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Imido-Supported Borohydrides of Titanium, Vanadium and Molybdenum

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New imido bis(borohydride) complexes $[(RN=)M(PMe_3)_2(\eta^2 BH_{4}_{2}$ [R = Ar, M = Ti (3); R = Ar, M = V (5); R = Ar, M = Mo (6); R = Ar', M = Mo (7); $Ar = 2,6-iPr_2C_6H_3$, $Ar' = 2,6-iPr_2$ Me₂C₆H₃] were prepared by the reaction of dichlorides $[(RN=)MCl_2(PMe_3)_n]$ (M = Ti, n = 2; M = V, n = 2, M = Mo, n = 3) with LiBH₄ (2 equiv) in THF. Compounds 3, 5, 6 and 7were studied by IR spectroscopy and X-ray diffraction, and an EPR spectroscopy study was performed for paramagnetic

Introduction

The imido ligand RN²⁻ has received significant attention as a useful spectator ligand owing to its isolobal relationship with the ubiquitous cyclopentadienyl (Cp) ligand and owing to the ease of tuning its electronic and steric properties by changing the imido R group.^[1,2] However, the imido ligand can be a potential reactive site, which, for instance, is evidenced in the coupling reactions with CO₂,^[3] alkynes,^[4] imines^[5] and silanes.^[6,7] Our groups are interested in developing the catalytic chemistry of (imido)early-transitionmetal complexes,^[4,6,8,9] which would circumvent the notorious cost and toxicity problems pertinent to late-transitionmetal catalysts. In particular, we are interested in studying imido-supported hydride complexes that could be precatalysts or reactive intermediates in catalytic reductions, such as hydrosilylation,^[9a,9b,9d,9e] hydroboration^[9c] or hydrogena-

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compound 5. In 3, the two borohydride units are orthogonal to each other as a result of the overlap of an antiphase combination of B-H orbitals with the empty d_{xy} orbital of Ti. In contrast, the d_{xv} orbital of the metal atom is singly occupied in 5 and fully occupied in 6 and 7, and both borohydride ligands are oriented in the same way, with the $B(\mu-H_2)M$ moieties orthogonal to the P-M-P vector.

tion. The chemistry of imido-supported metal hydrides is relatively undeveloped.^[10] Herein we report some of our efforts in preparing Group 4-6 metal hydride complexes.

Results and Discussion

Titanium

We have recently shown that the hydride complex $[(ArN=)Mo(PMe_3)_3(Cl)(H)]$ (1, Ar = 2,6-*i*Pr₂C₆H₃) catalyses the hydrosilylation of carbonyl substrates.^[9a] By taking into account that the covalent radius of molybdenum (1.29 Å) is comparable to that of titanium (1.32 Å),^[11] we targeted the preparation of the corresponding titanium complexes $[(ArN=)Ti(PMe_3)_n(Cl)(H)]$, which we expected to have interesting catalytic properties. Attempted direct substitution of the chlorido ligand in the precursor complex $[(ArN=)Ti(PMe_3)_2(Cl)_2]$ (2) for the hydrido ligand by L-Selectride {Li[CH(CH₃)CH₂CH₃]₃BH}, a method that worked well in the preparation of complex 1, resulted in an intractable mixture of products. The treatment of 2 with tBuOK followed by addition of H₃SiPh also resulted in a mixture of products, but the silane was not consumed, and there was no evidence for the hydride complex in the NMR spectroscopic data. In a separate set of experiments, we found that 2 does not react with H₃SiPh but reacts slowly with tBuOK to give a mixture of unidentified products. Use of a smaller alkoxide (LiOEt) resulted in decomposition of the Ti complex and evolution of free phosphane.

To prepare a masked form of the hydride, we treated complex 2 with 1 equiv. of $LiBH_4$. This reaction resulted in

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a 1:1 mixture of the starting complex **2** and the bis(borohydride) [(ArN=)Ti(PMe₃)₂(η^2 -BH₄)₂] (**3**). When 2 equiv. of LiBH₄ were used, complex **3** was obtained as the sole product [Equation (1)]. Complex **3** belongs to the very small class of (imido)transition-metal borohydride compounds,^[2c,2d,12-15] and is only the second example of an (imido)Ti borohydride that has been structurally characterized.^[15]



Complex 3 was characterized by NMR and IR spectroscopy, and its structure was confirmed by X-ray analysis. The ¹H NMR spectrum (C₆D₆, 23 °C) shows *i*Pr signals at δ = 4.34 (sept, J = 6.9 Hz, 2 H, CHMe₂) and 1.33 ppm (d, J = 6.9 Hz, 12 H, CHMe₂) and a doublet (J = 7.2 Hz, 18 H) for the PMe₃ ligands at $\delta = 1.06$ ppm. The borohydrido ligands give rise to a broad feature in the range $\delta = 0.0$ -1.5 ppm overlapped with the iPr and PMe₃ signals. Decoupling from ¹¹B leads only to a marginal sharpening of the signal, presumably due to the exchange between the bridging and terminal hydrido ligands. The presence of phosphane was confirmed by a ³¹P NMR spectroscopic signal at $\delta = -21.0$ ppm. The borohydrido ligand has a typical upfield ¹¹B{¹H} spectroscopic resonance at $\delta = -11.4$ ppm (t, $J_{\rm B,P}$ = 85.7 Hz) showing coupling to two equivalent phosphanes.

