Journal of Organometallic Chemistry, 121 (1976) 373—379
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THE PREPARATION OF $NbH_5(Me_2PCH_2CH_2Me_2)_2$ AND $NbHL_2(Me_2PCH_2CH_2PMe_2)_2$ (L = CO OR C_2H_4)

RICHARD R. SCHROCK *

*Central Research and Development Department **, E.I. du Pont de Nemours and Company, Wilmington, Delaware 19898 (U.S.A.)*

(Received May 19th, 1976)

Summary

MMe_5(dmpe) (M = Nb or Ta, dmpe = $Me_2PCH_2CH_2PMe_2$) reacts with H_2 (500 atm) and dmpe in THF at 60°C to give $MH_5(dmpe)_2$. $NbH_5(dmpe)_2$ readily reacts with two mol of CO or ethylene (L) to give $NbHL_2(dmpe)_2$. The exchange of the hydride ligand with the ethylene protons in $NbH(C_2H_4)_2(dmpe)_2$ is not rapid on the ^1H NMR time scale (60 MHz) at 95°C.

Introduction

Numerous polyhydride complexes of the type MH_xL_y (L = a tertiary phosphine ligand) are known [1]. Two typical examples are $WH_6(PMe_2Ph)_3$ [2] and $IrH_5(PMe_3)_2$ [3]. However, only one example is known where M is a metal from the Ti or V triads, $TaH_5(dmpe)_2$ [dmpe = $Me_2PCH_2CH_2PMe_2$] [4a]. It, and its analog, $NbH_5(dmpe)_2$, have now been prepared in good yield by cleaving the metal—carbon bond in MMe_5(dmpe) with H_2 in the presence of dmpe. This paper reports the details of the preparation of $NbH_5(dmpe)_2$, its characterization, and its reactions with CO or C_2H_4 (L) to give the derivatives, $NbHL_2(dmpe)_2$.

Results and discussion

The preparation of $MH_5(dmpe)_2$ (M = Nb, Ta)

$TaMe_5$(dmpe) apparently does not react rapidly with H_2 at 1 atm pressure and 25°C. However, at 500 atm and 60°C in the presence of 1 mol of dmpe, $TaMe_5$(dmpe) in THF is transformed into $TaH_5(dmpe)_2$. It was identified by its characteristic ^1H NMR spectrum [4a]. A spectrum of the crude product showed evidence of no other non-volatile species.

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* Current address: Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

** Contribution No. 2378.

The reaction between $NbMe_5(dmpe)$, H_2 (500 atm), and dmpe in THF at 60°C is entirely analogous. The resulting brownish-yellow solution probably contains a nearly quantitative yield of $NbH_5(dmpe)_2$ but since it slowly "decomposes" during workup (vide infra) the isolated yield of pure $NbH_5(dmpe)_2$ is only ca. 50%. A close examination of the reaction conditions showed that a large molar excess of H_2 at a high partial pressure is necessary to ensure complete reaction to $NbH_5(dmpe)_2$; in one instance the reaction (in 20 ml of THF) between 5.0 g of $NbMe_5(dmpe)$, 2.5 g of dmpe, and 100 atm H_2 at 60°C for 16 h gave impure $NbH_5(dmpe)_2$ in low yield.

Several preparations of metal hydride complexes from alkyl or aryl complexes and H_2 have been reported in the literature [5]. In most cases a plausible mechanism consists of "oxidative addition" of H_2 to the metal followed by "reductive elimination" of the alkane, for example;

$$RhRL_3 \xrightarrow{H_2} RhRH_2L_3 \xrightarrow{-RH} RhHL_3$$

However, d^0 alkyl complexes cannot react with H_2 strictly in this manner because the metal is already in its highest formal oxidation state. Yet several (besides the $MMe_5(dmpe)$ complexes described here) do, sometimes under fairly mild conditions. Three examples are $[TaPh_6]^-$ *, $Ti(\eta^5\text{-}C_5H_5)_2Me_2$ [6] and $Zr(\eta^5\text{-}C_5H_5)_2Me_2$ [7]. One possible mechanism for the first step at least is analogous to the reaction of Group I and II organometallic compounds (e.g., LiC_6H_5) with H_2[8]. More complex mechanisms such as reaction of H_2 with a decomposition product, of course, cannot be excluded.

