difference-Fourier maps revealed all 22 non-hydrogen atoms. Anisotropic least-squares refinement of all atoms followed by a difference-Fourier map revealed all but four of the hydrogen atoms, which were placed at idealized distances (1.00 Å for C-H) and angles (109.6° for H-C-H). Hydrogen atom contributions were included in the final structure factor calculation (B = 6 Å^2), but no refinement of their positional or thermal parameters was permitted. Final positional parameters (Table V) and selected distances and angles (Table IV) are given in the text. Other data have been deposited as supplementary material.

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Registry No. **1a**, 12354-85-7; **1b**, 36484-11-4; **1c**, 67841-74-1; **2a**, 80298-79-9; **2b**, 88704-26-1; **2c**, 88704-27-2; **3a**, 63179-49-7; **3b**, 63179-48-6; **3c**, 32761-86-7; **4b**, 90624-44-5; **5b**, 90624-45-6; **6a**, 84623-98-3; **7b**, 84624-05-5; **8a**, 90641-26-2; **9b**, 90624-46-7; **10a**, 90624-47-8; **10b**, 81971-45-1; **10c**, 90624-48-9; **11b**, 81971-44-0; **11c**, 88704-29-4; **12b**, 90624-49-0; **13b**, 90624-50-3; **14b**, 90624-51-4; **15b**, 90624-52-5; **16b**, 90624-53-6; **17b**, 90624-54-7; **18b**, 90624-55-8; **19b**, 90624-56-9; **20b**, 90624-57-0; **21b**, 90624-58-1; **22b**, 90624-59-2; **23b**, 90624-60-5; **24b**, 90624-61-6; **25b**, 90624-62-7; **26b**, 90624-63-8; **27b**, 90624-64-9; **28b**, 90624-65-0; **29b**, 90624-66-1; **30b**, 88704-31-8; **31b**, 90624-67-2; **32c**, 90624-68-3; **33c**, 90624-69-4; $(C_5Me_5)Rh(PMe_3)(C_2H_4)$, 86225-02-7; $CpRh(PEt_3)(C_2H_4)$, 90624-70-7.

Supplementary Material Available: Anisotropic thermal parameters (Table VII), calculated and observed structure factors (Table VIII), and bond distances and angles (Table IX) (15 pages). Ordering information is given on any current masthead page.

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Nine-Coordinate Hexahydride Complexes of Molybdenum and Tungsten

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The known complex $WH_6(PMe_2Ph)_3$ is prepared in 53% yield from $WCl_4(PMe_2Ph)_3$ and $NaH_2Al(OCH_2CH_2OMe)_2$ at -80 °C. It reacts with RNC (R = *t*-Bu) to give $[W(RNC)_5(PMe_2Ph)_2]^{2+}$. The corresponding molybdenum complexes MoH_6L_3 (L = PCy_3, PCy_2Ph, P(*i*-Pr)$_3$, P(*i*-Pr)$_2$Ph) were prepared from $MoCl_4(thf)_2$, L, and $NaAlH_2(OR)_2$ in ~5% yields as unstable oils. They were unambiguously characterized by ^1H NMR and especially $^{31}P\{^1H\}$ NMR spectroscopy. The role of the phosphine in stabilizing these new complexes is discussed. Attempts to prepare MH_9^{3-} (M = Mo, W) were unsuccessful. MoH_6L_3 and the unstable $MoH_5L_4^+$ are the only examples of nine-coordinate mononuclear molybdenum. Evidence for the existence of the latter complex is discussed. The coordination number concept is applied to related organometallic complexes such as $Cp_2MoH_3^+$.

In connection with our studies on C-H activation on alkanes,[1] we set out to make $MH_6(PR_3)_3$ (M = Mo, W). While the tungsten complexes (e.g., PR_3 = PMe_3, PMe_2Ph, or P(*i*-Pr)$_3$) can be made[2] from the reaction of $WCl_4(PR_3)_2$ with $NaBH_4$,[2] $LiAlH_4$,[3] or Na/Hg/H_2,[4] the molybdenum analogues were completely unknown.

