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THE FIRST ISOLATION AND SOME REACTIONS OF THE CATIONIC TRIHYDRIDES, $[M(\eta\text{-}C_5H_5)_2H_3]^+TsO^-$ (M = W, Mo)

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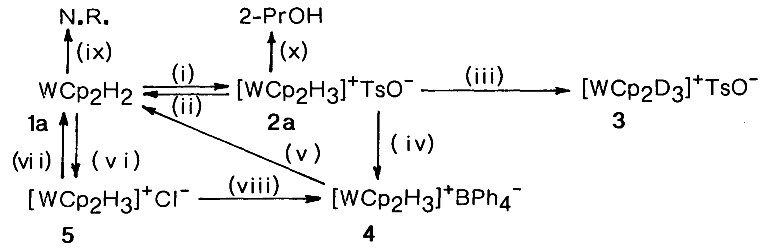
MCp_2H_2 [M = W (**1a**), Mo (**1b**); Cp = $\eta\text{-}C_5H_5$] was protonated with TsOH to give $[MCp_2H_3]^+TsO^-$ [M = W (**2a**), Mo (**2b**)], which was isolated and characterized spectroscopically. **2a** and **2b** reduced acetone to *i*-PrOH indicating their more hydridic nature as compared to **1a** and **1b**. Complex **2b** reacted with Lewis bases and allyl alcohols to give $[MoCp_2H(L)]^+TsO^-$ (L = CO, PPh_3, MeOH) and cyclic γ-hydroxyalkyl complexes, respectively.

Since the first preparation of the dihydrides MCp_2H_2 [M = W (**1a**) and Mo (**1b**); Cp = $\eta\text{-}C_5H_5$],1) it has been shown that they are easily protonated with the strong acids such as HCl and CF_3COOH to give cationic trihydrides $[MCp_2H_3]^+$ **2**. However, their chemistries have scarcely been studied partly because of the difficultly in their isolation in analytically pure states due to their tendencies to revert to the parent hydrides in the course of the attempted isolation.1,2) Recently we have found that the cationic trihydrides $[MCp_2H_3]^+A^-$ (M = Mo and W; A = Cl and RCOO), which were prepared *in situ* by the protonation of **1** with the corresponding acids, reduced organic carbonyl compounds to alcohols with the concomitant formation of MCp_2A_2.3) (Eq. 1)

$$\underset{\mathbf{1}}{\mathrm{MCp_2H_2}} + \mathrm{HA} \longrightarrow \underset{\mathbf{2}}{[\mathrm{MCp_2H_3}]^+\mathrm{A}^-} \xrightarrow{2{>}\mathrm{C{=}O/HA}} \mathrm{MCp_2A_2} + 2{>}\mathrm{CHOH} \qquad (1)$$

In the course of the studies on this line, we found that the trihydrido cation **2** can be successfully isolated as tosylates when the hydrides **1** are protonated with *p*-toluenesulfonic acid (TsOH) in non-aqueous solvent. Here we describe the isolation, characterization, and some chemistries of the cation **2**.

Addition of EtOH to an equimolar mixture of WCp_2H_2 **1a** and TsOH *in vacuo* afforded a colorless solution. After being stirred at room temperature for 0.5 h, solvent was evaporated off to leave off-white solid which was then washed with Et_2O, and recrystallized from EtOH to give white crystals of $[WCp_2H_3]^+TsO^-$ **2a**4) (yield, 62%) [Scheme 1, path (i)]. Similarly obtained was the molybdenum analogue of **2a**, $[MoCp_2H_3]^+TsO^-$ **2b**, by using Et_2O as solvent (crude yield, 94%) [Scheme 2, path (i)]. Complex **2b**, being so reactive that most of the common organic solvents react with it, could not be purified by the recrystallization, although its purity was confirmed by the comparison of its IR with that of tungsten analogue **2a** and by



Scheme 1. Reactions of $[WCp_2H_3]^+TsO^-$: (i) TsOH in EtOH, r.t., 62%; (ii) NaOH(aq), r.t., 57%; (iii) excess CD_3OD or D_2O, r.t.; (iv) $NaBPh_4$ in EtOH, r.t., 79%; (v) NaOH in H_2O/acetone, r.t., trace; (vi) HCl(aq), r.t.; (vii) NaOH(aq); (viii) $NaBPh_4$ in EtOH, r.t., 74% (based on **1a**); (ix) excess acetone; (x) excess acetone, r.t., 46 h, 67% (GLC yield).

characterizing some stable compounds derived from it (*vide infra*).

