173.5, 90.6, 86.9, 60.2, 59.9, 40.8, 34.0, 32.3, 28.4, 24.4, 14.2	5.43 (ddd, $J = 9.8, 7.5, 4.9$ Hz, 1 H), 5.28 (dd, $J = 7.8, 4.9$ Hz, 1 H), 4.11 (q, $J = 7.3$ Hz, 3 H), 2.55 (ddd, $J = 13.1, 7.8, 4.9$ Hz, 1 H), 2.24 (t, $J = 7.3$ Hz, 2 H), 1.88 (dd, $J = 7.5, 2.4$ Hz, 1 H), 1.55 (m, 3 H), 1.48 (dd, $J = 7.6, 2.8$ Hz, 1 H), 1.45 (m, 2 H), 1.25 (t, $J = 7.3$ Hz, 3 H), 1.07 (m, 1 H)
6f	287	287.0244 (287.0233)	3059, 3010, 2939, 2850, 2244, 2045, 1975, 1425, 1328, 1158, 1027, 980, 814, 547	211.9, 120.0, 85.8, 84.5, 65.6, 59.5, 38.7, 37.5, 30.6, 24.0, 17.3	5.35 (dd, $J = 6.0, 4.1$ Hz, 1 H), 5.29 (td, $J = 6.0, 1.8$ Hz, 1 H), 3.05 (m, 2 H), 2.26 (t, $J = 6.9$ Hz, 2 H), 2.05 (m, 1 H), 2.00 (dd, 10.8, 4.2 Hz, 1 H), 1.54 (m, 2 H), 1.35-1.28 (m, 3 H)
6g	273	189.0239 (189.0231) (M-3CO)	3032, 3000, 2942, 2847, 2468, 2250, 2049, 1962, 1424, 1350, 1165, 960	211.6, 119.3, 85.9, 84.3, 63.8, 59.0, 36.9, 34.6, 30.3, 15.6	5.79 (dd, $J = 6.1, 4.0$ Hz, 1 H), 5.31 (dd, $J = 6.1, 3.0$ Hz, 1 H), 3.04 (brs, 2 H), 2.30 (t, $J = 8.4$ Hz, 2 H), 2.19 (m, 1 H), 2.07 (dd, $J = 14.7, 4.7$ Hz, 1 H), 1.56 (m, 2 H), 1.24 (d, $J = 14.7$ Hz, 1 H)
6h	334	334.0504 (334.0504)	2987, 2849, 2465, 2043, 1964, 1734, 1628, 1539, 1455, 1373, 1241, 1186, 1030, 967, 861, 617	212.1, 173.4, 85.5, 84.5, 66.5, 60.2, 59.8, 39.3, 37.9, 34.2, 30.6, 23.5, 14.2	5.32 (dd, $J = 6.3, 4.1$ Hz, 1 H), 5.23 (td, $J = 6.1, 1.5$ Hz, 1 H), 4.07 (q, $J = 7.2$ Hz, 2 H), 3.08 (dd, $J = 6.4, 3.0$ Hz, 1 H), 3.00 (m, 1 H), 2.19 (t, $J = 7.3$ Hz, 2 H), 2.09 (m, 1 H), 1.92 (dd, $J = 10.4, 3.7$ Hz, 1 H), 1.51 (p, $J = 7.5$ Hz, 2 H), 1.17 (t, $J = 7.2$ Hz, 3 H), 1.28-1.05 (m, 3 H)
6l	364	364.0608 (364.0628)	2938, 2040, 1960, 1735, 1524, 1438, 1424, 1373, 1227, 1177, 1094, 1027, 925, 797, 614	211.3, 173.4, 139.8, 66.4, 60.2, 55.2, 54.2, 52.7, 39.4, 37.5, 34.3, 31.1, 23.6, 14.2	5.05 (dd, $J = 6.5, 2.2$ Hz, 1 H), 4.07 (q, $J = 7.2$ Hz, 2 H), 3.61 (s, 3 H), 3.25 (q, $J = 3.5$ Hz, 1 H), 2.70 (dd, $J = 6.4, 3.3$ Hz, 1 H), 2.25 (t, $J = 7.3$ Hz, 2 H), 2.00 (dd, $J = 10.8, 4.2$ Hz, 1 H), 1.90 (m, 1 H), 1.55 (m, 2 H), 1.30-1.20 (m, 3 H), 1.23 (t, $J = 7.3$ Hz, 3 H)
11	320	320.0347 (320.0292)	3056, 2990, 2934, 2852, 2050, 1978, 1726, 1609, 1447, 1373, 1330, 1185, 1092, 1031	211.9, 173.3, 85.6, 84.5, 65.6, 60.2, 59.5, 37.4, 34.5, 32.8, 30.4, 14.1	5.37 (dd, $J = 6.3, 4.4$ Hz, 1 H), 5.29 (td, $J = 4.9, 1.5$ Hz, 1 H), 4.11 (q, $J = 6.8$ Hz, 2 H), 3.08 (dd, $J = 6.4, 4.3$ Hz, 1 H), 3.03 (dd, $J = 4.0, 2.0$ Hz, 1 H), 2.23 (t, $J = 7.8$ Hz, 2 H), 2.13 (m, 1 H), 2.00 (dd, $J = 14.2, 3.9$ Hz, 1 H), 1.50 (m, 2 H), 1.30-1.21 (m, 4 H)
21	317	233.0503 (233.0496) (M-3CO)	3066, 3011, 2941, 2916, 2852, 2244, 2040, 1964, 1511, 1477, 1457, 1423, 1328, 1221, 1172, 1039, 967, 865, 635, 561	211.1, 139.8, 119.4, 66.2, 54.3, 54.2, 52.4, 38.7, 37.1, 31.6, 24.2, 17.2	5.03 (dd, $J = 6.5, 2.2$ Hz, 1 H), 3.61 (s, 3 H), 3.25 (m, 1 H), 2.60 (dd, $J = 6.5, 3.3$ , 1 H), 2.26 (t, $J = 6.9$ Hz, 2 H), 2.09 (dd, $J = 9.2, 3.5$ Hz, 1 H), 1.90 (m, 1 H), 1.56 (m, 2 H), 1.34-1.27 (m, 3 H)
25	301	301.0401 (301.0402)	3066, 2934, 2240, 2042, 1964, 1606, 1455, 1432, 1244, 1089	212.0, 139.8, 119.6, 85.6, 84.5, 66.3, 59.7, 39.0, 37.9, 30.6, 27.2, 25.6, 17.0	5.35 (t, $J = 5.3$ Hz, 1 H), 5.27 (dd, $J = 5.3, 4.9$ Hz, 1 H), 3.09 (brs, 1 H), 3.04 (brs, 1 H), 2.31 (t, $J = 6.8$ Hz, 2 H), 2.04 (m, 1 H), 1.97 (dd, $J = 10.2, 3.9$ Hz, 1 H), 1.58 (m, 2 H), 1.38-1.19 (m, 5 H)
28	308	252.0449 (252.0455) (M-2CO)	2982, 2047, 1960, 1726, 1603, 1449, 1375, 1182, 1028	211.0, 173.3, 90.8, 86.9, 77.0, 59.6, 40.9, 33.6, 28.0, 14.2	5.44 (ddd, $J = 9.8, 7.3, 4.9$ Hz, 1 H), 5.30 (dd, $J = 8.0, 4.9$ Hz, 1 H), 4.10 (q, $J = 7.3$ Hz, 2 H), 2.54 (td, $J = 13.1, 4.8$ Hz, 1 H), 2.24 (q, $J = 7.8$ Hz, 2 H), 1.86 (dd, $J = 7.3, 2.4$ Hz, 1 H), 1.75-1.48 (m, 3 H), 1.44 (dd, $J = 9.8, 2.4$ Hz, 1 H), 1.24 (t, $J = 7.32$ Hz, 3 H), 1.06 (m, 1 H)