Results and Discussion

An Improved Preparation of $WH_6(PMe_2Ph)_3$. We felt that a better synthetic route to these complexes might be developed in view of our experience with the corresponding tetrahydrides,[5a] the yields of which were increased from 2-4% (W) or 15-45% (Mo) to 50-70% by using the strongly nucleophilic organic-soluble $LiBEt_3H$ in place of $NaBH_4$. This modification was not useful for the synthesis of $WH_6(PMe_2Ph)_3$ from $WCl_4(PMe_2Ph)_3$. We therefore turned to the readily available aluminum-based reagent $NaH_2Al(OCH_2CH_2OMe)_2$. This gave some improvement, but substantial improvement was only obtained by cooling the reaction mixture to -78 °C. Under these conditions, yields of 50% were obtained[5b] as long as care was taken with the hydrolysis step (see Experimental Section). Similar attempts using other phosphines such as PCy_3 and PCy_2Ph (Cy = cyclohexyl) gave much lower yields (ca. 5%) of the corresponding $WH_6(PR_3)_3$ complexes.

Chemistry of $WH_6(PMe_2Ph)_3$. We were not able to dehydrogenate alkanes with $WH_6(PMe_2Ph)_3$ by heating it with *tert*-butylethylene and cyclopentane.[1,6a] Only $WH_4(PMe_2Ph)_4$ was detected in the products. This was also the case for the reactions with olefins such as cod, nbd, cyclohexadiene, and cyclopentene. Irradiation of $WH_6(PMe_2Ph)_3$ with light at 366 nm gave no photolysis products, and the starting material was recovered.

Table I. NMR Data for the New Molybdenum Hexahydrides

compd	^1H NMR[a] δ[b]	^2J(P,H)[c]	$^{31}P\{^1H\}$ NMR,[d] δ
$MoH_6(PCy_3)_3$	-4.42	36.3	62.3
$MoH_6(PCy_2Ph)_3$	-3.71	35	70.32
$MoH_6(P(i\text{-}Pr)_3)_3$	-4.63	35.6	52.54
$MoH_6(P(i\text{-}Pr)_2Ph)_3$	-4.00	35	57.89

[a] Assigned to Mo*H*; C_6D_6 solution. [b] Relative to internal Me_4Si. [c] Hz. [d] Assigned to Mo*P*; C_6D_6 solution; downfield from external 85% H_3PO_4.

In contrast to the corresponding reaction with $ReH_4(PPh_3)_2$,[6b] pyridine and piperidine do not react with the tungsten complex, but PMe_2Ph did react at 80 °C in benzene to give $WH_4(PMe_2Ph)_4$. As Walton[7] et al. have found for the Re complex (eq 1), A related complex $[W(CyNC)_5(dpe)]^{2+}$

$$ReH_4(PPh_3)_2 \xrightarrow{RNC} [Re(RNC)_4(PPh_3)_2]^+ \quad (1)$$

$$WH_6(PMe_2Ph)_3 \xrightarrow{RNC} [W(RNC)_5(PMe_2Ph)_2]^{2+} \quad (2)$$

(dpe = 1,2-bis(diphenylphosphino)ethane) has been obtained from $[W(CyNC)_7]^{2+}$ and dpe.[8] The formation of a cationic

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complex in eq 1 and 2 may at first sight appear puzzling, but the most reasonable explanation[8] is the protonolysis by trace acids (e.g., H_2O) of an intermediate, e.g., $WH_2(RNC)_3(PMe_2Ph)_2$. Disproportionation reactions may also play a role. In general, we find that the chemistry of $WH_6(PMe_2Ph)_3$ is much more restricted than that of the analogous $ReH_7(PPh_3)_2$.

Molybdenum Hexahydrides. Despite the fact that the analogous molybdenum complexes were not known, we felt that they would be accessible by using our new preparation. These might be more labile, we thought, and so react with alkanes.[6a] Indeed, reaction of $MoCl_4(thf)_2$ and 3 mol equiv of tertiary phosphine with $NaH_2Al(OCH_2CH_2OMe)_2$ gave $MoH_6(PR_3)_3$. The new hydrides were isolated in low yield (~5%) as air-sensitive orange-yellow oils, which decomposed within 3–5 h in solution under argon. They could not be chromatographically freed from the excess phosphine present, as the complex decomposed to a black material even on Florisil. Possibly, the presence of the excess phosphine is required to suppress decomposition of the hydride.

