CHEMISTRY LETTERS, pp. 1893-1896, 1991.

Preparation, Characterization, and X-Ray Structure Studies of Tertiary Phosphine Coordinated Molybdenocene

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$Cp_2MoH(OTs)$ ($Cp = \eta$-C_5H_5, $Ts = p$-$CH_3C_6H_4SO_2$), which was prepared from Cp_2MoH_2 by its treatment with TsOH in EtOH, reacted with tertiary phosphines and phosphite to give cationic $[Cp_2MoH(PR_3)]^+TsO^-$ where R = Ph, Et, OEt, Cy, and Bu^n. Deprotonation of the latter with NaOH in EtOH afforded $Cp_2Mo(PR_3)$; X-ray structure (R = Bu^n) and some reactions including those with alkyl halides and with H_2 to revert to Cp_2MoH_2 of which were studied.

Recently we reported the diastereoselective reduction of organic carbonyl compounds with the system composed of Cp_2MoH_2 (**1**) ($Cp = \eta$-C_5H_5) and acid (HA) such as RCO_2H, TsOH ($Ts = p$-$CH_3C_6H_4SO_2$), and HCl (Eq. 1).¹⁾

$$Cp_2MoH_2 + 2HA + 2R_2C{=}O \longrightarrow Cp_2MoA_2 + 2R_2CHOH \qquad (1)$$

In an effort to convert this reaction into catalytic one, we succeeded in obtaining and characterizing, including X-ray crystal structure analysis, a series of neutral tertiary phosphine derivatives of molybdenocene, $Cp_2Mo(PR_3)$ (**2**). The formation of **2** has so far been suggested by Azevedo *et al.* in the reaction of $[Cp_2MoH(PR_3)]^+PF_6^-$ with NaH²⁾ and by Geoffroy *et al.* in the photochemical reaction of **1** with PR_3 in isooctane.³⁾ Development of easy access to the complex of the type **2** and establishment of its structural characterization are important in view of the fact that it behaves as a highly reactive molybdenocene precursor.²,³⁾ In fact, complex **2** (R = Bu^n) reacted with H_2 under fairly moderate conditions to give **1** (*vide infra*).

Hydridotosylato complex $Cp_2MoH(OTs)$ (**3**), which was prepared in almost quantitative yield by the reaction of **1** with equimolar amount of $TsOH{\bullet}H_2O$ in ethanol at 80 °C,⁴,⁵⁾ was allowed to react with tertiary phosphines and phosphite to give cationic phosphine adducts of monohydride (**4**) (Eqs. 2 and 3 and Table 1).

$$\underset{\mathbf{1}}{Cp_2MoH_2} + TsOH{\bullet}H_2O \xrightarrow[80\ ^\circ C]{EtOH} \underset{\mathbf{3}}{Cp_2MoH(OTs)} + H_2 + H_2O \qquad (2)$$

$$\underset{\mathbf{3}}{Cp_2MoH(OTs) + PR_3} \overset{r.t.}{\rightleftharpoons} \underset{\mathbf{4}}{[Cp_2MoH(PR_3)]^+TsO^-} \qquad (3)$$

The complex **4** with $PR_3 = PPh_3$, which has been prepared by the reaction of $[Cp_2MoH_3]^+TsO^-$ with PPh_3,⁴⁾ was also formed in 82% yield by the direct reaction of **1** with TsOH in the presence of PPh_3 and acetone (Eq. 4). In the reaction of $[Cp_2MoH_3]^+TsO^-$ with PEt_3, the latter worked as a Lewis base to trap dissociated TsOH yielding $[P(H)Et_3]^+TsO^-$ together with **1**.⁴⁾ In contrast, the present route (Eqs. 2 and 3) can afford **4** with PEt_3 ligand successfully although its purification was somewhat difficult.