Table 5 (continues)

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
30	266 (M-2CO)	266.0605 (266.0612)	3059, 2982, 2040, 1967, 1728, 1452, 1377, 1277, 1261, 1186, 1030	211.9, 173.3, 94.6, 82.2, 60.3, 58.8, 57.7, 33.6, 28.8, 28.0, 20.2, 14.2	5.21 (dd, $J = 8.9, 4.9$ Hz, 1 H), 5.08 (dd, $J = 7.6, 5.1$ Hz, 1 H), 4.08 (q, $J = 7.1$ Hz, 2 H), 2.44-2.17 (m, 3 H), 1.68-1.47 (m, 4 H), 1.41 (d, $J = 6.2$ Hz, 3 H), 1.22 (t, $J = 7.1$ Hz, 3 H), 1.06 (m, 1 H)
32	322	294.0554 (294.0550) (M-CO)	3059, 2980, 2042, 1969, 1728, 1442, 1277, 1257, 1184, 1033	211.3, 173.4, 108.0, 86.7, 60.3, 55.6, 43.5, 33.7, 28.0, 24.6, 17.6, 14.2	5.22 (d, $J = 7.5$ Hz, 1 H), 4.10 (q, $J = 7.1$ Hz, 2 H), 2.41-2.23 (m, 4 H), 2.18 (s, 3 H), 1.89-1.47 (m, 4 H), 1.24 (t, $J = 7.1$ Hz, 3 H), 1.10 (m, 1 H)
35	280 (M-2CO)	280.0762 (280.0760) (M-2CO)	3053, 2982, 1961, 1423, 1377, 1273, 1186, 1030	212.0, 173.6, 94.5, 82.3, 60.2, 59.6, 57.6, 34.1, 32.5, 29.0, 24.4, 20.2, 14.2	5.24 (dd, $J = 9.2, 4.9$ Hz, 1 H), 5.12 (dd, $J = 7.8, 5.2$ Hz, 1 H), 4.12 (q, $J = 6.8$ Hz, 2 H), 2.44 (ddd, $J = 14.2, 7.3, 6.8$ Hz, 1 H), 2.33 (m, 1 H), 2.25 (t, $J = 7.3$ Hz, 2 H), 1.68-1.50 (m, 5 H), 1.44 (d, $J = 5.9$ Hz, 3 H), 1.26 (t, $J = 6.8$ Hz, 3 H), 1.08 (m, 1 H)
37	336	308.0711 (308.0703) (M-CO)	3061, 2932, 2042, 1977, 1728, 1440, 1377, 1263, 1184, 1032	211.3, 173.5, 107.8, 86.8, 60.1, 56.3, 43.3, 34.0, 32.3, 28.0, 24.3, 24.2, 14.1	5.17 (brd, $J = 7.6$ Hz, 1 H), 4.07 (q, $J = 7.1$ Hz, 2 H), 2.36 (td, $J = 7.6, 4.0$ Hz, 1 H), 2.19 (t, $J = 7.2$ Hz, 1 H), 2.13 (s, 3 H), 1.82 (m, 1 H), 1.57-1.32 (m, 6 H), 1.21 (t, $J = 7.1$ Hz, 3 H), 1.06 (m, 1 H)

The reaction mixture was stirred at  $-78^\circ\text{C}$  for 20 min. With the solution at  $-78^\circ\text{C}$ , carbon monoxide was added to the system via a syringe needle and was pressurized to ca. 2 psig (always keeping a positive pressure on the system) as measured by a regulator at the CO cylinder. The CO pressure was then released via an additional needle, and the CO was allowed to flow through the system for 20 s. A solution of a diene-iron complex (**4** or **7**, 2 mmol) in 3 mL of THF was added dropwise via syringe, the gas exit needle was removed, and the closed system was pressurized to ca. 14 psig with CO. The mixture was stirred at  $-78^\circ\text{C}$  for 2 h and  $25^\circ\text{C}$  for 2 h. After this time, the mixture was again cooled to  $-78^\circ\text{C}$ , the CO needle was removed, and the system was depressurized via insertion of a syringe needle into the septum, which was quickly removed when gas flow could no longer be heard. The reaction mixture was quenched with electrophiles (trifluoroacetic acid, iodomethane, or benzyl bromide, 5 molar equiv, Table 1) via a syringe needle and was stirred at  $25^\circ\text{C}$  for 2 h. After this time, the reaction mixture was diluted with a mixture of ethyl acetate/hexanes (1/2, 100 mL). The resultant solution was washed with water (100 mL  $\times$  3) and brine (100 mL  $\times$  3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography to give pure compound.

[(6-9- $\eta$ )-Ethyl *cis*-6,8-nonadienoate]tricarbonyliron Complex (**6c**): 93%.

[*exo*-4-[(1-4- $\eta$ )-1,3-Cyclohexadien-5-yl]butyronitrile]tricarbonyliron Complex (**6f**): as a yellow oil; 73%.

[*exo*-3-[(1-4- $\eta$ )-1,3-Cyclohexadien-5-yl]propionitrile]tricarbonyliron Complex (**6g**): as a yellow oil; 79%.

[Ethyl *exo*-4-[(1-4- $\eta$ )-1,3-cyclohexadien-5-yl]butyrate]tricarbonyliron Complex (**6h**): as a yellow oil; 79%.

[Ethyl 5-*exo*-4-[(1-4- $\eta$ )-2-methoxy-1,3-cyclohexadien-5-yl]butyrate] tricarbonyliron Complex (**6i**): as a yellow oil; 76%.

[Ethyl *exo*-3-[(1-4- $\eta$ )-1,3-cyclohexadien-5-yl]propionate]tricarbonyliron Complex (**11**): as a yellow oil; 83%.

[*exo*-4-[(1-4- $\eta$ )-2-Methoxy-1,3-cyclohexadien-5-yl]butyronitrile]tricarbonyliron Complex (**21**): as a yellow oil; 70%.

[*exo*-5-[(1-4- $\eta$ )-1,3-Cyclohexadien-5-yl]pentanenitrile]tricarbonyliron Complex (**25**): as a yellow oil; 66%.

[(5-8- $\eta$ )-Ethyl *cis*-5,7-octadienoate]tricarbonyliron complex (**28**): as a yellow oil; 95%.

[(5-8- $\eta$ )-Ethyl *cis*-5,7-*trans*-7-nonadienoate]tricarbonyliron Complex (**30**): as a yellow oil; 99%.

[(5-8- $\eta$ )-Ethyl 7-methyl-*cis*-5,7-octadienoate]tricarbonyliron Complex (**32**): as a yellow oil; 85%.

[(6-9- $\eta$ )-Ethyl *cis*-6,8-decadienoate]tricarbonyliron Complex (**35**): as a yellow oil; 82%.