The complexes were unambiguously characterized by ^1H and especially ^{31}P NMR spectroscopy (Table I). The Mo*H* quartet at δ −3.7 to −4.6 is in the region expected for these complexes ($WH_6(P(i\text{-}Pr)_2Ph)_3$ δ −3.4; $^2J(P,H)$ = 36 Hz[9]), and the coupling constants observed (35–36.3 Hz) are close to those expected. The tetrahydrides show smaller coupling constants (30–33 Hz).[5] The quartet splitting shows that three equivalent PR_3 ligands are present in these complexes. They are apparently fluxional because in the case of the $P(i\text{-}Pr)_2Ph$ complex, the hydride resonances broaden at 215 K and coalesce at 195 K. In the case of the tungsten analogue, similar changes occur at 210 and 190 K, respectively.[9]

To determine the number of hydrides present, we turned to ^{31}P NMR. It has previously been shown[10] that selective ^1H decoupling of the spectrum can remove coupling to protons and allow observation of the coupling to the hydrides. Examination of the resulting $(n + 1)$ binomial pattern leads to the value of n, the number of hydrides present. Placement of the decoupler frequency is straightforward for trialkyl- or triarylphosphines but less so for mixed alkylarylphosphines, where two separate proton frequencies must be decoupled. Our experience has been that the use of noise-band modulation to attempt to decouple both groups of protons is not successful. Instead, we have used simple selective decoupling set at the frequency of the proton resonance corresponding to the greatest number of PR_3 protons. We found no improvement by placing the decoupler at a position intermediate in frequency between those of the aryl and alkyl groups. In this way we found that coupling to one set of protons was eliminated and coupling to the other set was reduced sufficiently by off-resonance effects. The success of this method may be a consequence of the relatively high values (~30 Hz) of the $^2J(P,H)$ coupling to the Mo*H* groups compared to the lower values (~7 Hz) for coupling to the PR_3 protons. We also used the resolution-enhancement capabilities of the instrument with success. These methods were used in the cases of the PCy_3 and $P(i\text{-}Pr)_2Ph$ complexes, and an unambiguous septet was observed in each case. This result confirms the hexahydride formulation. The fully decoupled ^{31}P NMR spectra showed two singlets, one for the free phosphine and the other for the hexahydride, suggesting that no other phosphorus-containing species were present in significant amounts. Some of this work has appeared in a communication.[5b]

The Choice of Phosphine. The choice of phosphine ligand is an important factor in the preparation of these new complexes. In each case, strongly basic, large-cone-angle ligands[11] were successful. The basicity of the phosphine seems to be required to stabilize the Mo(VI) center against loss of H_2. Hydrides appear to be more electron withdrawing in the case of Mo than W, to judge from recent XPS studies.[12] In line with these observations, $WH_4(PR_3)_4$ can be protonated to give the stable $WH_5(PR_3)_4^+$,[13] and even $WH_5(P(O\text{-}i\text{-}Pr)_3)_4^+$ has been reported.[14] The molybdenum analogues $MoH_5(PR_3)_4^+$ (see below) rapidly lose H_2.

The high-cone-angle phosphines (PCy_3 (179°), PCy_2Ph (168°), $P(i\text{-}Pr)_2Ph$ (155°)) that were successfully used prevent the formation of the more stable MoH_4L_4 species as happens[3,15] for PEt_3 (130°), PMe_2Ph (127°), and $PMePh_2$ (136°).[2] Similar effects are observed for the tungsten hydrides. PMe_3 (118°) gives WH_2L_5 and WH_4L_4 while $P(i\text{-}Pr)_3$ (160°) gives only WH_6L_3.[16]

It is often held[17] that bulky phosphines promote the formation of complexes of unusually low coordination numbers and valencies. Just the opposite is true for polyhydride complexes, as we see here.

Attempts To Prepare MH_9^{3-}. In view of the existence of MH_9^{2-} (M = Re, Tc)[18] we tried to synthesize the analogous complexes MH_9^{3-} (M = Mo, W). Many attempts to obtain these by reaction of Na_2WO_4, WCl_6, $MoOCl_4$, and MoO_3 with hydridoaluminates, metallic sodium, or hydrazine were unsuccessful; no hydridic complexes were detected. We did not examine the case of OsH_9^-, however.