Characterization of $NbH_5(dmpe)_2$

$NbH_5(dmpe)_2$ is a pale yellow, waxy, crystalline solid which is stable under N_2 for at least several days at 25°C. It readily dissolves in pentane from which it can be recrystallized at −30°C in ca. 80% yield. Treatment (in toluene) with 5.7 mol of gaseous HCl for 16 h gave 5.0 mol of H_2. Using 10 mol of DCl, 4.7 mol of a mixture of 26% H_2, 47% HD, and 27% D_2 evolved. Its infrared spectrum shows a strong, broad resonance at ca. 1520 cm^{-1} (in Nujol) which can be assigned to $\nu(M{-}H)$.

The ^1H NMR spectrum of $NbH_5(dmpe)_2$ in C_6D_6 at 25°C consists of a quintet at τ 12.04 ($^2J(HP) = 39$ Hz) and a broad resonance for the dmpe protons (CH_3 and CH_2 combined) at τ 8.57 ppm. The relative areas as $5 \pm 0.5 : 32$. The fact that the the hydride resonance is a quintet confirms that the hydride ligands are coupled to four phosphorus nuclei which are equivalent on the ^1H NMR time scale at 25°C. The ^1H NMR spectrum at −80°C in toluene-d_8 is virtually identical.

The $^{31}P\{^1H\}$ NMR spectrum in toluene at −80°C shows a single resonance 39.5 ppm below external 85% H_3PO_4. The half-height width at this temperature is ca. 10 Hz. At 0°C this resonance is considerably broader (ca. 90 Hz) due to coupling of ^{31}P to ^{93}Nb (100% abundant, $I = 9/2$). Loss of H_2 or one end of a dmpe ligand is probably not responsible for the broadening since the hydride resonance in the ^1H NMR spectrum is a sharp quintet at both −80°C at 25°C.

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* The reaction of $[Li(THF)_4]^+[TaPh_6]^-$ (U. Klabunde, manuscript in preparation) and H_2 (1500 psi) in THF in the presence of dmpe at 45°C for 5 h was the original preparation of $TaH_5(dmpe)_2$ developed by Tebbe [4a].

Also note that the ^{31}P resonance in the $^{31}P\{^1H\}$NMR spectrum of $TaH_5(dmpe)_2$ [4a] does not broaden in this manner, in part, at least, because the electric quadrupole moment for Ta is relatively large *. Selective decoupling of the dmpe protons at —80°C gave a poorly resolved binomial sextet in the ^{31}P spectrum ($^2J(PH) \approx 32$ Hz; cf. $^2J(HP)$ above), consistent with the presence of five hydride ligands.

Both ^1H NMR and ^{31}P NMR spectra suggest that the barrier to interconversion of idealized structures for $NbH_5(dmpe)_2$ in solution is low. In fact, no polyhydride complexes which are at least seven-coordinate show a preferred geometry in solution under conditions which are normally accessible in a low temperature NMR experiment [1].