[(6-9- $\eta$ )-Ethyl 8-methyl-*cis*-6,8-nonadienoate]tri-

Table 6. Spectral Data for Compounds 9-22

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) cm <sup>-1</sup>	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
9	222	222.1255 (222.1238)	3032, 2942, 2716, 1736, 1514, 1472, 1457, 1384, 1378, 1375, 1186, 1018, 998, 984	203.3, 173.8, 133.1, 124.5, 60.4, 52.9, 45.5, 32.9, 29.2, 26.9, 20.4, 14.2	9.59 (s, 1 H, H10), 5.94 (dt, $J = 9.8, 3.3$ Hz, 1 H, H7), 5.67 (dd, $J = 9.8, 2.7$ Hz, 1 H, H8), 4.15 (dq, $J = 1.6, 7.2$ Hz, 2 H, H12), 3.23 (brs, 1 H), 2.56 (dt, $J = 11.0, 3.8$ Hz, 1 H), 2.49 (m, 1 H), 2.29 (m, 1 H), 1.87-1.64 (m, 6 H), 1.28 (t, $J = 7.2$ Hz, 3 H, H13)
12a	208	208.1100 (208.1089)	3036, 2984, 2950, 2906, 2838, 2722, 2252, 1715, 1585, 1434, 1371, 1291, 1097, 1033	202.5, 174.8, 130.7, 127.3, 60.7, 54.8, 52.6, 39.3, 35.7, 34.7, 33.1, 14.2	9.85 (s, 1 H), 6.03 (dd, $J = 8.8, 7.3$ Hz, 1 H, Ha), 5.44 (dd, $J = 9.3, 3.0$ Hz, 1 H), 4.12 (q, $J = 7.3$ Hz, 2 H), 3.01 (m, 2 H), 2.80 (dd, $J = 4.4, 4.9$ Hz, 1 H, Hb), 2.73 (brs, 1 H), 2.47 (m, 1 H), 2.33 (m, 1 H), 1.94-1.82 (m, 2 H), 1.26 (t, $J = 7.3$ Hz, 3 H)
12b	208	208.1100 (208.1102)	3060, 2952, 2042, 1969, 1721, 1606, 1440, 1371, 1283, 1195, 1043	202.6, 173.0, 128.2, 127.9, 60.5, 56.3, 52.5, 38.3, 34.6, 33.8, 33.4, 14.3	9.85 (s, 1 H), 5.86 (dd, $J = 8.3, 6.4$ Hz, 1 H, Ha), 5.64 (dt, $J = 9.3, 3.6$ Hz, 1 H), 4.12 (2 q, $J = 7.3$ Hz, 2 H), 3.14 (m, 2 H), 2.69 (brs, 1 H), 2.58 (brs, 1 H, Hb), 2.49 (brd, $J = 18.6$ Hz, 1 H), 2.32 (m, 1 H), 2.02-1.96 (m, 2 H), 1.26 (t, $J = 7.3$ Hz, 3 H)
13	236	236.1412 (236.1412)	3035, 2934, 1732, 1634, 1428, 1370, 1302, 1245, 1180, 1044, 1021	208.6, 173.8, 132.0, 124.3, 60.2, 54.2, 46.0, 33.4, 33.2, 29.4, 27.5, 26.8, 20.1, 14.2	5.74 (dt, $J = 9.9, 3.3$ Hz, 1 H), 5.50 (dd, $J = 9.9, 6.1$ Hz, 1 H), 4.02 (2 q, $J = 7.1$ Hz, 2 H), 3.17 (brs, 1 H), 2.43 (m, 2 H), 2.29 (m, 1 H), 2.05 (s, 3 H), 1.70-1.58 (m, 6 H), 1.18 (t, $J = 7.1$ Hz, 3 H)
14a	175	175.0997 (175.0986)	3066, 3036, 2938, 2236, 1710, 1637, 1449, 1428, 1374, 1286, 1140, 1097, 927, 920	201.7, 134.3, 124.5, 121.3, 48.7, 32.3, 29.9, 29.5, 28.8, 26.5, 20.8	9.50 (d, $J = 2.9$ Hz, 1 H), 5.92 (dt, $J = 9.8, 3.4$ Hz, 1 H), 5.59 (dd, $J = 9.8, 6.4$ Hz, 1 H), 3.08 (brs, 1 H), 2.78 (m, 1 H), 2.74 (brs, 1 H), 2.60 (brs, 1 H), 2.40 (dd, $J = 19.5, 6.8$ Hz, 1 H), 1.96-1.73 (m, 5 H)
14b	175	175.0997 (175.1001)	3064, 3046, 2940, 2240, 1725, 1607, 1447, 1425, 1374, 1287, 1153, 1090, 1023, 951, 932	201.4, 134.6, 123.1, 121.0, 51.4, 32.3, 31.8, 31.1, 28.9, 26.1, 22.2	9.55 (brs, 1 H), 6.10 (dt, $J = 9.8, 3.4$ Hz, 1 H), 5.9 (dd, $J = 9.8, 6.3$ Hz, 1 H), 3.13 (brs, 1 H), 2.71 (dt, $J = 11.2, 3.9$ Hz, 1 H), 2.52 (brs, 1 H), 2.40 (dd, $J = 19.5, 6.8$ Hz, 1 H), 2.24 (brs, 1 H), 1.90-1.83 (m, 4 H), 1.60 (m, 1 H)
15a	189	189.1153 (189.1145)	3392, 3048, 3030, 2930, 2252, 1707, 1424, 1354, 1285, 1243, 1178	207.5, 133.3, 124.6, 121.6, 50.0, 33.4, 30.7, 29.6, 27.7, 26.5, 20.5	5.90 (dd, $J = 9.3, 6.8$ Hz, 1 H), 5.61 (dt, $J = 9.3, 3.2$ Hz, 1 H), 3.07 (m, 1 H), 2.99 (m, 1 H), 2.77 (brs, 1 H), 2.59 (brd, $J = 18.3$ Hz, 1 H), 2.41 (m, 1 H), 2.16 (s, 3 H), 2.03 (dd, $J = 9.28, 4.39$ Hz, 2 H), 1.82 (dd, $J = 18.5, 1.9$ Hz, 1 H), 1.20 (m, 2 H)
15b	189	189.1153 (189.1147)	3064, 2988, 2934, 2308, 1732, 1634, 1442, 1428, 1370, 1302, 1245, 1220, 1180, 1092, 1021, 937	207.0, 133.8, 123.1, 121.2, 52.9, 33.0, 32.0, 31.8, 29.2, 27.0, 26.6, 21.9	6.01 (dt, $J = 9.8, 3.4$ Hz, 1 H), 5.88 (dd, $J = 9.8, 6.2$ Hz, 1 H), 3.15 (brs, 1 H), 2.69 (brd, $J = 11.0$ Hz, 1 H), 2.52 (brs, 1 H), 2.43 (dd, $J = 19.5, 6.8$ Hz, 1 H), 2.25 (brs, 1 H), 2.11 (s, 3 H), 1.86-1.72 (m, 4 H), 1.58 (m, 1 H)
16a	256	256.1466 (256.1446)	3682, 3032, 2934, 2236, 1709, 1604, 1494, 1452, 1422, 1335, 1103, 922	206.3, 133.9, 133.4, 129.4, 128.7, 128.6, 128.0, 126.9, 124.3, 121.0, 49.2, 46.0, 33.3, 30.7, 30.2, 29.3, 27.6, 20.5	7.31 (t, $J = 7.3$ Hz, 2 H), 7.26 (d, $J = 7.0$ Hz, 1 H), 7.16 (d, $J = 7.4$ Hz, 2 H), 5.92 (dt, $J = 9.8, 3.4$ Hz, 1 H), 5.59 (dd, $J = 7.1, 6.4$ Hz, 1 H), 3.77 (s, 2 H), 3.12 (brs, 1 H), 2.93 (d, $J = 11.2$ Hz, 1 H), 2.78 (brs, 1 H), 2.60 (brs, 1 H), 2.42 (m, 1 H), 1.92-1.72 (m, 5 H)
16b	256	256.1466 (256.1448)	3680, 3060, 3032, 2936, 2238, 1710, 1605, 1495, 1451, 1422, 1342, 1283, 1124, 1090, 924	206.3, 133.9, 133.7, 129.2, 128.6, 126.9, 122.9, 121.0, 51.7, 46.0, 33.0, 32.8, 29.3, 27.0, 21.8	7.32 (t, $J = 6.8$ Hz, 2 H), 7.26 (d, $J = 7.3$ Hz, 1 H), 7.16 (d, $J = 7.4$ Hz, 1 H), 6.03 (dt, $J = 9.8, 3.4$ Hz, 1 H), 5.85 (dd, $J = 10.0, 6.4$ Hz, 1 H), 3.75 (s, 2 H), 3.19 (brs, 1 H), 2.67 (d, $J = 11.2$ Hz, 1 H), 2.64 (brs, 1 H), 2.42 (dd, $J = 19.5, 6.8$ Hz, 1 H), 2.40 (brs, 1 H), 1.84-1.78 (m, 4 H), 1.57 (m, 1 H)

