Alkylation of the (η4-Cyclohexa-1,3-diene)(η5-cyclopentadienyl)(dicarbonyl)-molybdenum Hexafluorophosphate with the Highly Functionalized Zinc–Copper Reagents RCu(CN)ZnI

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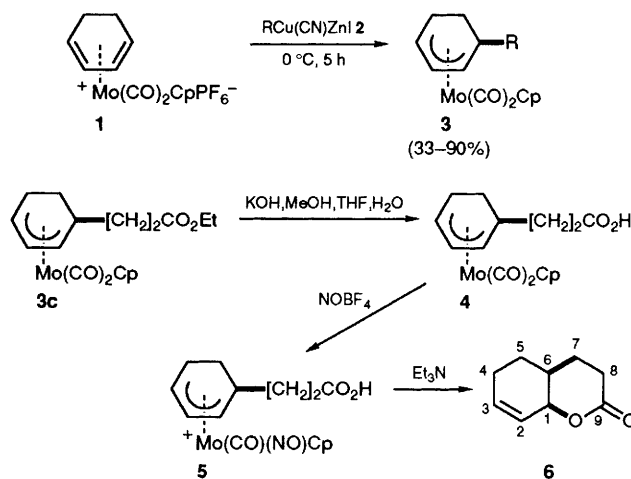
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The addition of a variety of the highly functionalized zinc–copper reagents RCu(CN)ZnI to the title cation at the terminus of the coordinated diene ligand gives [Mo(π-allyl)(CO)₂(Cp)] (Cp = cyclopentadienyl) complexes with the functionalized side-chain at the C-4 position of the ring: intramolecular cyclisation of the (π-allyl)molybdenum complex **4** containing a pendant propanoic acid unit generates the δ-lactone derivative **6**.

The addition of various nucleophiles at the terminal position of the [Mo(η4-cyclohexa-1,3-diene)(CO)₂(Cp)]+ cation **1** offers an easy access to a variety of [Mo(π-allyl)(CO)₂(Cp)] complexes (Cp = cyclopentadienyl).[1] Detachment of the metal moiety can be performed efficiently by using iodolactonisation–ozonisation procedures to give useful organic intermediates.[2] Alternatively, the resulting (π-allyl)molybdenum complexes can be further activated towards nucleophilic additions by hydride abstraction on treatment with triphenylcarbenium hexafluorophosphate (Ph₃CPF₆) 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.[3] 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 **1**.[1] Among these, the stabilized enolates add most efficiently to the cation. However, the rections can only introduce a two carbon atom side chain at the C-4 position of the [Mo(π-allyl)(CO)₂(Cp)] complexes. Surprisingly, reports on the addition of organocopper derivatives to cation **1** are rare[4] and the reactions proceed in low yields (ca. 35%);[4] this has been confirmed in our preliminary investigations (Table 1, 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 transmetallation of the corresponding functionalized zinc organometallic compounds with CuCN·2LiCl in tetrahydrofuran (THF).[5] We now report that the highly functionalized copper reagents **2a–h** add efficiently at the terminal position of the coordinated diene ligand of cation **1** to generate [Mo(π-allyl)(CO)₂(Cp)] complexes **3a–h** with a functionalized side-chain at the C-4 position. The reaction of **2i** 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 **1** was prepared in five steps from cyclohexene (62% overall yield) following the literature procedures.[1] Slow

addition of a THF solution of the highly functionalized copper reagents RCu(CN)ZnI (1.2 mol. equiv.) to a stirred suspension of cation **1** 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 [Mo(π-allyl)(CO)₂(Cp)] complexes **3a–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 **2c** appeared to be less reactive even in the presence of hexamethylphosphoramide (HMPA).[6] The *trans* relationship between the nucleophile and the metal moiety of complex **3** was assigned based upon comparison of their ¹H NMR spectra with the spectra of [Mo(π-allyl)(CO)₂(Cp)] complexes made by Faller and Pearson. Further manipulation of the resulting complexes **3** was demonstrated as follows. Hydrolysis of the ester **3c** using KOH in MeOH–THF–H₂O at 23 °C gave the corresponding acid **4** in 87% yield. The carboxylic acid **4** was converted to cation **5** by ligand exchange (NOBF₄), followed by addition of
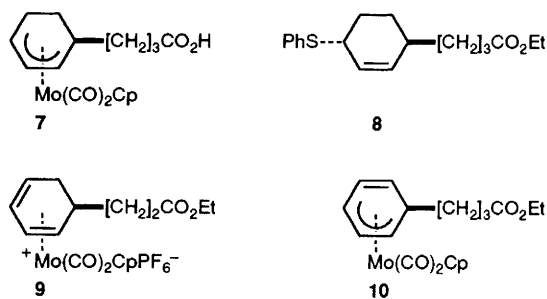
Scheme 1 Formation of functionalized [Mo(π-allyl)(CO)₂(Cp)] complexes **3** and the δ-lactone **6**. R may contain an ester, a nitrile, an acetoxy, a benzoyloxy or a benzyl group.

Table 1 Reaction of cation **1** with the highly functionalized RCu(CN)ZnI

Entry	RCu(CN)ZnI **2**	Product **3**[a]	Yield (%)
1	**a**; R = [CH₂]₄CO₂Et	**3a**	90
2	**b**; R = [CH₂]₃CO₂Et	**3b**	90
3	**c**; R = [CH₂]₂CO₂Et	**3c**	33
4	**d**; R = [CH₂]₄CN	**3d**	58
5	**e**; R = [CH₂]₃CN	**3e**	41
6	**f**; R = [CH₂]₄OAc	**3f**	51
7	**g**; R = [CH₂]₄OCOPh	**3g**	57
8	**h**; R = CH₂Ph	**3h**	57
9	(**2i**; Bu₂CuLi)	**3i**	18

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

triethylamine to produce the δ-lactone **6** (35%, two steps).[7] The δ-lactone **6** 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 **5** (I_2, MeCN, 23 °C) also gave the lactone **6** in 27% yield. The cis-stereochemistry of the δ-lactone **6** 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-γ-lactones reported by Pearson.[7] However, under the same reaction conditions, intramolecular cyclisation of the carboxylic acid **7**, derived from **3b** (Table 1, entry 2), did not occur. This might be due to the difficulty of formation of the seven-membered-ring. Bromination of complex **3b** (bromine, 1.1 mol. equiv.; CH_2Cl_2; −78 °C; 2 h), followed by addition of NaSPh (THF, −78 °C, 3 h) gave the cyclohexene derivative **8** in 53% yield.[8] Complex **3b** was further converted into the cationic diene complex **9** by treatment with Ph_3CPF_6. Deprotonation of **9** with lithium diisopropylamide (LDA) gave complex **10** as the major product.

In conclusion, we have demonstrated that the addition of the highly functionalized copper reagents RCu(CN)ZnI to the [Mo(η^4-cyclohexa-1,3-diene)(CO)$_2$(Cp)] cation **1** occurred at the terminus of the diene system to furnish polyfunctionalized [Mo(π-allyl)(CO)$_2$Cp] complexes. Further activation of the resulting (π-allyl)molybdenum complexes to the new cations can be accomplished by ligand exchange using NOBF$_4$ or by hydride abstraction adding Ph_3CPF_6.

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