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Preliminary communication

TUNGSTEN AND MOLYBDENUM PHOSPHINE HEXAHYDRIDES: THE FIRST EXAMPLES OF NINE COORDINATION AMONG MONONUCLEAR MOLYBDENUM COMPLEXES

ROBERT H. CRABTREE* and GREGORY G. HLATKY
Sterling Chemistry Laboratory, Yale University, 225 Prospect St., New Haven, CT 06511 (U.S.A.)

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Summary

An improved preparation and some reactions of $WH_6(PMe_2Ph)_3$ are described. This method has been extended to prepare the novel $MoH_6(PR_3)_3$ compounds, the first mononuclear nine-coordinate molybdenum complexes.

Nine coordination in the *d*-block series is limited to the second and third rows of Groups V—VII. Given the low steric demand of the hydride ligand, it is not surprising that these mononuclear nine-coordinate compounds are polyhydrides of the type $MH_9{}^{2-}$ and $MH_x(PR_3)_y$ [1].

To date, within the Group VI metals, only tungsten forms the nine-coordinate complexes $MH_6(PR_3)_3$ [2] and $[MH_5(PR_3)_4]^+$ [3]. The hexahydride $WH_6(PMe_2Ph)_3$ (I) has been prepared in 10—25% yield by reaction of $WCl_4(PMe_2Ph)_2$ with $NaBH_4$ [2a], $LiAlH_4$ [4], and $H_2/Na/Hg$ [5]. We have found the reaction of $WCl_4(PMe_2Ph)_3$ with $NaH_2Al(OCH_2CH_2OCH_3)_2$ to be a much better method of preparing I.

In a typical reaction, 10 ml of a 3.4 *M* solution of $NaH_2Al(OCH_2CH_2OCH_3)_2$ in toluene (Aldrich) were added to 75 ml of THF in an inert atmosphere and the solution cooled to —78°C. Solid $WCl_4(PMe_2Ph)_3$ [6] (2.16 g; 2.92 mol) was added slowly to the solution and the mixture allowed to warm slowly to room temperature and it was stirred overnight. For ease of work-up, the solvent was removed in vacuo and replaced with 100 ml Et_2O. The aluminium hydride was hydrolyzed with 10% aqueous NaOH; the ether layer was decanted, dried with $MgSO_4$, and filtered. The hexahydride was isolated by evaporation and purified by recrystallization from hexane. Yield was 0.92 g (53%). Anal.: Found, C, 47.50; H, 6.62. $C_{24}H_{39}P_3W$ calcd.: C, 47.70; H,

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6.50%. ^1H NMR (C_6D_6): δ—1.91 (quartet, J(PH) 36 Hz, J(WH) 27.8 Hz), 1.76 (t, J(PH) 4 Hz), 7.08 (mult.) ppm. Extensions of this procedure to other phosphines (PCy_3, PPr^i_3, PCy_2Ph {Cy = cyclohexyl}) gave lower yields of the hexahydrides.

Previous work in our group has shown that the solvento complexes $[IrH_2S_2(PPh_3)_2]^+$ (S = acetone, H_2O) can dehydrogenate alkanes [7]. We wished to extend the range of known solvento complexes of the earlier transition metals. Caulton et al. have prepared $[MoH_2(CH_3CN)_x(PR_3)_y]^{2+}$ (x = 2,3; y = 4,3) from $MoH_4(PR_3)_4$ and $AgBF_4$ or HBF_4 in CH_3CN [8]. HBF_4 reacts rapidly with I in CH_3CN to give $[WH_2(CH_3CN)_3(PMe_2Ph)_3][BF_4]_2$ (II) in 86% yield. Anal.: Found: C, 40.11; H, 4.78. $C_{33}H_{44}B_2F_8N_3P_3W$ calcd.: C, 40.17; H, 4.94%. ^1H NMR (CD_3CN): δ—0.30 (quartet, J(PH) 52.8 Hz), 1.81 (d, J(PH) 8.5 Hz), 2.24 (s), 7.43 (mult.) ppm. ^{31}P (selective ligand ^1H) NMR (CD_3CN): δ +3.45 (tt, J(WP) 165 Hz). Attempts to prepare solvento complexes with other donors (MeOH, acetone, DMF, PhCN) gave only oily products; no alkane activation has yet been observed with any of the complexes.

Molybdenum hexahydrides similar to I have never been observed up to now; indeed, no mononuclear nine-coordinate molybdenum complexes of any type exist*. We find, however, that the preparation similar to that used for I, but starting from $MoCl_4(THF)_2$ (1.5 mmol) and 3.0 mol equivalents PR_3, also gives the $MoH_6(PR_3)_3$ complexes (III) (eq. 1).

The hexahydrides IIIa—IIId are obtained in very low yield (<5%) as air-sensitive, unstable oils containing excess phosphine. They cannot be chromatographed and we have been unable to obtain pure samples. We have based their formulation as hexahydrides on the NMR spectra (Table 1). All four

$$MoCl_4(THF)_2 \xrightarrow[3\ PR_3,\ THF,\ -78^\circ C]{NaH_2Al(OCH_2CH_2OCH_3)_2} MoH_6(PR_3)_3 \qquad (1)$$

(IIIa: PR_3 = PCy_3,
IIIb: PR_3 = PCy_2Ph,
IIIc: PR_3 = PPr^i_3,
IIId: PR_3 = PPr^i_2Ph)

TABLE 1

NMR DATA FOR THE MOLYBDENUM HEXAHYDRIDES IIIa—IIId

Compound	^1H [a]		$^{31}P\{^1H\}$ [d]
	δ [b]	^2J(PH) [c]	δ
IIIa	—4.42	36.3	62.83
IIIb	—3.71	35	70.32
IIIc	—4.63	35.6	52.54
IIId	—4.00	35	57.89

[a] MoH resonance, C_6D_6 solution. [b] ppm from internal TMS. [c] In Hz. [d] MoP resonance, C_6D_6 solution, ppm downfield from external 85% H_3PO_4.

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*Certain trinuclear clusters containing nine-coordinate molybdenum atoms are known [9].

compounds show a sharp 1/3/3/1 quartet in the high-field ^1H NMR region, indicating the presence of three equivalent phosphines in a fluxional molecule. A variable-temperature NMR study of IIId shows that the quartet begins to broaden at 215 K and at 195 K the hydride resonances appear only as a broad peak. The dynamic behavior of IIId is similar to that of the tungsten analogue $WH_6(PPr^i_2Ph)_3$, in which the same spectral changes occurred about 5° lower than in IIId [2b].

The number of hydride ligands was determined from the ^{31}P NMR spectra of IIIa and IIId. On selectively decoupling the aliphatic protons on the ligand, the resonance is split into a septet, thus confirming the hexahydride formulation.

The role of the phosphines in IIIa—IIId appears to be twofold: not only does their steric bulk preclude coordination of more than three phosphines, but their high basicity also helps to stabilize the otherwise unstable MoH_6 group; the smaller and less basic phosphines (PMe_2Ph, $PMePh_2$) give only $MoH_4(PR_3)_4$. The tungsten hexahydrides are similarly dependent on the steric bulk of the phosphines: PMe_3 and PPr^i_3 have comparable Lewis bascities, but only WH_4L_4 and WH_2L_5 are known for PMe_3 [10], while PPr^i_3 gives only $WH_6(PPr^i_3)_3$ [2b]. The electronic nature of the phosphine seems to be less important in tungsten(VI) polyhydrides, where even $[WH_5(P(OPr^i)_3)_4]^+$ has been reported [3b].

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