Table 6 (continues)

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
17a	161	161.0840 (161.0855)	3484, 3054, 2928, 2852, 2238, 1709, 1607, 1433, 1378, 1306, 1289, 1148, 1086, 1042, 1007, 963, 931, 905	200.4, 128.5, 128.4, 122.2, 54.7, 40.3, 37.8, 35.5, 34.1, 33.0	9.85 (s, 1 H), 5.96 (brdd, $J = 9.0, 6.9$ Hz, 1 H), 5.63 (dt, $J = 9.3, 2.4$ Hz, 1 H), 3.08 (m, 1 H), 3.03 (dd, $J = 9.3, 3.4$ Hz, 1 H), 2.92 (brs, 1 H), 2.85 (brs, 1 H), 2.50 (d, $J = 19.0$ Hz, 1 H), 2.36 (m, 1 H), 2.05 (dd, $J = 13.7, 9.3$ Hz, 1 H), 1.94 (td, $J = 19.1, 2.0$ Hz, 1 H)
18a	175	175.0997 (175.0986)	3040, 2959, 2236, 1707, 1605, 1426, 1360, 1247, 1180, 1092	206.2, 128.6, 127.9, 122.6, 56.2, 41.2, 37.2, 35.5, 34.2, 33.1, 28.4	5.90 (dd, $J = 9.4, 6.9$ Hz, 1 H), 5.56 (dt, $J = 9.3, 3.2$ Hz, 1 H), 3.03 (m, 1 H), 2.97 (d, $J = 7.8, 3.9$ Hz, 2 H), 2.81 (brs, 1 H), 2.58 (d, $J = 18.6$ Hz, 1 H), 2.33 (m, 1 H), 2.22 (s, 3 H), 2.04 (dd, $J = 9.3, 6.9$ Hz, 1 H), 1.84 (dd, $J = 18.6, 1.9$ Hz, 1 H)
18b	175	175.0997 (175.0977)	3030, 2960, 2240, 1706, 1608, 1451, 1360, 1255, 1183	206.0, 128.8, 127.6, 121.2, 57.5, 38.7, 36.4, 35.4, 34.1, 33.7, 28.4	5.99 (dd, $J = 9.8, 6.4$ Hz, 1 H), 5.72 (dt, $J = 9.8, 3.2$ Hz, 1 H), 3.06 (dd, $J = 8.8, 5.4$ Hz, 1 H), 3.01 (dd, $J = 11.2, 5.4$ Hz, 1 H), 2.71 (brs, 1 H), 2.60 (d, $J = 19.1$ Hz, 1 H), 2.57 (brs, 1 H), 2.48 (m, 1 H), 2.18 (s, 3 H), 1.92 (dd, $J = 19.1, 3.2$ Hz, 1 H), 1.82 (dd, $J = 14.2, 6.3$ Hz, 1 H)
19b	251	251.1310 (251.1308)	3044, 2956, 2240, 1708, 1638, 1600, 1495, 1451, 1350, 1232, 1185, 1108, 1075, 1031, 919	205.5, 133.9, 129.3, 128.9, 127.5, 127.1, 121.2, 55.6, 47.9, 38.5, 36.4, 36.3, 34.2, 33.8	7.32 (t, $J = 6.8$ Hz, 2 H), 7.23 (d, $J = 6.8$ Hz, 1 H), 7.16 (d, $J = 6.8$ Hz, 2 H), 6.01 (dd, $J = 9.3, 6.4$ Hz, 1 H), 5.74 (dd, $J = 9.6, 3.9$ Hz, 1 H), 3.78 (s, 2 H), 3.06 (m, 1 H), 3.0 (ddd, $J = 17.0, 11.7, 5.4$ Hz, 1 H), 2.74 (brs, 1 H), 2.66 (brs, 1 H), 2.63 (d, $J = 19.0$ Hz, 1 H), 2.46 (ddd, $J = 11.2, 7.3, 1.9$ Hz, 1 H), 1.94 (dd, $J = 17.5, 2.0$ Hz, 1 H), 1.81 (dd, $J = 14.2, 6.3$ Hz, 1 H)
20	210	210.1255 (210.1252)	2978, 2931, 2860, 2360, 2341, 2040, 1967, 1762, 1635, 1546, 1516	231.7, 173.6, 60.7, 47.7, 45.4, 39.7, 33.2, 31.0, 28.9, 25.7, 22.6, 14.0	4.12 (2 q, $J = 6.8$ Hz, 2 H), 2.87 (brs, 1 H), 2.69 (m, 1 H), 2.53 (dd, $J = 13.2, 8.8$ Hz, 2 H), 2.40 (m, 2 H), 2.09 (m, 2 H), 1.91-1.75 (m, 5 H), 1.30 (t, $J = 7.3$ Hz, 3 H)
22a	163	163.0997 (163.0996)	3686, 3048, 2936, 2308, 2238, 1708, 1606, 1456, 1431, 1426, 1292, 1284, 1111, 935, 923	206.9, 121.3, 46.8, 46.2, 32.8, 32.4, 29.2, 28.6, 28.0, 20.6	2.80 (brs, 1 H), 2.57 (dd, $J = 17.7, 8.4$ Hz, 2 H), 2.38 (m, 2 H), 2.16 (dt, $J = 18.0, 3.6$ Hz, 2 H), 1.92-1.54 (m, 6 H)
22b	163	163.0997 (163.1004)	3686, 3070, 2989, 2306, 2242, 1708, 1607, 1443, 1428, 1283, 1079, 942, 923	209.9, 119.9, 46.2, 39.1, 31.7, 31.0, 30.8, 27.7, 24.9, 24.6	2.81 (brd, $J = 15.3$ Hz, 1 H), 2.77 (brs, 1 H), 2.53 (dd, $J = 19.0, 8.2$ Hz, 1 H), 2.49 (dd, $J = 19.0, 7.8$ Hz, 1 H), 2.16 (m, 3 H), 1.87-1.78 (m, 6 H)

carbonyliron Complex (37): as a yellow oil; 83%.

(1R\*,2S\*,5S\*,9R\*)-2-Carboethoxy-9-formylbicyclo [3.3.1]non-7-ene (9): as a colorless liquid; 82%.

(1R\*,2S\*,5S\*,9R\*)-2-Carboethoxy-9-formylbicyclo [3.3.1]non-7-ene (2,4-Dinitrophenyl)hydrazone (10): as a yellow solid; mp 172-173 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3686, 3060, 2986, 1720, 1618, 1519, 1443, 1438, 1431, 1427, 1335, 1286, 928  $cm^{-1}$ ; <sup>1</sup>H NMR (400 M Hz, CDCl<sub>3</sub>)  $\delta$  10.99 (s, 1 H), 9.12 (d,  $J = 2.5$  Hz, 1 H), 8.30 (dd,  $J = 9.5, 2.5$  Hz, 1 H),

7.89 (d,  $J = 9.5$  Hz, 1 H), 7.46 (d,  $J = 5.0$  Hz, 1 H), 5.99 (dt,  $J = 8.8, 4.5$  Hz, 1 H), 5.65 (dd,  $J = 8.7, 5.8$  Hz, 1 H), 4.15 (2 q,  $J = 7.3$  Hz, 2 H), 2.79 (m, 1 H), 2.62 (m, 2 H), 2.35 (m, 1 H), 1.86-1.66 (m, 6 H), 1.30 (t,  $J = 7.3$  Hz, 3 H); <sup>13</sup>C NMR (100.4 MHz, CDCl<sub>3</sub>)  $\delta$  173.7, 154.0, 145.1, 137.8, 132.3, 129.9, 128.9, 124.3, 123.5, 116.4, 60.4, 45.7, 43.9, 34.9, 33.4, 29.5, 29.2, 20.2, 14.2; MS (70 eV)  $m/z$  (rel intensity) 402 ( $M^+$ , 15), 401 (48), 384 (56), 328 (10), 207 (20), 167 (13), 150 (68), 130 (100); HRMS (EI)  $m/z$  calcd for



