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Preliminary communication

New Molybdenocene Dihydrocarbyls

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Abstract

The preparation and characterization of $[Mo(\eta^5\text{-}C_5H_5)_2R_2)]$ $(R = C_2H_5, {}^nC_4H_9, C_6H_5)$ and $[Mo(\eta^5\text{-}C_5H_5)_2R_2]$ PF_6 $(R = C_2H_5, {}^nC_4H_9)$ are described. Cyclic voltammograms in CH_3CN and CH_2Cl_2 show that the reversible 1-electron oxidation of $[Mo(\eta^5\text{-}C_5H_5)_2R_2]$ $(R = C_2H_5, {}^nC_4H_9)$ occurs at higher potentials (ca. −210 mV) than that for $[Mo(\eta^5\text{-}C_5H_5)_2(CH_3)_2]$ (ca. −270 mV).

The results of thermochemical [1] and photochemical [2] studies on $[M(Cp)_2)(CH_3)_2]$ * $(M = Mo,W)$ complexes led us to attempt the preparation of higher dihydrocarbyl derivatives $[M(Cp)_2R_2]$ bearing either bulkier and/or β-hydrogen-containing R groups. A number of W derivatives of this type were recently reported by Cooper and his coworkers, who described some of their very interesting chemistry and electrochemistry [3]. However, except for the metallocycle $[Mo(Cp)_2(CH_2)_4]$ [4] no β-hydrogen containing $[Mo(Cp)_2R_2]$ compounds have been reported. The reason for this seems to lie in the fact that the reaction of the dihalides $[Mo(Cp)_2X_2]$ with RMgX $(R = C_2H_5, {}^iC_3H_7)$ leads to $[Mo(Cp)_2H(\eta^2\text{-alkene})]^+$ through facile β-elimination in the intermediate $[Mo(Cp)_2R]^+$ generated by halide abstraction from $[Mo(Cp)_2$ RX] (5). Introduction of AlR_3 $(R = C_2H_5, {}^nC_4H_9)$ in place of RMgX in reactions in toluene gave, in our hands, the same result. Since Et_2O coordinates strongly with AlR_3 we thought that this solvent might to some extent retard the chloride abstraction from $[Mo(Cp)_2XR]$ and so favour the formation of the sought dialkyl. This was, indeed, found to be the case and we were able to prepare $[Mo(Cp)_2R_2]$ (**1**, $R = C_2H_5$;**2**, $R = {}^nC_4H_9$) from $[Mo(Cp)_2Cl_2]$ and the corresponding trialkylaluminium in Et_2O. However, these reactions were found to be difficult to reproduce. The observation that $Li[Al({}^nC_4H_9)_4]$ gave **2** much more cleanly than $Al({}^nC_4H_9)_3$ prompted us to try RLi reagents.

Treatment of a suspension of $[Mo(Cp)_2I_2]$ in Et_2O at −10°C with a 100% excess of RLi $(R = C_2H_5; {}^nC_4H_9)$ followed by warming to room temperature gives

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* $Cp = \eta^5\text{-}C_5H_5$ throughout this paper

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Table 1

Analytical and ^{1}H NMR data

Compound	m/e [a]	Analysis found (calc) (%)		^{1}H NMR
		C	H	δ(multiplicity, area, assignment)
1 $[Mo(Cp)_2(C_2H_5)_2]$	286	59.4(59.2)	7.2(7.1)	4.5(s,10, η-$C_5\mathit{H}_5$), 1.37(t, $J_{H,H}$ 7Hz, 6, $C\mathit{H}_3$), 0.69(q, J_{H-H} 7Hz, 4, $C\mathit{H}_2$) [b]
2 $[Mo(Cp)_2(^nC_4H_9)_2]$	342	63.2(63.5)	8.5(8.3)	4.07(s, 10, η-$C_5\mathit{H}_5$), 1.59–0.34(c, 18, $C_4\mathit{H}_9$) [b]
3 $[Mo(Cp)_2(C_6H_5)_2]$	–	–	–	7.43–7.34(c, 4, o-$C_6\mathit{H}_5$), 6.8–6.74(c, 6, m,p-$C_6\mathit{H}_5$), 4.94(s, 10, η-$C_5\mathit{H}_5$) [c]
4 $[Mo(Cp)_2(C_2H_5)_2]\,PF_6$	–	38.8(39.1)	4.5(4.7)	–
5 $[Mo(Cp)_2(^nC_4H_9)_2]\,PF_6$	–	44.9(44.5)	5.8(5.8)	–

[a] Parent ion peak (^{98}Mo). [b] δ relative to external TMS, in C_6H_6-d_6. [c] δ relative to internal TMS in Me_2CO-d_6.

an orange solution. The unchanged RLi is destroyed with EtOH, the solution evaporated and the orange products extracted with pentane and recrystallized from EtOH at −60°C. The yields, although not very high (ca. 20%) are reproducible when the di-iodide is used as starting material. The given formulation is confirmed by the analytical and spectroscopic data shown in Table 1. The $Mo(Cp)_2$ moiety is recognized by the characteristic peaks in the IR spectrum and the sharp singlet at ca. δ 4 ppm in the ^{1}H NMR spectrum. The parent-ion peaks of **1** and **2** were observed in the mass spectra.