Both cations **2a** and **2b** are unstable to air even in the solid state, the latter being more easily decomposed by air. Complex **2a** is soluble in protic solvents such as alcohols, whereas **2b** reacted with these solvents releasing H_2. In the IR spectra, M-H stretching bands were observed at 1935m cm^{-1} (**2a**) and 1950w/1890w cm^{-1} (**2b**), which are higher frequencies than those of the parent hydrides, **1a** and **1b** (1920 and 1840 cm^{-1}, respectively). ^1H NMR spectrum of **2a** in CD_3OD showed only one singlet signal assignable to the Cp protons at δ 5.67 which was lower than the parent **1a** by about 1 ppm. When the spectrum was taken in CH_3OH, hydride signals were observed at around -6.4 ppm as a broad A_2B pattern (J = 8.2 Hz), which was again lower than the W-H signal of **1a** by about 7 ppm. These spectral evidences are all in accord with the increased magnetic deshielding effect in cations **2** induced by the cationic metal center.

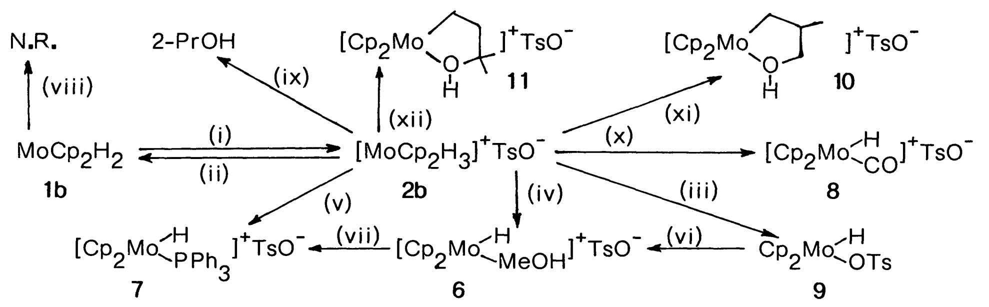
On treatment with aqueous NaOH, tungsten complex **2a** reverted to the dihydride **1a** [Scheme 1 (ii)]. Dissolution of **2a** in large excess of CD_3OD or D_2O resulted in an H/D exchange of the hydride, and $[WCp_2D_3]^+TsO^-$ **3**$^{5)}$ was recovered from the solution [Scheme 1 (iii)] indicating the existence of the equilibrium as shown in Eq. 2 in the solution.

$$\underset{\textbf{2a}}{[WCp_2H_3]^+TsO^-} \rightleftharpoons \underset{\textbf{1a}}{WCp_2H_2} + TsOH \qquad (2)$$

Treatment of **2a** with $NaBPh_4$ in EtOH gave tetraphenylborate complex $[WCp_2H_3]^+BPh_4^-$ **4**$^{6)}$ [Scheme 1 (iv)]. Alternatively, **4** was obtained by treating $[WCp_2H_3]^+Cl^-$ **5**, which had been formed *in situ* by protonation of **1a** with HCl, with $NaBPh_4$ [Scheme 1 (vi) and (viii)].

According to Labinger and Komadina who proposed that hydridic character of the transition metal hydrides can be assessed by their ability to reduce ketones,$^{7)}$ the hydrides of the present cationic complexes **2a** and **2b** were found to be more hydridic than the parent neutral dihydrides **1a** and **1b**, since the former hydrogenated acetone to 2-propanol whereas the latter did not [Scheme 1 (ix), (x) and Scheme 2 (viii), (ix)].