PCy_3 ligand in **4d** was found to be replaced easily with PPh_3, which suggests the existence of an equi-

Table 1. Preparation (Eq. 3) and Spectroscopic Properties of Cationic Complexes **4**[a)]

					IR /cm^{-1} c)	^{1}H NMR/ppm d)	
PR_3/mmol	**3**/mmol	Solvents/cm^{-3}	Time/h	Yield of **4**/%[b)]	ν(Mo-H)	δ(Cp)	δ(Mo-H)
PPh_3 (**a**) 2.68	1.34	EtOH 10	20	58 (94)	1820	4.96 (1.8)	-8.06 (34)
PEt_3 (**b**) 1.26	0.63	THF 10	10	e) (92)	1855	5.11 (1.5)	-8.51 (35)
$P(OEt)_3$ (**c**) 1.22	0.81	THF 10	4	50 (85)	1865	5.23 (1.8)	-8.69 (39)
PCy_3[f)] (**d**) 1.76	1.17	THF 10	22	17 (34)	1865	5.15 (1.2)	-8.38 (35)
PBu^n_3 (**e**) 0.74	0.49	THF 10	15	73 (96)	1845	5.13 (2.4)	-8.51 (35)

a) All complexes except for $PR_3 = PEt_3$ gave satisfactory analytical results. b) Crude yields in parentheses. c) KBr disc. d) 270 MHz in CD_3OD, *J*(P–H) in Hz are in parentheses. e) Not crystallizable. f) Cy = *cyclo*-C_6H_{12}.

$$\underset{\mathbf{1}}{Cp_2MoH_2} + TsOH + PPh_3 + (CH_3)_2C{=}O \xrightarrow{EtOH} \underset{\mathbf{4}}{[Cp_2MoH(PPh_3)]^+TsO^-} + (CH_3)_2CHOH \quad (4)$$

librium as shown in Eq. 3. The cationic complex analogous to **4** with a halide counter anion has been prepared by Dias *et al.* starting from Cp_2MoHX (X = Cl, Br, and I)[6)] for $PR_3 = PPh_3$, PMe_2Ph, PEt_2Ph,[7)] and the X-ray structure of $[Cp_2MoH(PPh_3)]^+I^-$ was determined to be a distorted tetrahedron.[2)]

Treatment of the cationic complex **4** with an equivalent NaOH in EtOH afforded phosphine-adduct of molybdenocene **2** (Eq. 5).[8)] When $PR_3 = PCy_3$, **2d** was not formed but some uncharacterizable products were yielded together with **1**. In the case of $PR_3 = PEt_3$, the reaction was carried out *in situ* since isolation of corresponding **4b** in a pure state was difficult.

$$\underset{\mathbf{4}}{[Cp_2MoH(PR_3)]^+TsO^-} + NaOH \xrightarrow{EtOH} \underset{\mathbf{2}}{Cp_2Mo(PR_3)} + NaOTs + H_2O \quad (5)$$

The phosphine derivatives of molybdenocene of the type **2** have been prepared for $PR_3 = PPh_3$ and PEt_3 independently by Azevedo *et al.*[2)] and Geoffroy *et al.*[3)] However, the present route finds an advantage over the previous routes in that it works under milder reaction conditions and thence it is convenient for the preparation of a series of complexes with a variety of tertiary phosphines and phosphite ligands. Complex **2c** reverted to the cationic hydrido complex **4c** on treatment with TsOH (Scheme 1).

Since it was difficult to obtain satisfactory analytical results for complex **2** due to its highly sensitive nature to the air, characterization by means of X-ray crystal structure analysis was attempted. A reddish brown prismatic crystal of **2e** ($PR_3 = PBu^n_3$) suitable for X-ray analysis was obtained by recrystallization from hexane. A full-matrix least-squares refinement procedure was used with anisotropic thermal parameters for the non-hydrogen atoms of the complex. The hydrogen atoms were placed at distance of C–H = 1.00 Å and included in least-square calculations without refinement of their parameters. ORTEP drawing of the molecule is shown in Fig. 1.[9)]

The molecule consists of wedge-formed two Cp rings coordinated to molybdenum in a mutually eclipsed conformation and a tributylphosphine ligand. Mo-P distance of 2.494(3) Å is a little shorter than that reported for $[Cp_2MoH(PPh_3)]^+I^-$ [2.501(4) Å].[2)] Mean bond distances between molybdenum and Cp carbons (2.287