Table 7. Spectral Data for Compounds 29, 31, 33, 34, 36, 38

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
29	196	196.1099 (196.1106)	3074, 2964, 1724, 1458, 1376, 1253, 1194, 1039	221.7, 174.7, 60.4, 52.0, 45.3, 36.8, 30.5, 28.1, 25.0, 14.1	4.16 (q, $J = 7.1$ Hz, 2 H), 3.03 (dq, $J = 9.5, 3.8$ Hz, 1 H, Ha), 2.69 (td, $J = 9.5, 4.9$ Hz, 1 H, Hb), 2.52 (q, $J = 7.3$ Hz, 1 H), 2.32 (dd, $J = 8.8, 7.3$ Hz, 2 H), 2.17 (dt, $J = 13.2, 7.8$ Hz, 1 H), 2.08 (m, 1 H), 1.92 (q, $J = 8.0$ Hz, 2 H), 1.82 (m, 2 H), 1.28 (t, $J = 5.0$ Hz, 3 H)
31	210	210.1255 (210.1249)	2970, 1729, 1454, 1375, 1185, 1039	220.8, 173.1, 60.3, 50.4, 48.8, 44.7, 39.9, 31.9, 27.6, 26.3, 14.3, 12.8	4.14 (dq, $J = 4.3, 7.1$ Hz, 2 H), 3.00 (dt, $J = 10.5, 7.7$ Hz, 1 H, Hb), 2.86 (dt, $J = 10.7, 7.0$ Hz, 1 H, Hd), 2.73 (td, $J = 7.7, 1.2$ Hz, 1 H, Hc), 2.31 (qd, $J = 13.8, 6.8$ Hz, 1 H, Ha), 2.16 (dd, $J = 19.4, 7.4$ Hz, 1 H), 1.94 (dd, $J = 10.2, 2.4$ Hz, 1 H), 1.79 (m, 1 H), 1.67 (m, 1 H), 1.61 (m, 1 H), 1.25 (t, $J = 7.1$ Hz, 3 H), 1.01 (d, $J = 6.7$ Hz, 3 H), 1.03 (m, 1 H)
33	210	210.1255 (210.1240)	2968, 1728, 1454, 1378, 1252, 1192, 1035	221.9, 175.4, 60.5, 54.7, 50.5, 44.5, 43.6, 32.4, 30.7, 28.2, 16.4, 14.1	4.14 (m, 2 H), 3.06 (dd, $J = 10.0, 7.2$ Hz, 1 H, Hd), 2.71 (ddd, $J = 10.0, 7.3, 3.2$ Hz, 1 H, He), 2.50 (m, 2 H, Hc, Hf), 2.34 (dd, $J = 18.6, 8.1$ Hz, 1 H, Hb), 2.08 (m, 1 H), 1.94 (m, 1 H, Ha), 1.83 (m, 3 H), 1.25 (t, $J = 7.1$ Hz, 3 H), 1.09 (d, $J = 6.8$ Hz, 3 H)
34	210	210.1255 (210.1261)	2944, 1731, 1446, 1237, 1201, 1174, 1029	220.0, 174.0, 60.2, 48.4, 42.1, 37.3, 36.8, 23.6, 22.2, 20.5, 14.2	4.09 (q, $J = 7.3$ Hz, 2 H), 2.62 (m, 2 H, Hb, Hd), 2.36 (dd, $J = 19.0, 8.0$ Hz, 1 H), 2.20 (dt, $J = 11.9, 6.0$ Hz, 1 H, Ha), 2.13 (dd, $J = 19.0, 6.0$ Hz, 1 H), 1.80 (m, 4 H, Ha and others), 1.54 (m, 2 H), 1.20 (t, $J = 7.0$ Hz, 3 H), 1.13 (m, 2 H)
36	224	224.1412 (224.1410)	2974, 1730, 1423, 1284, 1195, 1172	220.0, 172.1, 60.2, 49.0, 41.8, 40.0, 34.5, 29.3, 24.6, 22.6, 22.0, 16.8, 14.2	4.18 (2 q, $J = 6.9$ Hz, 2 H), 2.78 (ddd, $J = 11.2, 10.3, 5.5$ Hz, 1 H, Ha), 2.71 (ddd, $J = 11.7, 5.5, 3.1$ Hz, 1 H, Hb), 2.49 (dq, $J = 9.6, 7.6$ Hz, 1 H, Hd), 2.29 (td, $J = 11.0, 4.8$ Hz, 1 H, Hc), 2.20 (ddd, $J = 12.0, 10.3, 9.6$ Hz, 1 H, Hf), 1.84 (m, 2 H), 1.68 (m, 2 H), 1.47 (dd, $J = 12.0, 6.9$ Hz, 1 H, He), 1.27 (t, $J = 6.8$ Hz, 3 H), 1.22 (m, 2 H), 1.11 (d, $J = 7.8$ Hz, 3 H)
38	224	224.1412 (224.1410)	2943, 1732, 1631, 1448, 1377, 1286, 1269, 1182, 1032	220.0, 174.5, 60.3, 47.3, 46.6, 41.5, 39.5, 32.0, 25.2, 24.4, 22.3, 19.0, 14.2	4.18 (2 q, $J = 6.9$ Hz, 2 H), 2.76 (m, 2 H, Ha, Hd), 2.60 (8 lines, $J = 8.8, 7.0, 3.3$ Hz, 1 H, Hc), 2.46 (dd, $J = 18.0, 8.3$ Hz, 1 H), 2.26 (dd, $J = 8.8, 7.8$ Hz, 1 H, Hb), 2.08 (dd, $J = 18.0, 3.4$ Hz, 1 H), 1.80 (m, 2 H), 1.68 (m, 1 H), 1.50 (m, 1 H), 1.46 (m, 1 H), 1.29 (t, $J = 7.0$ Hz, 3 H), 1.22 (m, 1 H), 1.09 (d, $J = 7.3$ Hz, 3 H)

C<sub>19</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub> (M<sup>+</sup>) 402.1539, found 402.1547.

(1R\*,2S\*,4S\*,8R\*)-2-Carboethoxy-8-formylbicyclo[3.2.1]oct-6-ene (12a): as a colorless liquid; 25%.

(1R\*,2R\*,4S\*,8R\*)-2-Carboethoxy-8-formylbicyclo[3.2.1]oct-6-ene (12b): as a colorless liquid; 12%.

(1R\*,2S\*,5S\*,9R\*)-2-Carboethoxy-9-acetylbicyclo[3.3.1]non-7-ene (13): as a colorless liquid; 40%.

(1S\*,2S\*,5S\*,9R\*)-2-Cyano-9-formylbicyclo[3.3.1]non-7-ene (14a): as a light orange solid; mp 105.0-05.5 °C (hexane/ethyl acetate); 27%.

(1S\*,2R\*,5S\*,9R\*)-2-Cyano-9-formylbicyclo[3.3.1]non-7-ene (14b): as a red liquid; 52%

(1S\*,2S\*,5S\*,9R\*)-2-Cyano-9-acetylbicyclo[3.3.1]non-7-ene (15a): as a yellow liquid; 14%.

(1S\*,2R\*,5S\*,9R\*)-2-Cyano-9-acetylbicyclo[3.3.1]non-7-ene (15b): as a colorless solid; mp 112-112.5 °C (hexane/ethyl acetate); 28%.