The highly reactive molybdenum cation **2b** reacted with some Lewis bases (L) to give Mo(IV) monohydrides $[MoCp_2H(L)]^+TsO^-$ [L = MeOH (**6**),$^{8)}$ PPh_3 (**7**),$^{9)}$ and CO



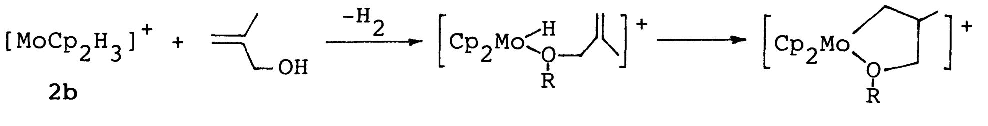
Scheme 2. Reactions of $[MoCp_2H_3]^+TsO^-$: (i) TsOH in Et_2O, r.t., 2 h, 94% (crude yield); (ii) PEt_3 in EtOH, r.t., 50 min, 53%; (iii) 50 °C in THF, 3 h, 61%; (iv) MeOH, 50 °C, 3 h, 96%; (v) PPh_3 in EtOH, r.t., 17 h, 93%; (vi) MeOH, r.t., 44 h, 97%; (vii) PPh_3 in THF, r.t., 19 h, 94%; (viii) excess acetone; (ix) excess acetone, r.t., 22 h, 153% (GLC yield); (x) CO, 1 atm, in EtOH, r.t., 121 h, 59%; (xi) $CH_2=CH(CH_3)CH_2OH$, 50 °C, 5 h, 79%; (xii) $CH_2=CHC(CH_3)_2OH$, 80 °C, 15 h, 44%.

(**8**)[10]] with accompanying evolution of one mole of H_2 [Scheme 2 (iv), (v), and (x)]. As is reported for $NbCp_2H_3$ which is isoelectronic with **2b**, these reactions may follow the following path in which the intermediary monohydride cation is involved.[11] Complexes **7** and **8** have been prepared by Green *et al.* *via* different routes.[12]

$$\underset{\mathbf{2b}}{[MoCp_2H_3]^+TsO^-} \xrightarrow{\Delta \quad -H_2} [MoCp_2H]^+TsO^- \xrightarrow{L} \underset{\mathbf{6}\ -\ \mathbf{8}}{[MoCp_2H(L)]^+TsO^-} \qquad (3)$$

The more basic tertiary phosphine, PEt_3, neutralized **2b** reverting it to dihydride **1b** [Scheme 2 (ii)]. On the contrary, when **2b** was warmed in a weak base such as tetrahydrofuran (THF), a very unstable neutral monohydride, of which structure was tentatively assigned to $MoCp_2H(OTs)$ **9**,[13] was isolated. Complex **9** was converted into MeOH adduct **6** quantitatively by just dissolving the former in MeOH [Scheme 2 (iii) and (vi)]. The ligating MeOH in **6** was displaced with PPh_3 to give **7** by treating **6** with PPh_3 in THF [Scheme 2 (vii)].

Heating **2b** with substituted allyl alcohols such as $CH_2=C(CH_3)CH_2OH$ and $CH_2=CHC(CH_3)_2OH$ afforded cyclic γ-hydroxyalkyl complexes **10** and **11**, respectively, together with H_2, possibly as a result of the double bond insertion into the Mo-H bond *via* an intermediate of the type **6** alcohol adducts [Scheme 2 (xi) and (xii)]. Characterization of **10** and **11** was achieved by IR and ^1H- and ^{13}C-NMR spectroscopies.[14,15]



2b **10** (4)

In the present studies, cationic trihydride complexes which have TsO^- as a counter anion were prepared by the reaction of dihydrides with *p*-toluenesulfonic acid and were successfully isolated possibly owing to a weak coordinating ability of the tosylato ligand to the central metal. It was found that the isolated trihydride complexes, especially when the central metal was molybdenum, showed high reactivities toward Lewis bases and allylic alcohols to give a variety of new derivatives. Furthermore, their highly oxophilic properties, induced by the high oxidation state of the central metal, allow the application of these complexes for various organic reactions such as selective reduction of the carbonyl group.$^{3)}$

References

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3) T. Igarashi, M. Natori, N. Sekizuka, and T. Ito, 31st Symposium on Organometallic Chemistry, Japan, A206, 1984, Tsukuba.