When a pentane or hexane solution of $NbH_5(dmpe)_2$ stands (under N_2) at 25°C for several days, greenish-brown microcrystals slowly form. The $^{31}P\{^1H\}$NMR spectrum of this apparent decomposition product shows at least four approximately equally intense resonances while its ^1H NMR spectrum still shows a weak quintet hydride resonance which is, however, shifted 1—2 ppm to higher field than observed in $NbH_5(dmpe)_2$. In one instance this material could not be cleanly transformed into $NbH_5(dmpe)_2$ under the conditions used for its preparation (500 atm H_2 at 60°C in THF). These results auger against the proposition that $NbH_5(dmpe)_2$ spontaneously and reversibly loses 1 or 2 mol of H_2 under molecular nitrogen to give stable $NbH_3(dmpe)_2$ or $NbH(dmpe)_2$. In the presence of typical π-acid ligands such as CO or ethylene, however, 2 mol of H_2 evolve briskly (vide infra). In contrast, $TaH_5(dmpe)_2$ is comparatively stable toward loss of H_2, even in the presence of CO or C_2H_4 [4b]. The comparative "lability"of complexes of second row metals vs. those of third row metals is, of course, a well-recognized phenomenon not only for polyhydride species [1] but for many other types of complexes throughout the transition series.

The reaction of $NbH_5(dmpe)_2$ with CO

$NbH_5(dmpe)_2$ in pentane reacts with CO (30 psi) at 25°C to give an orange solution from which orange needles crystallize at —30°C. An infrared spectrum (Nujol) shows a weak to medium band at 1550 cm^{-1} and a strong band at 1700—1750 cm^{-1}, consistent with ν(M—H) and ν(C≡O) modes, respectively.

The ^1H NMR spectrum of $NbH(CO)_2(dmpe)_2$ in C_6D_6 at 25°C shows a triplet of triplets at τ 14.46 ($^2J(HP) = 92$ Hz, $^2J(HP') = 14$ Hz) and two poorly resolved doublets due to two types of dmpe methyl groups. Its ^{31}P NMR spectrum at —80°C (undecoupled) consists of a broad doublet 49 ppm downfield from external 85% H_3PO_4 ($^2J(PH) \approx 89$ Hz; cf. $^2J(HP) = 92$ Hz above) and a broad singlet at 27 ppm. On decoupling all protons, the two ^{31}P resonances collapse to two identical non-first-order doublets ($^2J(PP') \approx 25$ Hz). These findings are analogous to those for $TaH(CO)_2(dmpe)_2$ [4,10]. Furthermore, X-ray examination of a single crystal [11] showed that $NbH(CO)_2(dmpe)_2$ and $TaH(CO)_2(dmpe)_2$ are indeed isomorphous and, therefore, presumably isostructural.

The reaction of $NbH_5(dmpe)_2$ with ethylene

The reaction of 1.0 mmol of $NbH_5(dmpe)_2$ in 10 ml of pentane with 4.0 mmol

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* See ref. 9 for a discussion of proton coupling to ^{51}V in $V(\eta^7\text{-}C_7H_7)(CO)_3$.

of C_2H_4 (ca. 1 atm) at 25° C for 16 h gave 1.8 mol of H_2, a trace of ethane, and a yellow solution from which yellow crystals of what is postulated to be $NbH(C_2H_4)_2(dmpe)_2$ could be isolated at —30° C. The remaining ethylene, 2.0 mmol, was likewise measured by Toepler pump techniques and identified by mass spectroscopy. An identical reaction between 1.0 mmol of $NbH_5(dmpe)_2$ and 6 mmol of C_2D_4 gave 1.8 mmol of a mixture of 21% H_2, 44% HD, and 35% D_2 and yellow crystals of "$NbH(C_2D_4)_2(dmpe)_2$". Though transition metal complexes containing both a hydride ligand and a coordinated olefin are rare, the experimental evidence below clearly supports the $NbH(C_2H_4)_2(dmpe)_2$ formulation.

The infrared spectrum (in Nujol) of $NbH(C_2H_4)_2(dmpe)_2$ shows a weak absorption at 1550 cm^{-1}, almost identical to that found in the spectrum of $NbH(CO)_2$ $(dmpe)_2$. A shoulder at 3020 cm^{-1} is consistent with an olefinic ν(CH) stretching mode. The infrared spectrum of "$NbH(C_2D_4)_2(dmpe)_2$" shows a weaker ν(MH) absorption at 1550 cm^{-1} and a pattern of four peaks at ca. 2290, 2220, 2200, and 2170 cm^{-1} (relatively, strong, weak, medium, strong) due to wholly or partially deuterated coordinated ethylene. No shoulder at 3020 cm^{-1} was visible.