On the Existence of the Nine-Coordinate $MoH_5L_4^+$. Many polyhydrides protonate, although the protonated form is usually unstable and loses H_2. One exception is $WH_5L_4^+$, for which several examples are known[13,14] (e.g., L = dpe, $PHPh_2$, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$, $PBuPh_2$, and, surprisingly, $P(O\text{-}i\text{-}Pr)_3$). If the corresponding $MoH_5L_4^+$ salts existed, they would constitute further examples of nine-coordinate molybdenum. Caulton[19] has shown that MoH_4L_4 gives $[MoH_2S_2L_2]^{2+}$ with HBF_4 in MeCN (=S).[20a] We showed[20b] that even in the absence of a coordinating solvent an unexpected reaction occurs (eq 3). A plausible first step in both

$$MoH_4L_4 + 4HBF_4 \rightarrow [(L_3H_2Mo)_2(\mu\text{-}F)_3]BF_4 + 2H_2 + 3BF_3 \quad (3)$$

of these reactions is initial protonation of the MoH_4L_4 to give $MoH_5L_4^+$. In order to gather further evidence, we examined $MoH_4(PMePh_2)_4$ in CD_2Cl_2 at −60 °C by ^1H NMR. In the absence of acid, a broad quintet was observed at δ −2.65, as expected for a fluxional molecule near the coalescence temperature. On the addition of CF_3SO_3H (1 equiv) at −60 °C, the original NMR resonance was replaced by a sharp quintet at δ −1.89. No hydrogen evolution was observed at this temperature, and the reaction was reversible by the addition of NEt_3.

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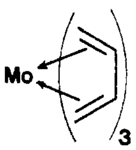
The most reasonable interpretation of this result is the protonation of the MoH_4L_4 complex (eq 4) to give a nine-

$$MoH_4(PMePh_2)_4 \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} MoH_5(PMePh_2)_4^+ \qquad (4)$$

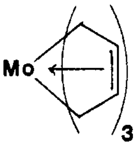
coordinate species $MoH_5L_4^+$. This nine-coordinate complex would be expected to be more fluxional than the eight-coordinate starting material, leading to the sharpening of the quintet. The shift in the resonance suggests the protonated complex is formed to an appreciable extent and is not merely an intermediate in proton exchange (which would also sharpen the resonances).

Unfortunately, attempts to measure the $^{31}P\{^1H\}$ NMR spectrum of the product were frustrated by solubility and viscosity problems, so we were not able to confirm the formulation in this way. This type of protonation, such as is shown is eq 4, is probably general for all polyhydrides having lone pairs available, i.e., other than d^0 complexes.

Nine-Coordination. Nine-coordination is rare for second-row d-block transition metals,[21a] and apart from certain trinuclear clusters,[21b] $MoH_6(PR_3)_3$ appears to be the only unambiguous stable example of nine-coordinate molybdenum. There are, however, complexes that one might regard as having a virtual coordination number of 9: $Cp_2MoH_3^+$, for example. If we regard a pair of ligand electrons as occupying a coordination position, then $Cp_2MoH_3^+$ is nine-coordinate. The lowest number should perhaps be chosen in doubtful cases; Mo(1,3-butadiene)$_3$ might better be thought of as six-coordinate (structure A) rather than nine-coordinate, which would follow



A



B

if structure B were chosen to represent the molecule. It will be seen that on the basis of this criterion any 18-electron d^0 complex has a virtual coordination number of 9. Because the same ambiguities[22] that arise in the assignment of oxidation states also make the d^n assignment equally ambiguous, these virtual coordination numbers should be treated with caution. We conclude that nine-coordination is rare because the early metals are often d^0 but rarely 18-electron and the later metals are often 18-electron but rarely d^0. It is perhaps for this reason most examples of nine-coordination come from groups 5 to 7.

Experimental Section

All reactions were carried out in an atmosphere of prepurified argon. Glassware was oven-dried before use. thf, petroleum ether, and benzene were distilled from sodium/benzophenone and stored over molecular sieves in argon. ^1H NMR spectra were recorded on JEOL FX-90 and Bruker HX-270 instruments. ^{31}P NMR spectra were recorded at 32.2 MHz on a Varian CFT-20 spectrometer. Microanalyses were performed by Galbraith Laboratories Inc. (Knoxville, TN). Ligands, $MoCl_5$, and WCl_6 were obtained from Alfa-Ventron or Strem Chemical Co.