4) **2a**: IR (KBr) 1930m cm^{-1} (W-H); ^1H NMR (CD_3OD) δ = 5.67 (10H, s, Cp); ^1H NMR (CH_3OH) δ =*ca.* -6.40 [3H, A_2B multiplet, ^2J(H-H) = 8.2 Hz, W-H]. Resonances due to the TsO^- protons are omitted throughout. Found: C, 41.58; H, 4.18; S, 6.57%. Calcd for $C_{17}H_{20}O_3SW$: C, 41.82; H, 4.13; S, 6.57%.

5) **3**: IR (KBr) 1390m cm^{-1} (W-D).

6) **4**: IR (KBr) 1940w cm^{-1} (W-H).

7) J. A. Labinger and K. H. Komadina, *J. Organometal. Chem.*, 155, C25 (1978).

8) **6**: brown crystals; IR (KBr) 1840m (Mo-H) and 2400 - 2800 cm^{-1} (OH); ^1H NMR (CD_3OD) δ = 5.32 (10H, s, Cp); ^1H NMR (CH_3OH) δ = -9.33 (1H, s, Mo-H).

9) **7**: yellow crystals; IR (KBr) 1830m cm^{-1} (Mo-H); ^1H NMR (CD_3OD) δ = 7.5 - 8.0 (15H, m, PPh_3) and 4.92 [10H, d, ^3J(P-H) = 2.6 Hz, Cp]; ^1H NMR (CH_3OH) δ = -8.09 [1H, d, ^2J(P-H) = 33 Hz, Mo-H].

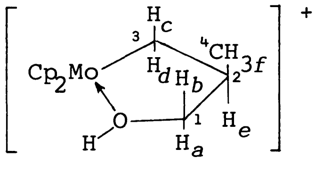
10) **8**: yellow crystals;IR (KBr) 1870m cm^{-1} (Mo-H); ^1H NMR (CD_3OD) δ = 5.73 (10H, s, Cp) and -8.43 (1H, s, Mo-H); ^{13}C NMR (CD_3OD) δ = 223 (CO) and 88.9 (Cp).

11) T. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.*, 93, 3793 (1971).

12) F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1244, and references cited therein.

13) **9**: brown powder; IR (KBr) 1875m cm^{-1} (Mo-H).

14) **10**: brown crystals; IR (KBr) 2400 - 2800 cm^{-1} (OH); ^1H NMR (CD_3OD) δ = 5.30 (5H, s, Cp), 5.22 (5H, s, Cp), 3.80 (1H, m, H_a), 2.75 [1H, dd, $^3J(H_bH_e)$ = 8.3 Hz, $^2J(H_aH_b)$ = 11.6 Hz, H_b], 2.12 (1H, apparent d, H_d), 1.56 [1H, apparent t, J = *ca.* 8.3 Hz, H_e], 1.35 [1H, d, $^2J(H_cH_d)$ = 10.7 Hz, H_c], and 0.98 [3H, d, $^3J(H_fH_e)$ = 5.3 Hz, H_f]; ^{13}C NMR (CD_3OD) δ = 96.97 (d, Cp), 96.43 (d, Cp), 77.90 (t, C_1), 39.11 (d, C_2), 23.84 (t, C_3), and 17.23 (quart, C_4).



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15) **11**: brown crystals; IR (KBr) 2500 - 2800 cm^{-1} (OH); ^1H NMR (CD_3OD) δ = 5.27 (10H, s, Cp), 1.90 [2H, apparent t, ^3J(HH) = 6.4 Hz, $Mo-CH_2$], 1.45 [2H, apparent t, ^3J(HH) = 6.6 Hz, $Mo-C-CH_2$], and 1.17 (6H, s, CMe_2).

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