The ^{1}H NMR spectrum of $NbH(C_2H_4)_2(dmpe)_2$ in C_6D_6 shows a hydride resonance at τ 12.94 (a poor triple triplet with $^2J(HP') \approx 21$ and $^2J(HP) \approx 102$ Hz, cf. the hydride resonance in the ^{1}H NMR spectrum of $NbH(CO)_2(dmpe)_2$ above), two doublets (τ 8.47 and 8.81; $J(CH_3P) = 6$ and 4 Hz, respectively) and two poorly resolved triplets (τ 9.06 and 9.66, $J(CH_3P) \approx 3$ and 2 Hz, respectively) assigned to dmpe methyl groups, and a broad peak (ca. 15 Hz wide) at τ 10.82 which integrates as 2 protons vs. the single hydride. The dmpe CH_2 resonances propably lie under the dmpe CH_3 resonances. Apparently the remaining six ethylene proton resonances are masked by the dmpe CH_3 and CH_2 resonances since the total relative intensity in the dmpe region is 38. The ^{1}H NMR spectrum of "$NbH(C_2D_4)_2(dmpe)_2$" confirms this postulate. Not only are the hydride and τ 10.82 ethylene proton peaks very weak but much intensity is lost from under the dmpe methyl resonances, most clearly at ca. τ 9.7 where a broad peak similar to that at τ 10.82 lies under the τ 9.66 dmpe methyl triplet in the spectrum of $NbH(C_2H_4)_2(dmpe)_2$. These results also suggest that hydrogen atoms have been incorporated into coordinated C_2D_4, consistent with finding an $H_2/HD/D_2$ mixture above the solution after reaction of C_2D_4 with $NbH_5(dmpe)_2$ (vide supra).

The ^{31}P NMR spectrum of $NbH(C_2H_4)_2(dmpe)_2$ is also similar to that of $NbH(CO)_2(dmpe)_2$. The undecoupled spectrum consists of a broad peak at 48 ppm and a poorly resolved doublet at 10 ppm ($^2J(PH) \approx 95$ Hz; cf. $^2J(HP) \approx 102$ above) downfield of 85% external H_3PO_4. On decoupling all protons the upper peak becomes a triplet ($J = 18$ Hz) and the lower peak sharpens somewhat and shows some structure but is still rather broad. That two doublets are not obtained, as in the case of $NbH(CO)_2(dmpe)_2$, is probably due to lower symmetry in $NbH(C_2H_4)_2(dmpe)_2$, which makes all P nuclei, and at least four of the eight dmpe methyl groups (see ^{1}H NMR results above) nonequivalent. However, the P nuclei are found in basically two magnetic environments according to the ^{31}P chemical shifts; the triple triplet pattern for the hydride resonance supports this postulate.

Comparison of the $^{13}C\{^1H\}$NMR spectrum of $NbH(C_2H_4)_2(dmpe)_2$ with that of "$NbH(C_2D_4)_2(dmpe)_2$" allows one to assign the resonances due to coordinated ethylene since the Overhauser enhancement is slight when an ethylene ^{13}C atom has D instead of H attached. Two peaks 35 and 32 ppm downfield from TMS in toluene-d_8 are as intense as the other major ^{13}C resonances in the spectrum of $NbH(C_2H_4)_2(dmpe)_2$. They are essentially absent in the $^{13}C\{^1H\}$spectrum of "$NbH(C_2D_4)_2(dmpe)_2$" (other peaks are unchanged) and can therefore be assigned to roughly two types of carbon atoms in the coordinated ethylenes.