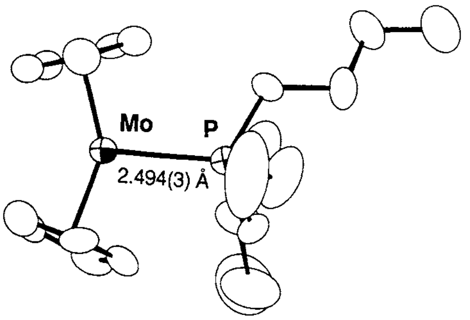


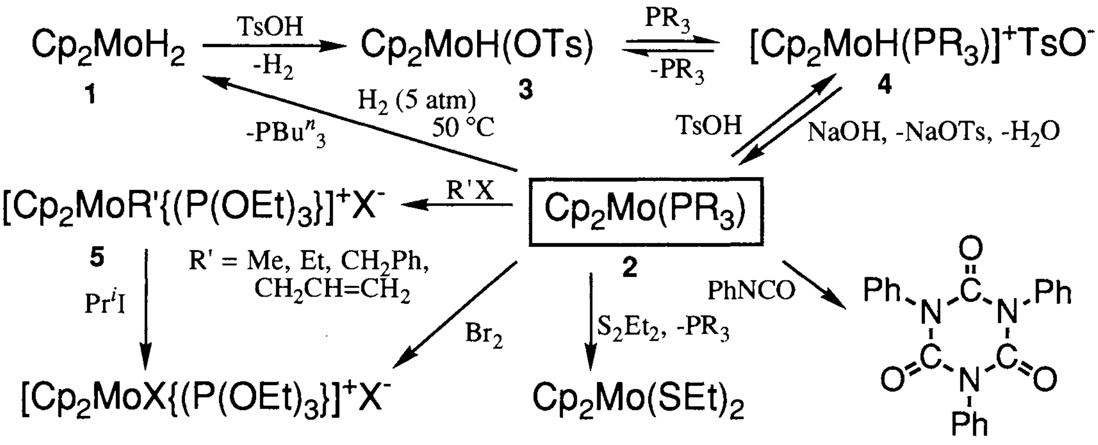
Fig. 1. Structure of $Cp_2Mo(PBu^n{}_3)$ (**2e**).

and 2.273 Å) are not unusual for this type of complexes.[2)]

Complex **2** reacted with alkyl halides (R'X) to give corresponding cationic alkyl complexes $[Cp_2MoR'(PR_3)]^+X^-$ (**5**) (Scheme 1). Recently Azevedo *et al.* have isolated **5** (R' = Me, R = Ph, X = PF_6^-) by an *in situ* reaction between **2a** and MeI and determined its X-ray structure.[2)] They mentioned that alkyl halide other than MeI did not work similarly and failed to obtain analogous alkyl complexes. When complex **2c** with PR_3 = $P(OEt)_3$ was allowed to react with EtI, $PhCH_2Br$, and CH_2=CH-CH_2I as well as MeI, the orange colored corresponding alkyl derivatives (yields 72, 20, and 63%, respectively) as well as methyl complex (yield 63%) were obtained (Scheme 1). The product in the reaction of allyl iodide was found to possess η^1-allyl ligand on the basis of spectral evidence.[10)] The reaction between **2** (R = OEt) and Pr^iI afforded violet $[Cp_2MoI\{P(OEt)_3\}]^+I^-$ (yield 74%) instead of an *i*-propyl derivative, probably *via* a rather unstable intermediary $[Cp_2MoPr^i(PR_3)]^+I^-$. The analogous cationic bromo complex, $[Cp_2MoBr\{P(OEt)_3\}]^+Br^-$,was obtained as a dark colored solid by the reaction of $Cp_2Mo\{P(OEt)_3\}$ (**2c**) with bromine in THF at room temperature (Scheme 1).

As reported for the PPh_3 derivative of **2**,[2)] the other type **2** complexes with PR_3 = $P(OEt)_3$ and $PBu^n{}_3$ reacted similarly with diethyl disulfide at 50 °C to give $Cp_2Mo(SEt)_2$ possibly *via* an oxidative addition involving S-S bond cleavage. Furthermore, $Cp_2Mo(PBu^n{}_3)$ (**2e**) was found to activate dihydrogen under fairly mild conditions. Thus, the reaction of **2e** with 5 atm of H_2 in benzene at 50 °C for 4 h yielded dihydride **1** in 38% yield (Scheme). The rest of the complexes **2** other than **2e** failed to react with H_2. Probably, feasibility of a dissociation of the phosphine ligand in **2e** due to its bulkiness may play an important role in this reaction.

