CHEMISTRY LETTERS, pp. 1699-1702, 1985.

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

Tadashi IGARASHI and Takashi ITO^{*} Departmentof Materials Chemistry, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240

 MCp_2H_2 [M = W (1a), Mo (1b); Cp = $n-C_5H_5$] 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, PPh₃, MeOH) and cyclic γ -hydroxyalkyl complexes, respectively.

Since the first preparation of the dihydrides MCp_2H_2 [M = W (1a) and Mo (1b); $Cp = n-C_5H_5$],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)

$$\begin{array}{c} 2 \geq C = O/HA \\ MCp_2H_2 + HA \longrightarrow [MCp_2H_3]^+A^- \longrightarrow MCp_2A_2 + 2 \geq CHOH \\ 1 \end{array}$$
(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 $[WCp_2H_3]^+TsO^-$ 2a⁴ (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



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 H₂. 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 CD₃OD 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 CH₃OH, hydride signals were observed at around -6.4 ppm as a broad A₂B 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.

$$[WCp_2H_3]^{\dagger}TsO^{-} \longrightarrow WCp_2H_2 + TsOH$$
(2)
2a 1a (2)

Treatment of 2a with NaBPh₄ in EtOH gave tetraphenylborate complex $[WCp_2H_3]^+BPh_4^-$ 4⁶⁾ [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 NaBPh₄ [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) PPh₃ (7),⁹ and CO



Scheme 2. Reactions of $[MoCp_2H_3]^{+}TsO^{-}$: (i) TsOH in Et₂O, r.t., 2 h, 94% (crude yield); (ii) PEt₃ in EtOH, r.t., 50 min, 53%; (iii) 50 °C in THF, 3 h, 61%; (iv) MeOH, 50 °C, 3 h, 96%; (v) PPh₃ in EtOH, r.t., 17 h, 93%; (vi) MeOH, r.t., 44 h, 97%; (vii) PPh₃ 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) CH₂= CH(CH₃)CH₂OH, 50 °C, 5 h, 79%; (xii) CH₂=CHC(CH₃)₂OH, 80 °C, 15 h, 44%.

 $(8)^{10}$] with accompanying evolution of one mole of H₂ [Scheme 2 (iv), (v), and (x)]. As is reported for NbCp₂H₃ 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)

$$[MoCp_{2}H_{3}]^{+}TsO^{-} \xrightarrow{\Delta - H_{2}} [MoCp_{2}H]^{+}TsO^{-} \xrightarrow{L} [MoCp_{2}H(L)]^{+}TsO^{-}$$
(3)
2b 6 - 8

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 PPh₃ to give **7** by treating **6** with PPh₃ 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 ¹³C-NMR spectroscopies.^{14,15})



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

- 1) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 1961, 4854.
- 2) M. J. Calhodra and A. R. Dias, J. Organometal. Chem., <u>198</u>, 41 (1980); Rev. Port. Quim., <u>23</u>, 12 (1981).
- 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 (CD₃OD) $\delta = 5.67$ (10H, s, Cp); ¹H NMR (CH₃OH) $\delta = ca. -6.40$ [3H, A₂B 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 C₁₇H₂₀O₃SW: 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 (CD₃OD) δ = 5.32 (10H, s, Cp); ¹H NMR (CH₃OH) δ = -9.33 (1H, s, Mo-H).
- 9) 7: yellow crystals; IR (KBr) 1830m cm⁻¹ (Mo-H); ¹H NMR (CD₃OD) δ = 7.5 8.0 (15H, m, PPh₃) and 4.92 [10H, d, ³J(P-H) = 2.6 Hz, Cp]; ¹H NMR (CH₃OH) 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 (CD₃OD) δ = 5.73 (10H, s, Cp) and -8.43 (1H, s, Mo-H); ¹³C NMR (CD₃OD) δ = 223 (CO) and 88.9 (Cp).
- 11) T. N. Tebbe and G. W. Parshall, J. Am. Chem. Soc., <u>93</u>, 3793 (1971).
- 12) F. W. S. Benfield and M. L. H. Green, J. Chem. Soc., Dalton Trans., <u>1974</u>, 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 (CD₃OD) 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]; ¹³C NMR (CD₃OD) δ = 96.97 (d, Cp), 96.43 (d, Cp), 77.90 (t, C₁), 39.11 (d, C₂), 23.84 (t, C₃), and 17.23 (quart, C₄).



15) 11: brown crystals; IR (KBr) 2500 - 2800 cm⁻¹ (OH); ¹H NMR (CD₃OD) δ = 5.27 (10H, s, Cp), 1.90 [2H, apparent t, ³J(HH) = 6.4 Hz, Mo-CH₂], 1.45 [2H, apparent t, ³J(HH) = 6.6 Hz, Mo-C-CH₂], and 1.17 (6H, s, CMe₂).

(Received September 3, 1985)