Though these data do not prove the $NbH(C_2H_4)_2(dmpe)_2$ formulation, they do support it strongly. The formulation seems especially reasonable in view of the suggested formation of the isoelectronic species, $[MoH(C_2H_4)_2(diphos)_2]^+$ (diphos = $Ph_2PCH_2CH_2PPh_2$), by protonation of $Mo(C_2H_4)_2(diphos)_2$ [12]. Based on the ^1H, ^{31}P, and ^{13}C NMR data above, a reasonable gross structure for $NbH(C_2H_4)_2(dmpe)_2$ would be analogous to that of $TaH(CO)_2(dmpe)_2$. The apparent lower symmetry of $NbH(C_2H_4)_2(dmpe)_2$ vs. $NbH(CO)_2(dmpe)_2$ could be ascribed to the fact that C_2H_4 is sterically more demanding than CO and not cylindrically symmetric about the bond to Nb. Thus an idealized molecular geometry is less favorable.

The exchange of the hydride ligand with ethylene protons in $NbH(C_2H_4)_2(dmpe)_2$

None of the NMR data (including the $^{13}C\{^1H\}$NMR data) suggests that any significant amount of D from C_2D_4 is incorporated into the dmpe ligands under the fairly mild conditions employed in preparation of "$NbH(C_2D_4)_2(dmpe)_2$". On the other hand, Nb—H does scramble to some extent with D in C_2D_4 during preparation of "$NbH(C_2D_4)_2(dmpe)_2$" judging from the 57% D present as HD and D_2 in the 2 mol of evolved gas (vide supra).

A rough estimate of the rate of the hydride/ethylene exchange can be made based on the fact that the spectrum of a sample of $NbH(C_2H_4)_2(dmpe)_2$ in toluene-d_8 at 95°C (60 MHz) is identical to the spectrum at 25°C. In particular the hydride triple triplet resonance at τ 12.94 remains distinct and shows no broadening characteristic of the onset of exchange with ethylene protons. This behavior contrasts markedly with that observed for $[MoH(C_2H_4)_2(diphos)_2]^+$ in CD_2Cl_2 where four protons on one of the ethylene ligands equilibrate with the hydride ligand rapidly on the ^1H NMR time scale (100 MHz) at +7°C by a postulated reversible formation of an ethyl ligand [12]. These data therefore confirm that the rate of exchange in $NbH(C_2H_4)_2(dmpe)_2$ is considerably slower. Though $NbH(C_2H_4)_2(dmpe)_2$ differs from isoelectronic $[MoH(C_2H_4)_2(diphos)_2]^+$ in several obvious ways (and perhaps structurally as well), it is not obvious why the hydride in the former should be so much more reluctant to transfer to ethylene.

Experimental

All operations were done under nitrogen, either in standard glassware or in a Vacuum Atmospheres HE43-2 drybox. $Nb(CH_3)_5(dmpe)$ and $Ta(CH_3)_5(dmpe)$ were prepared as previously reported [13]. Reactions in which H_2 or C_2H_4 uptake or evolution was to be measured were done in sealed vials to which a break-seal was attached. Hydrogen was measured quantitatively by Toepler pump techniques after passing the gas through a liquid nitrogen trap. Ethylene was similarly measured after warming the trap to —78°C (acetone/dry ice). Each was identified by mass spectroscopy. Elemental C and H analyses were done at the Central Research and Development Department.

Preparation of $TaH_5(dmpe)_2$

A mixture of 1.5 g of $Ta(CH_3)_5$(dmpe) and 0.60 g of dmpe in 4 ml of THF was shaken under 500 atm of H_2 in a 10 ml stainless steel bomb at 60°C for 16 h. Removal of the THF in vacuo left 0.6 g of white $TaH_5(dmpe)_2$ (some was lost during the isolation procedure). Its IR and ^1H NMR spectra were identical to those reported [4a].