(1S\*,2S\*,5S\*,9R\*)-2-Cyano-9-(2-phenyl-1-oxoethyl)bicyclo[3.3.1]non-7-ene (16a): as a yellow liquid; 16%.

(1S\*,2R\*,5S\*,9R\*)-2-Cyano-9-(2-phenyl-1-oxoethyl)

Table 8. Spectral Data for Compounds 57

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
57a	328	328.0398 (328.0407)	3069, 2993, 2961, 2928, 1979, 1912, 1883, 1728, 1620, 1470, 1426, 1375, 1157	231.6, 172.8, 99.1, 97.8, 66.3, 60.4, 35.3, 33.4, 28.6, 14.2	5.97 (brm, 2 H), 4.82 (brm, 2 H), 4.08 (q, $J = 7.0$ Hz, 2 H), 3.69 (t, $J = 8.5$ Hz, 2 H), 2.96 (m, 1 H), 2.02 (t, $J = 7.5$ Hz, 2 H), 1.23 (t, $J = 7.0$ Hz, 3 H), 0.56 (q, $J = 7.5$ Hz, 2 H)
57b	342	342.0554 (342.0556)	3020, 2996, 2942, 1977, 1910, 1881, 1728, 1609, 1424, 1101	231.8, 173.2, 98.9, 97.8, 67.2, 60.3, 38.2, 35.8, 33.7, 19.2, 14.2	5.96 (brm, 2 H), 4.79 (brm, 2 H), 4.09 (q, $J = 7.3$ Hz, 2 H), 3.71 (t, $J = 8.8$ Hz, 2 H), 2.92 (m, 1 H), 2.08 (t, $J = 7.8$ Hz, 2 H), 1.36 (q, $J = 7.8$ Hz, 2 H), 1.23 (t, $J = 7.3$ Hz, 3 H), 0.27 (q, $J = 7.8$ Hz, 2 H)
57c	356	356.0710 (356.0712)	3067, 3046, 2992, 2940, 1977, 1910, 1879, 1728, 1620, 1424, 1252	231.9, 173.4, 98.8, 97.8, 67.7, 60.2, 38.6, 35.9, 34.0, 24.3, 23.2, 14.2	5.95 (brs, 2 H), 4.77 (brs, 2 H), 4.10 (q, $J = 7.2$ Hz, 2 H), 3.70 (t, $J = 8.6$ Hz, 2 H), 2.90 (m, 1 H), 2.17 (t, $J = 7.3$ Hz, 2 H), 1.39 (m, 2 H), 1.23 (t, $J = 7.2$ Hz, 3 H), 1.06 (m, 2 H), 0.25 (m, 2 H)
57d	281	281.0141 (281.0143)	3053, 2249, 1981, 1915, 1888, 1609, 1530, 1472, 1424	231.1, 118.8, 99.1, 97.2, 64.0, 34.9, 33.0, 12.0	6.00 (brs, 2 H), 4.87 (brs, 2 H), 3.68 (t, $J = 8.6$ Hz, 2 H), 3.10 (m, 1 H), 2.06 (t, $J = 7.3$ Hz, 2 H), 0.55 (q, $J = 7.3$ Hz, 2 H)
57e	295	295.0297 (295.0300)	3067, 3046, 2994, 2930, 2857, 2251, 1979, 1913, 1883, 1609, 1424	231.5, 119.0, 97.8, 92.6, 66.0, 37.6, 35.5, 19.9, 16.8	5.99 (brs, 2 H), 4.82 (m, 2 H), 3.68 (t, $J = 8.6$ Hz, 2 H), 2.95 (m, 1 H), 2.15 (t, $J = 7.3$ Hz, 2 H), 1.40 (m, 2 H), 0.40 (q, $J = 7.8$ Hz, 2 H)
57f	309	309.0453 (309.0458)	3040, 2942, 2863, 2251, 1977, 1906, 1882, 1470, 1425, 1373	231.7, 119.3, 98.9, 97.8, 67.0, 38.0, 35.9, 24.8, 22.9, 16.9	5.97 (brs, 2 H), 4.80 (m, 2 H), 3.70 (t, $J = 8.8$ Hz, 2 H), 2.92 (m, 1 H), 2.23 (t, $J = 7.1$ Hz, 2 H), 1.44 (m, 2 H), 1.20 (m, 2 H), 0.27 (q, $J = 7.8$ Hz, 2 H)
57g	318	318.0344 (318.0341)	3082, 3030, 1977, 1912, 1883, 1609, 1424	232.0, 137.0, 129.5, 128.6, 126.6, 99.4, 98.1, 67.7, 45.0, 38.5	7.22 (m, 3 H), 6.94 (m, 2 H), 6.03 (m, 2 H), 4.85 (m, 2 H), 3.64 (t, $J = 8.8$ Hz, 2 H), 3.20 (m, 1 H), 1.52 (d, $J = 7.8$ Hz, 2 H)
57h	268	268.0188 (268.0187)	3073, 3040, 1977, 1912, 1881, 1640, 1607, 1424, 1277, 1258	231.7, 132.6, 117.4, 99.0, 97.8, 67.4, 43.2, 36.1	6.08 (m, 2 H), 5.53 (m, 1 H), 5.05-4.90 (m, 4 H), 3.81 (t, $J = 8.8$ Hz, 2 H), 3.12 (m, 1 H), 1.10 (t, $J = 7.3$ Hz, 2 H)

hyl)bicyclo[3.3.1]non-7-ene (16b): as a colorless solid; mp 122.0-122.5 °C; 33%.

(1S\*,2S\*,4S\*,8R\*)-2-Cyano-8-formylbicyclo[3.2.1]-oct-6-ene (17a): 28% as a yellow oil; 28%.

17b: as a colorless solid; 17%. Compound 17b slowly decomposed in the air. Further identification of 17b was not successful.

(1S\*,2S\*,4S\*,8R\*)-2-Cyano-8-acetylbicyclo[3.2.1]-oct-6-ene (18a): as a yellow oil; 9%.

(1S\*,2R\*,4S\*,8R\*)-2-Cyano-8-acetylbicyclo[3.2.1]-oct-6-ene (18b): as a colorless liquid; 6%.

(1S\*,2R\*,4S\*,8R\*)-8-(2-Phenyl-1-oxoethyl)bicy-

clo[3.2.1]oct-6-ene (19b): 14% Only 19b was isolated as a colorless and analytically pure compound.

19a: 2%.

(1R\*,2S\*,5S\*)-2-Carboethoxy-8-oxobicyclo[3.3.1]nonane (20): as a colorless oil; 74%.

(1R\*,2S\*,5S\*)-2-Cyano-8-oxobicyclo[3.3.1]nonane (22a): as a white solid; mp 103.0-103.5 °C; 21%.

(1R\*,2R\*,5S\*)-2-Cyano-8-oxobicyclo[3.3.1]nonane (22b): as a colorless liquid; 21%.