The molecular structure of 3 is shown in Figure 1. The geometry can be described as pseudo-trigonal-bipyramidal if one considers the borohydride groups as occupying one site each in the basal plane and two mutually trans phosphane ligands being in the apical positions. Since a crystallographic plane of symmetry runs through the nitrogen, the titanium and two boron atoms, the phosphane groups are equivalent. The Ti-P distance of 2.5834(3) Å is normal. The Ti=N distance of 1.7203(12) Å is close to the mean imidotitanium bond of 1.722 Å (average of 339 structures in the CCDC, in the range 1.656–1.962 Å).^[8b,16] Interestingly, the two borohydrido ligands are twisted relative to each other, so that one of the TiH₂B units lies in the TiB₂N plane, and the other is orthogonal to this plane and roughly coplanar with the P–P axis. The phosphane ligands deviate from the latter borohydride, so that the P(1)-Ti(1)-P(1a) bond angle of 159.33(2)° is significantly less than straight. This difference in borohydride orientation results in an overlap with different d orbitals of titanium and leads to different Ti-B bond lengths. If one assumes that the z axis lies along the Ti–N vector and that the x axis is collinear with the P-P'vector, then the hydride atoms of ligand B(1) overlap with the d_{z^2} orbital (Scheme 1a), whereas borohydride B(2) overlaps with the d_{xy} orbital (Scheme 1b).^[17] Because the empty d_{xy} orbital of Ti is not shared with any other ligand, the Ti-B(2) bond is shorter than the Ti-B(1) bond, 2.345(2)

versus 2.4836(19) Å, respectively. In contrast, the d_{z^2} orbital of the (ArN)Ti(PMe₃)₂ fragment is strongly antibonding with respect to the Ti–N σ -bond and hence is lying higher in energy than d_{xy} , which results in a weaker bonding with the B(1)H₄ ligand. In other known borohydride complexes of titanium, the η^2 -coordinated BH₄ ligands show Ti–B distances comparable with that in **3** {e.g., 2.37(1) Å in [Cp₂Ti(η^2 -BH₄)]^[18]}, whereas the η^3 -borohydride groups give rise to much shorter contacts, such as 2.17(1) Å in [Cp₂CITi(η^3 -BH₄)]^[19] and 2.265(8) Å in the imido borohydride complex [Ti(NAr){ArNC(Me)CHC(Me)CH*t*Bu}(η^3 -BH₄)].^[15] Similar short Ti–B contacts [2.27(1) Å] are also observed for the B–H side-on-coordinated borohydrido ligand in complex [Ti(PMe₃)₂(BH₄)₃].^[20]



Figure 1. Molecular structure of complex **3**. Hydrogen atoms except for those of the BH_4^- ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–P(1)[P(1a)] 2.5834(3), Ti(1)–N(1) 1.7203(12), Ti(1)–B(1) 2.4836(19), Ti(1)–B(2) 2.345(2); P(1)–Ti(1)–P(1a) 159.33(2), B(1)–Ti(1)–B(2) 119.47(8), B(1)–Ti(1)–P(1)[P(1a)] 81.675(11), B(2)–Ti(1)–P(1)[P(1a)] 99.408(11), N(1)–Ti(1)–P(1)[P(1a)] 90.865(12), N(1)–Ti(1)–B(1) 131.02(6), N(1)–Ti(1)–B(2) 109.51(7).



Scheme 1. Selected orbital interactions in **3** for the interaction of the borohydride ligands with the titanium atom.

Attempts to convert complex **3** into an active hydride form were unsuccessful. Complex **3** does not undergo BH_3 abstraction with added PMe_3 , nor does it react with $PhSiH_3$ in the absence or presence of phosphane.

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Vanadium

Similar to the titanium complex, reaction of $[(ArN=)-V(PMe_3)_2(Cl)_2]$ (4, Ar = 2,6-*i*Pr₂C₆H₃) with LiBH₄ (2 equiv.) leads to the bis(borohydride) $[(ArN=)V(PMe_3)_2-(\eta^2-BH_4)_2]$ (5), [Equation (2)]. Complex 5 has a d¹ configuration and thus is EPR-active.



The room-temperature EPR spectrum of **5** is shown in Figure 2 along with its simulation. The spectrum is similar to that of the previously reported rare example of a (imido)-bis(phosphane)V^{IV} complex^[21] and consists of eight overlapping 1:2:1 triplets. The pattern arises from coupling to the I = 7/2 ⁵¹V nucleus and two equivalent I = 1/2 ³¹P nuclei. The simulation yields $g_{iso} = 1.977$, A_{iso} (⁵¹V) = 216 MHz (7.71 mT) and A_{iso} (³¹P) = 98.3 MHz (3.51 mT). Hyperfine splittings from the imido nitrogen atom and hydrido protons are too small to be resolved.