Preparation of $NbH_5(dmpe)_2$

A mixture of 15.7 g of $Nb(CH_3)_5$(dmpe) and 7.5 g of dmpe in 200 ml of THF were drawn into an evacuated 400 ml bomb which was then pressurized to 500 atm with H_2, heated to 60°C and rocked for 16 h. The bomb was bled till only a few atmospheres pressure remained and then inverted. The brownish-yellow solution was then blown out carefully into a nitrogen-filled flask. The THF was removed in vacuo and the residue was dissolved in 200 ml of pentane. The solution was treated with dry activated charcoal, filtered, and stood at —30°C overnight to give 11.2 g of yellow, waxy $NbH_5(dmpe)_2$. An additional 1.0 g was isolated similarly after removing 150 ml of pentane in vacuo; total crude yield 12.2 g (62%). The crude product was dissolved in 125 ml of pentane, treated with charcoal, etc., and stood at —30°C overnight to give 9.5 g of pure, pale yellow $NbH_5(dmpe)_2$.

Found: C, 36.01; H, 9.30. $NbC_{12}H_{37}P_4$ calcd.: C, 36.20; H, 9.36%. The hydride quintet resonance in the ^1H NMR spectrum confirms the presence of four phosphorus atoms (see text).

Preparation of $NbH(CO)_2(dmpe)_2$

A solution of 0.79 g $NbH_5(dmpe)_2$ in 10 ml of pentane was placed in a 300 ml pressure bottle. The bottle was flushed twice with CO, then pressurized to 30 psi. After stirring for 16 h, the pressure was relieved and ca. 20 ml of hexane added to dissolve the orange solid. The solution was filtered through a fine glass frit to remove the haze. Long orange needles crystallized in the filtrate on standing at —30°C overnight; yield 0.70 g (79%).

Found: C, 37.35, H, 7.39. $NbC_{14}H_{33}P_4O_2$ calcd.: C, 37.36; H, 7.38%. The determination by X-rays that $NbH(CO)_2(dmpe)_2$ is isomorphous with $TaH(CO)_2$ $(dmpe)_2$ is conclusive support for its formulation.

Preparation of $NbH(C_2H_4)_2(dmpe)_2$

A procedure analogous to the above using 1.50 g $NbH_5(dmpe)_2$ under 30 psi of C_2H_4 gave 1.44 g of pale yellow $NbH(C_2H_4)_2(dmpe)_2$ (83% yield).

Found: C, 42.48; H, 9.19. $NbC_{16}H_{41}P_4$ calcd.: C, 42.69; 9.17%.

References

1 Transition Metal Hydrides, E.L. Muetterties, (Ed.), Marcel Dekker, Inc., New York, 1971.
2 J.R. Moss and B.L. Shaw, Chem. Commun., (1968) 632.
3 E.K. Barefield, Inorg. Syn., 15 (1974) 34.
4 (a) F.N. Tebbe, J. Amer. Chem. Soc., 95 (1973) 5823; (b) F.N. Tebbe, unpublished observations.
5 Transition Metal Hydrides, E.L. Muetterties, (Ed.), Marcel Dekker, Inc., New York, 1971, p. 213.
6 K. Clauss and H. Bestian, Ann. Chem., 654 (1962) 8.
7 P.C. Wailes, H. Weigold and A.P. Bell, J. Organometal. Chem., 34 (1972) 155.

8 H. Gilman, A.L. Jacoby and H. Ludeman, J. Amer. Chem. Soc., 60 (1938) 2336.
9 G.M. Whitesides and H.L. Mitchell, J. Amer. Chem. Soc., 91 (1969) 2245.
10 P. Meakin, L.J. Guggenberger, F.N. Tebbe and J.P. Jesson, Inorg. Chem., 13 (1974) 1025.
11 L.J. Guggenberger, Central Research and Development Department.
12 J.W. Byrne, H.U. Blaser and J.A. Osborn, J. Amer. Chem. Soc., 97 (1975) 3871.
13 R.R. Schrock and P. Meakin, J. Amer. Chem. Soc., 96 (1974) 5288.