A crystal structure study of **2** has confirmed this structure and will be described elsewhere in connection with thermochemical studies on **1** and **2** [6].

Reaction of $[Mo(Cp)_2Br_2]$ with PhMgBr [7 *] led to very small (ca. 5%) yield of a recrystallized dark orange compound **3** which is rather thermally unstable. We could not obtain reproducible elemental analyses or mass spectra owing to the thermal lability of **3**, but the spectroscopic data (Table 1) are consistent with the formulation as $[Mo(Cp)_2Ph_2]$. Typical C_6H_5 and $Mo(Cp)_2$ peaks are present in the IR spectrum. The ^{1}H NMR spectrum shows the C_5H_5 singlet and two complex resonances for the C_6H_5 protons similar to those reported for the $[W(Cp)_2Me(Ph)]$ analog [8].

Both **1** and **2** react readily with anhydrous HCl, in Et_2O, to give $[Mo(Cp)_2Cl_2]$ and the corresponding alkanes. Reaction of **1** and **2** with $[Fe(Cp)_2]\,PF_6$, in Me_2CO gives (after extraction of the formed ferrocene with toluene and recrystallization of the remaining residue from Me_2CO/Et_2O) greenish-gray crystals analysing correctly for $[Mo(Cp)_2R_2]\,PF_6$ (**4**, $R = C_2H_5$ **5**, $R = {}^nC_4H_9$). The IR spectra of **4** and **5** are virtually identical to those of **1** and **2**, respectively, except for the PF_6 anion peaks. Both compounds are paramagnetic. The ESR spectra obtained for the microcrystalline solids at 77 K show signals typical of an axially symmetrical g tensor with $g_\perp$ and $g_\parallel$ values in the region expected for this type of cations [9]: **4**, $g_\parallel = 2.01(1)$, $g_\perp = 2.04(1)$ and **5**, $g_\parallel = 2.07(9)$, $g_\perp = 2.00(7)$.

The ease of oxidation of **1** and **2** to give stable 17-electron cations, (**4**,**5**) prompted the study of the electrochemical behaviour of the dialkyls. The cyclic

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Electrochemical data [a]

Complex	ΔE_p (mV)		$(E_a + E_c)/2$ (mV)		i_a/i_c	
	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2
1	90	135	−215	−207	1.03	0.98
2	80	90	−220	−215	0.97	1.00
6	–	60	–	−270	–	1.00

[a] Experimental conditions: cyclic voltametry was performed at room temperature on solutions 1.0×10^{-3} *M* in substrate and 0.10 *M* on $[^nBu_4N]\ PF_6$ as supporting electrolyte at scan rate of 100 mV s^{-1}. The auxiliary and working electrodes were respectively a Pt wire coil and a 2 mm Pt sheet, and the reference electrode was a saturated calomel calibrated relative to a 1.0×10^{-3} *M* solution of ferrocene in acetonitrile containing 0.10 *M* $LiClO_4$.

voltammograms of complexes **1** and **2** recorded in acetonitrile and dichloromethane solutions between the solvent limits (ca. −1.5 V and 1.6 V) exhibited a chemically reversible oxidation at ca. −215 mV at scan rates between 20 and 500 mV s^{-1}. However, when the solvent was CH_2Cl_2 a second irreversible wave was found at ca. 1.05 V for **1**, and ca. 1.2 V for **2**. The data for the former oxidation are shown in Table 2, together with the value reported for the dimethyl derivative $[Mo(Cp)_2(CH_3)_2]$ **6** [10,11*]. From the measured potentials it can be seen that both **1** and **2** are more difficult to oxidize than **6**, in contrast to what was expected from consideration of inductive effects. On the other hand, inductive effects readily account for the fact that **2** is slightly easier to oxidize than **1**. Similar observations on the $[W(Cp)_2R_2]$ family of complexes have been interpreted on the basis of a stabilizing agostic interaction between an α-C–H bond of the alkyl ligand and the halffilled "Alcock" orbital in the oxidized $[W(Cp)_2R_2]^+$ species [3]. According to this argument, steric repulsion between the β-hydrogen atoms of the alkyl ligand and the Cp rings will decrease the importance of the α-C–H agostic stabilization. Thus $[Mo(Cp)_2\text{-}(C_2H_5)_2]^+$ will be less stabilized than $[Mo(Cp)_2(CH_3)_2]^+$, in agreement with the experimental oxidation potentials. On the other hand, $[Mo(Cp)_2(C_2H_5)_2]^+$ and $[Mo(Cp)_2(^nC_4H_9)_2]^+$ will not differ very much with regard to the α-C–H agostic stabilization and the higher positive inductive effect of $^nC_4H_9$ relative to C_2H_5 becomes dominant, therefore making **2** slightly easier to oxidize than **1**. The comparison between the Mo and W systems is even more striking when it is seen that the shift in potential, observed when C_2H_5 is substituted for CH_3, is 65 mV for W (in CH_3CN) [3] and 63 mV for Mo (in CH_2Cl_2). Whether this coincidence is merely accidental remains to be established through more detailed and extensive studies on the Mo system currently in progress in our laboratories, including MO calculations to ascertain the nature of the Mo–α-CH interaction.

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