(1R\*,2S\*,6S\*,10R\*)-2-Cyano-10-formylbicyclo-[4.3.1]dec-8-ene (2,4-nitrophenyl)hydrazone (26): as a yellow solid; mp 155-156 °C; 5%; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3682, 3306,

Table 9. Spectral Data for Compounds 65

Compd. No.	MS(EI) $m/z, M^+$	High MS(EI) Calcd.(Found)	IR(CH <sub>2</sub> Cl <sub>2</sub> ) $cm^{-1}$	<sup>13</sup> C NMR (100.4 MHz) $\delta$	<sup>1</sup> H NMR (400.0 MHz) $\delta$
65a	428	428.0885 (428.0887)	2990, 1932, 1849, 1731, 1373, 1242, 1046	236.0, 235.5, 173.7, 92.0, 60.2, 59.0, 56.8, 55.7, 39.0, 34.3, 31.7, 27.7, 25.2, 23.2, 18.7, 14.2	5.28 (s, 5 H, Cp), 4.18 (m, 3 H, C2 and C12), 3.72 (m, 1 H, C1 or C3), 3.63 (m, 1 H, C1 or C3), 2.30 (t, 2 H, $J = 7.32$ Hz, C10), 1.95 (m, 1 H, C6), 1.71-1.39 (m, 8 H, C4, C6, C7, C8 and C9), 1.26 (t, 3 H, $J = 7.32$ Hz, C13), 0.82 (m, 1 H, C5), 0.50 (m, 1 H, C5)
65b	414	414.0728 (414.0709)	3078, 2972, 1934, 1851, 1727, 1606, 1459, 1430, 1375, 1349, 1241, 1192, 1096, 1029	236.0, 235.5, 173.7, 92.0, 60.2, 58.6, 56.9, 55.7, 38.8, 34.5, 31.5, 23.5, 23.3, 18.7, 14.2	5.29 (s, 5 H, Cp), 4.16-4.11 (m, 3 H, C2 and C11), 3.70 (m, 1 H, C1 or C3), 3.63 (m, 1 H, C1 or C3), 2.27-2.33 (m, 3 H, C4 and C9), 1.95 (m, 1 H, C6), 1.73-1.42 (m, 5H, C6, C7 and C8), 1.25 (dd, 3 H, $J = 6.91, 6.78$ Hz, C12), 0.86 (m, 1 H, C5), 0.50 (m, 1 H, C5)
65c	400	400.0566 (400.0576)	3050, 2936, 1933, 1852, 1726, 1447, 1423, 1373, 1183, 1112, 1071, 1034	235.9, 235.4, 173.9, 92.1, 60.3, 57.8, 57.0, 55.8, 34.1, 33.1, 31.6, 23.1, 18.7, 14.2	5.26 (s, 5 H, Cp), 4.16-4.07 (m, 3 H), 3.68 (m, 1 H), 3.56 (m, 1 H), 2.35 (t, $J = 7.8$ Hz, 2 H), 1.93 (m, 1 H), 1.82 (m, 1H), 1.71 (m, 2 H), 1.67 (m, 1 H), 1.23 (t, $J = 7.1$ Hz, 3 H), 0.79 (m, 1 H), 0.46 (m, 1H)
65d	381	381.0626 (381.0630)	3082, 2932, 2306, 1993, 1851, 1609, 1458, 1275, 1182, 1160, 1113, 1011	235.0, 234.4, 118.8, 91.1, 57.3, 55.9, 54.7, 37.5, 30.6, 26.2, 24.6, 22.4, 17.8, 16.2	5.29 (s, 5 H, Cp), 4.16 (m, 1 H, C2), 3.69 (m, 1 H, C1 or C3), 3.59 (m, 1 H, C1 or C3), 2.36 (t, $J = 7.32$ Hz, 2 H, C10), 1.96 (m, 1 H, C6), 1.78-1.57 (m, 7 H, C7, C8, C9 and C4), 1.25 (m, 1 H, C6), 0.79 (m, 1 H, C5), 0.51 (m, 1 H, C5)
65e	367	367.0470 (367.0450)	3060, 2930, 2306, 1935, 1853, 1606, 1423, 1277, 1252, 1160, 1113, 1011	235.9, 234.9, 120.0, 92.1, 58.0, 57.0, 55.7, 38.2, 31.3, 24.0, 23.2, 18.6, 17.4	5.29 (s, 5 H, Cp), 4.15 (m, 1 H, C2), 3.71 (m, 1 H, C1 or C3), 3.58 (m, 1 H, C1 or C3), 2.34 (m, 2 H, C9), 1.96 (m, 1 H, C6), 1.78-1.57 (m, 5 H, C7, C8 and C4), 1.24 (m, 1 H, C6), 0.79 (m, 1 H, C5), 0.51 (m, 1 H, C5)
65f	414	414.0729 (414.0739)	3062, 2936, 1934, 1851, 1731, 1606, 1425, 1367, 1240, 1038	236.0, 235.6, 171.2, 92.0, 64.5, 58.9, 56.9, 55.7, 38.9, 31.7, 28.8, 24.5, 23.2, 23.0, 18.7	5.30 (s, 5 H, Cp), 4.18-4.03 (m, 3 H, C2 and C10), 3.71-3.60 (m, 2 H, C1 and C3), 2.31 (m, 1 H, C4), 2.06 (s, 3 H, C12), 1.95 (m, 1 H, C6), 1.66-1.22 (m, 7 H, C6, C7, C8 and C9), 0.8 (m, 1 H, C5), 0.5 (m, 1 H, C5)
65g	476	476.0885 (476.0875)	3085, 2936, 1934, 1851, 1712, 1605, 1439, 1423, 1314, 1254, 1176, 1071	236.1, 235.5, 166.6, 132.8, 130.5, 129.5, 128.3, 92.0, 64.9, 58.9, 56.9, 55.7, 38.9, 31.7, 28.9, 24.6, 23.3, 18.7	8.05-8.00 (m, 2 H, Ph), 7.54-7.39 (m, 3 H, Ph), 5.26 (s, 5 H, Cp), 4.31 (dd, 2 H, $J = 6.50, 6.59$ Hz, C10), 4.12 (dd, 1 H, $J = 7.18, 7.19$ Hz, C2), 3.68-3.58 (m, 2 H, C1 and C3), 1.90 (m, 1 H, C6), 1.75 (m, 1 H, C4), 1.58-1.48 (m, 5 H, C7, C8 and C9), 1.27 (m, 1 H, C9), 0.86-0.79 (m, 2 H, C5 and C6), 0.45 (m, 1 H, C5)
65h	390	390.0517 (390.0511)	3060, 2930, 1935, 1852, 1606, 1425, 1253	235.9, 235.4, 141.2, 129.2, 128.2, 125.8, 92.0, 58.4, 56.7, 55.9, 45.7, 34.0, 22.9, 18.6	7.26-7.08 (m, 5 H, Ph), 5.22 (s, 5 H, Cp), 4.12 (dd, 1 H, $J = 7.18, 7.14$ Hz, C2), 3.67 (m, 1 H, C1 or C3), 3.45 (m, 1 H, C1 or C3), 2.68 (m, 1 H, C7), 1.99-1.92 (m, 2 H, C4 and C6), 1.57 (m, 1 H, C6), 0.77 (m, 1H, C5), 0.38 (m, 1 H, C5)
65i	356	356.0668 (356.0670)	2928, 2860, 1931, 1849, 1620, 1457, 1422	236.1, 235.6, 92.0, 59.5, 26.9, 55.5, 39.1, 31.7, 30.4, 23.3, 18.7, 14.6	5.28 (s, 5 H, Cp), 4.15 (dd, 1 H, $J = 6.84, 7.36$ Hz, C2), 3.70 (m, 1 H, C1 or C3), 3.66 (m, 1 H, C1 or C3), 1.93 (m, 1 H, C6), 1.68 (m, 1 H, C4), 1.58 (m, 1 H, C7), 1.47 (m, 1 H, C7), 1.40-1.33 (m, 5 H, C6, C8 and C9), 0.90 (dd, 3 H, $J = 6.84, 7.32$ Hz, C10), 0.82 (m, 1 H, C5), 0.46 (m, 1 H, C5)

3060, 2984, 2932, 2238, 2042, 1617, 1594, 1517, 1425, 1334, 1284, 1139, 1086  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.98 (s, 1 H) 9.04 (d,  $J = 2.44$  Hz, 1 H) 8.23 (dd,  $J = 9.28$ , 2.44 Hz, 1 H), 7.83 (d,  $J = 9.28$  Hz, 1 H), 7.44 (d,  $J = 3.91$  Hz, 1 H), 5.94 (dd,  $J = 8.0$ , 4.8 Hz, 1 H), 5.55 (dt,  $J = 8.0$ , 3.1 Hz, 1 H), 3.15 (br s, 1 H), 2.96 (br d,  $J = 12.7$  Hz, 2 H), 2.36 (m, 2 H), 1.78-1.66 (m, 3 H), 1.54 (m, 4 H);  $^{13}\text{C}$  NMR (100.4 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 145.0, 138.0, 130.1, 130.0, 129.5, 129.0, 126.2, 123.4, 116.6, 39.2, 37.4, 35.2, 33.4, 30.8, 30.4, 29.7, 21.6; MS (70 eV)  $m/z$  (rel intensity) 369 ( $\text{M}^+$ , 14), 285 (18), 227 (18), 187 (37), 145 (37), 91 (100); HRMS (EI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_5\text{O}_4$  ( $\text{M}^+$ ) 369.1437, found 369.1445.