Hexahydridotris(dimethylphenylphosphine)tungsten(VI). $WCl_4(PMe_2Ph)_3$ was prepared from $WCl_4(PPh_3)_2$ by a literature procedure.[23] $WCl_4(PMe_2Ph)_3$ (2.16 g, 2.92 mmol) was slowly added to a cold (−80 °C, CO_2–acetone bath) solution of $NaH_2Al(OCH_2CH_2OMe)_2$ (Aldrich Chemical Co., 3.4 M, 10 mL, 34 mmol) in thf (75 mL). The mixture was allowed to warm slowly to room temperature and was stirred overnight. The solvents were evaporated in vacuo, and benzene was (50 mL) added. The aluminohydride was *carefully* hydrolyzed with 10% aqueous NaOH (10 mL). The benzene layer was decanted, dried with Na_2SO_4, and filtered. The solvent was evaporated, and Et_2O (20 mL) and hexane (50 mL) were added. The precipitated product was filtered, washed with hexane, and dried in vacuo. The crude product so obtained was recrystallized by dissolution in Et_2O (100 mL), addition of $MgSO_4$ (1 g) to decolorize the mixture, and filtration. The volume of the filtrate was slowly reduced in vacuo until the onset of precipitation, when the mixture was cooled to −20 °C. The colorless needles so formed were collected, washed with hexane, and dried in vacuo to give 0.92 g (53%) yield. Anal. Calcd (found) for $C_{24}H_{39}P_3W$: C, 47.70 (47.50); H, 6.50 (6.62). ^1H NMR (C_6D_6): δ −1.91 (q, $^2J(P,H) = 36$ Hz, $^1J(W,H) = 27$ Hz, WH), 1.76, (t, $^2J(P,H) = 4$ Hz, PMe), 7.08 (complex Ph).

Hexahydridotris(tricyclohexylphosphine)molybdenum(VI). $MoCl_4(thf)_2$[24] (0.57 g, 1.5 mmol) and PCy_3 (0.90 g, 3.3 mmol) were refluxed in thf (30 mL) for 15 min. The deep red solution was then cooled to −80 °C. $NaH_2Al(OCH_2CH_2OMe)_2$ solution (3.4 M, 5 mL, 17 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo, and Et_2O (50 mL) was added. The aluminohydride was hydrolyzed with 10% aqueous NaOH, and the ether layer was decanted. After being dried with $MgSO_4$, the ether layer was filtered and evaporated in vacuo. The residue was extracted with hexane (3 × 15 mL), and the extracts were combined and evaporated to give an orange-yellow oil (0.3 g). This contained $MoH_6(PCy_3)_3$ as shown by ^1H and ^{31}P NMR (see text). The analogous complexes of the other phosphines (see Table I) were prepared similarly.

Pentakis(*tert*-butyl isocyanide)bis(dimethylphenylphosphine)tungsten(II) Hexafluorophosphate. $WH_6(PMe_2Ph)_3)_2$ (155 mg; 0.25 mmol) and *tert*-butyl isocyanide (0.4 mL, 5 mmol) were refluxed in MeOH (10 mL) for 4 h. The orange solution was cooled and the solvent evaporated. Acetone (35 mL) saturated with KPF_6 was added to the residue, and the resulting solution was filtered and evaporated. The residue was extracted with CH_2Cl_2 (30 mL) and the resulting mixture evaporated to give a third residue, which was taken up in Me_2CO (3 mL). Slow addition of Et_2O precipitated an orange solid, which was filtered and recrystallized from CH_2Cl_2/Et_2O to give a 50-mg (16%) yield. Anal. Calcd (found) for $C_{36}H_{67}P_4W{\cdot}0.33CH_2Cl_2$: C, 41.25 (41.08); H, 5.67 (5.80); N, 5.80 (5.76). IR (KBr): 2150 (s), 2075 (s), 2065 (s) cm^{-1}.

Action of PMe_2Ph on $WH_6(PMe_2Ph)_3$. $WH_6(PMe_2Ph)_3$ (100 mg, 0.165 mmol) was refluxed in benzene (10 mL) with PMe_2Ph (0.3 mL). After 4 h, the clear yellow solution was evaporated. The residue was dissolved in C_6D_6, and the ^1H NMR spectrum showed that only $WH_4(PMe_2Ph)_4$ was present.[4]

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Registry No. $WH_6(PMe_2Ph)_3$, 20540-07-2; $WCl_4(PMe_2Ph)_3$, 47690-18-6; $MoH_6(PCy_3)_3$, 84430-71-7; $MoCl_4(thf)_2$, 16998-75-7; $[W(t\text{-}BuNC)_5(PMe_2Ph)_2](PF_6)_2$, 90790-90-2; $MoH_6(PCy_2Ph)_3$, 84430-72-8; $MoH_6(P(i\text{-}Pr)_3)_3$, 84430-73-9; $MoH_6(P(i\text{-}Pr)_2Ph)_3$, 84430-74-0; $MoH_4(PMePh_2)_4$, 32109-07-2; $MoH_5(PMePh_2)_4^+$, 90790-91-3.

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