Finally, complex **2c** was found to catalyze selective trimerization of phenyl isocyanate to give triphenyl isocyanurate (Scheme 1). In a typical experiment (not optimized), phenyl isocyanate (1.9 cm^3) and **2c** (0.43 mmol) in hexane (15 cm^3) were stirred *in vacuo* at room temperature for 18.5 h. During the period, a colorless precipitate accumulated gradually in the flask, which was filtered and recrystallized from acetone. 44% of phenyl isocyanate was converted into isocyanurate (589% for **2c**), which was identified by IR and mass spectrometry.



Scheme 1.

Although isocyanate is known to be trimerized by Lewis base such as tertiary amine,[11)] a control experiment using $P(OEt)_3$ as catalyst in place of **2c** did not give the cyclic trimer. Cyclo-addition reaction to give heterometallacycle in the reaction of $Cp_2Mo=O$ with PhNCO and the coupling of PhNCO with coordinated carbonyl ligand in $Cp_2W(CO)$ to give metallacycloimides have been reported.[12–14)]

We are grateful to Prof. K. Osakada of Tokyo Institute of Technology and Dr. S. Kurishima for X-ray structure analysis and to Dr. M. Tanaka of Tokyo Institute of Technology for elemental analysis. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (No. 02650621). T. I. thanks to Iwatani Scholarship and Shinsei-Shigen Kyokai for financial support.

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5) **3**: IR (KBr) 1875 cm^{-1} [ν(Mo-H)]; ^1H NMR (CD_3OD) δ 5.3 (s, *Cp*), δ -9,4 ppm (s, Mo-*H*); E.A. Found: C, 51.77; H, 4.70; S, 7.91%. Calcd for $C_{17}H_{18}MoO_3S$: C, 51.26; H, 4.55; S, 8.05%.

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8) $Cp_2Mo\{P(OEt)_3\}$ (**2c**), yield 76%; ^1H NMR (C_6D_6) $\delta = 4.19$ [5H, d, Cp, *J*(H-P) = 4.88 Hz]; $^{31}P\{^1H\}$ NMR (C_6D_6) $\delta = 206.9$ ppm down field from external PPh_3. $Cp_2Mo(PBu^n{}_3)$ (**2e**), yield 60%; ^1H NMR (C_6D_6) $\delta = 3.99$ [5H, d, Cp, *J*(H-P) = 4.29 Hz]; $^{31}P\{^1H\}$ NMR (C_6D_6) $\delta = 42.0$ ppm down field from external PPh_3.

9) Crystal data: $C_{22}H_{37}MoP$, M = 428.454, orthorhombic, space group *P*bca, a = 18.193(5), b = 25.414(3), c = 9.541(2) Å, V = 4411.3 $Å^3$, Z = 8, $D_c = 1.29$ g cm^{-3}, λ (Mo Kα) = 0.71069 Å, R = 0.080, Rw = 0.073 for 1697 reflections [$F_o > 3\sigma(F_o)$].

10) $[Cp_2Mo(\eta^1\text{-}C_3H_5)\{P(OEt)_3\}]^+I^-$, ^1H NMR (CD_3OD) $\delta = 5.21$ [5H, d, Cp, *J*(H-P) = 2.0 Hz], 1.85 [2H, t, Mo-CH_2-, *J*(H-P) = 7.44 Hz]; ^{13}C NMR (CD_3OD) $\delta = 94.2$ (s, Cp), 8.3 [d, Mo-CH_2-, *J*(C-P) = 14.3 Hz]. Although the η^1-allyl derivative was not able to be isolated analytically pure due to contamination of $[Cp_2MoI\{P(OEt)_3\}]^+I^-$ in the product, satisfactory analytical results were obtained for the rest of the alkyl complexes reported here.

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(Received July 23, 1991)