**(1R\*,2R\*,5R\*)-2-Carbethoxy-6-oxobicyclo[3.3.0]octane (29):** as a colorless liquid; 55%.

**(1R\*,2R\*,5R\*,7S\*)-2-Carbethoxy-7-methyl-6-oxobicyclo[3.3.0]octane (31):** as a colorless liquid; 34%.

**(1R\*,2R\*,5R\*,8R\*)-2-Carbethoxy-8-methyl-6-oxobicyclo[3.3.0]octane (33):** as a colorless liquid; 30%.

**(1R\*,2R\*,6R\*)-2-Carbethoxy-7-oxobicyclo[4.3.0]nonane (34):** as a colorless liquid; 54%.

**(1R\*,2R\*,6R\*,8S\*)-2-Carbethoxy-8-methyl-7-oxobicyclo[4.3.0]nonane (36):** as a colorless liquid; 25%.

**(1R\*,2R\*,6R\*,9S\*)-2-Carbethoxy-9-methyl-7-oxobicyclo[4.3.0]nonane (38):** as a colorless liquid; 28%.

**[Ethyl *exo*-3-[(1-6- $\eta$ )-cycloheptatrien-7-yl]-propionate]tricarbonylchromium (57a):** as a brown-red oil; 96%.

**[Ethyl *exo*-4-[(1-6- $\eta$ )-cycloheptatrien-7-yl]-butyrate]tricarbonylchromium (57b):** as a brown-red oil; 96%.

**[Ethyl *exo*-5-[(1-6- $\eta$ )-cycloheptatrien-7-yl]-valerate]tricarbonylchromium (57c):** as a brown-red oil; 88%.

**[*exo*-3-[(1-6- $\eta$ )-Cycloheptatrien-7-yl]propionitrile]tricarbonylchromium (57d):** as a brown-red oil; 69%.

**[*exo*-4-[(1-6- $\eta$ )-Cycloheptatrien-7-yl]butyronitrile]tricarbonylchromium (57e):** as a brown-red oil; 69%.

**[*exo*-5-[(1-6- $\eta$ )-Cycloheptatrien-7-yl]valeronitrile]tricarbonylchromium (57f):** as a brown-red oil; 96%.

**[*exo*-Phenyl[(1-6- $\eta$ )-cycloheptatrien-7-yl]methane]tricarbonylchromium (57g):** as a brown-red oil; 89%.

**[*exo*-3-[(1-6- $\eta$ )-Cycloheptatrien-7-yl]propene]tricarbonylchromium (57h):** as a brown-red oil; 84%.

**10-(Ethoxycarbonyl)bicyclo[5.3.0]dec-1(7),2-diene (58a) and 8-(Ethoxycarbonyl)bicyclo[5.3.0]dec-1(7),2-diene (58b):** IR ( $\text{CH}_2\text{Cl}_2$ ) 2996, 2930, 2870, 1725, 1609, 1424, 1375, 1182  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  5.82-5.72 (m, 2 H), 4.18-4.09 (m, 2 H), 3.47 (m, 1 H), 2.65-1.74 (m, 10 H), 1.28-1.24 (m, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.4 MHz)  $\delta$  175.6, 175.1, 144.8, 137.6, 135.4, 133.3, 132.2,

130.1, 124.3, 123.3, 60.3, 56.7, 55.3, 38.9, 37.5, 32.3, 31.1, 30.9, 30.7, 26.9, 26.7, 24.3, 24.1, 14.2; MS (30 eV)  $m/z$  (rel intensity) 206 ( $\text{M}^+$ , 27), 133 (100), 119 (11), 105 (19), 91 (32); HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_2$  206.1302, Found 206.1312.

**(1S\*,7R\*,11S\*)-2-Acetyl-11-(ethoxycarbonyl)bicyclo[5.4.0]undec-2,4-diene (62):** IR ( $\text{CH}_2\text{Cl}_2$ ) 3072, 3055, 2995, 2940, 1723, 1659, 1601, 1427, 1375, 1182  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz)  $\delta$  6.84 (d,  $J = 7.8$  Hz, 1 H), 6.14 (dd,  $J = 10.7$ , 8.3 Hz, 1 H), 5.91 (m, 1 H), 4.14 (q,  $J = 6.8$  Hz, 2 H), 3.26 (dd,  $J = 12.0$ , 2.8 Hz, 1 H), 2.71-2.61 (m, 2 H), 2.44 (m, 1 H), 2.34 (s, 3 H), 2.12 (m, 1 H), 1.82-1.23 (m, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.4 MHz)  $\delta$  199.4, 174.3, 144.8, 139.5, 133.7, 122.8, 60.0, 47.3, 41.8, 34.8, 27.8, 27.6, 26.1, 25.5, 21.8, 14.1; MS (30 eV)  $m/z$  (rel intensity) 262 ( $\text{M}^+$ , 77), 216 (23), 188 (37), 145 (100), 105 (9), 91 (17); HRMS (EI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3$  262.1563, Found 262.1567.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[Ethyl 4-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]pentarate] molybdenum (65a):** as a yellow oil; 90%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[Ethyl 4-*exo*-[(1-3-*h*)-cyclohexen-4-yl]butyrate] molybdenum (65b):** as a yellow oil; 90%.

**Dicarbonyl( $\eta^5$ -Cyclopentadienyl)[Ethyl 3-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]propionate] molybdenum (65c):** as a yellow oil; 73%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[4-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]pentanonitrile] molybdenum (65d):** as a yellow oil; 58%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[4-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]butyronitrile] molybdenum (65e):** as a yellow oil; 41%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[4-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]butyl acetate] molybdenum (65f):** as a yellow oil; 51%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[4-*exo*-[(1-3- $\eta$ )-cyclohexen-4-yl]butyl benzoate] molybdenum (65g):** as a yellow oil; 57%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[(1-3- $\eta$ )-cyclohexen-4-yl]phenylmethyl] molybdenum (65h):** as a yellow oil; 57%.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[4-*exo*-(1-3- $\eta$ )-cyclohexen-4-yl]n-butyl] molybdenum (65i):** 18%.

**2-Hydroxycyclohex-3-enyl propionic acid Lactone (68):** IR ( $\text{CH}_2\text{Cl}_2$ ) 3022, 2930, 1724, 1432, 1360, 1335, 1206, 1048  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  6.02 (m, 1 H), 5.82 (m, 1 H), 4.78 (br m, 1 H), 2.52 (m, 2 H), 2.21-2.00 (m, 4 H), 1.73-1.60 (m, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.4 MHz)  $\delta$  172.1, 132.7, 124.5, 74.9, 30.9, 28.3, 24.1, 24.0, 23.7; MS (30 eV)  $m/z$  (rel intensity) 152 ( $\text{M}^+$ , 48), 124 (38), 96 (52),

80 (86), 67 (26), 55 (100); HRMS (EI)  $m/z$  calcd for  $C_9H_{12}O_2$  152.0834, Found 152.0928.

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Functionalized zinc-copper reagents; Intramolecular cyclization.

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