Figure 2. Room-temperature EPR spectrum of 5 and its simulation.

The molecular structure of **5** is shown in Figure 3. Although the overall appearance is similar to that of complex **3**, there is an essential structural difference. Namely, both borohydride moieties are oriented in the same way so that the VH₂B units are orthogonal to the VNP₂ plane, with two bridging ligands from opposite borohydride groups lying *trans* to each other and two other bridging hydrido ligands *trans* to the imido ligand. As a result, the V–H(bridge) bonds are very different: 1.856 and 1.857 Å for the mutually *trans* hydrido ligands and 1.999 and 2.048 Å for the hydrido ligands *trans* to imido. The two V–B distances in **5** are very close: 2.432(2) and 2.419(3) Å^[22] and are comparable with the Ti–B distance to the borohydrido ligand in **3** that has the same orientation. These structural features can be explained by the single occupancy of the d_{xy} orbital shown in Scheme 1b. Two phosphane ligands of **5** are related by a crystallographic symmetry plane. The V–P bond is 2.4782(5) Å, a value slightly lower than that in the related $[V(=NAr)Cl_2(PMe_2Ph)_2]$ [2.489(2) and 2.517(2) Å].^[17] The V=N imido bond of 1.6835(15) Å is in the expected range;^[17,23,24] however, it is shorter than the Ti=N bond in **3** [1.7203(12) Å], despite the ionic radius of five-coordinate vanadium(IV) being marginally larger than the ionic radius of titanium(IV), 0.53 versus 0.51 Å, respectively.^[25] We believe that the difference in the imido–metal bond lengths in **3** and **5** may reflect the different orientation of the borohyd-

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Figure 3. Molecular structure of complex **5**. Hydrogen atoms except for BH_4^- ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–N(1) 1.6835(15), V(1)–P(1)[P(1a)] 2.4782(5), V(1)–B(1) 2.432(2), V(1)–B(2) 2.419(3); P(1)–V(1)–P(1a) 172.50(2), B(1)–V(1)–B(2) 119.24(9), B(1)–V(1)–P(1)[P(1a)] 86.571(13), B(2)–V(1)–P(1)[P(1a)] 90.352(13), N(1)–V(1)–B(1) 123.88(8), N(1)–V(1)–B(2) 116.88(9), N(1)–V(1)–P(1)[P(1a)] 93.170(11).

Molybdenum

Borohydrides $[(ArN=)Mo(PMe_3)_2(\eta^2-BH_4)_2]$ (6) and $[(Ar'N=)Mo(PMe_3)_2(\eta^2-BH_4)_2]$ (7, $Ar' = 2,6-Me_2C_6H_3)$ were prepared by the addition of LiBH₄ (2 equiv) in THF to the dichloride precursors $[(RN=)Mo(Cl)_2(PMe_3)_3]$ [R = Ar' and Ar, respectively; Equation (3)].



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The higher solubility of derivative 6 in nonpolar solvents allowed for its easy extraction with hexanes to furnish, after filtration and removal of volatiles, the compound in 51% isolated yield. Complex 7 was isolated in 67% yield by means of extraction with toluene and recrystallization from Et₂O. Both 6 and 7 were characterized by NMR and IR spectroscopy, and X-ray analyses. The ¹H NMR spectra of 6 and 7 show broad resonances for the BH₄ groups at δ = -0.02 and -0.03 ppm, respectively. Lowering the temperature allowed for observation of separate signals for the bridging and terminal hydrido ligands at $\delta = -5.43$ (br. s, 2) H, B-H_{bridge}) and -1.16 ppm (br. s, 2 H, B-H_{term}) for 6 and at $\delta = -5.38$ (br. s, 2 H, B–H_{bridge}) and -1.10 ppm (br. s, 2 H, B-H_{term}) for 7. ³¹P NMR spectra for both 6 and 7 do not show any significant temperature dependence and feature a singlet for two equivalent *trans*-PMe₃ groups at δ = 1.1 and 1.9 ppm, respectively. As for related compounds 3 and 5, IR spectra show multiple bands in the B-H region, in accord with the presence of two η^2 -coordinated borohydrido ligands: 1950, 1969, 2013, 2102, 2266, 2378, and 2405 cm⁻¹ for **6** and 2111, 2189, 2269, 2371, and 2395 cm⁻¹ for 7.^[26] In the large variety of structurally characterized molybdenum, and Group 6 in general, boro-

hydride complexes,^[27] compounds 6 and 7 are only the sec-

ond and third examples, respectively, of (imido)Mo boro-

hydrides.[14] The molecular structure of 6 is shown in Figure 4. The structure of its Ar' analogue 7 is very similar and is given in the Supporting Information. Complex 6 is isostructural with vanadium complex 5, with both borohydride groups orthogonal to the MoNP2 plane and one bridging hydrido atom of each $Mo(\mu-H)_2B$ unit lying *trans* to the imido group. The trans-PMe₃ ligands are coplanar with the other two hydrido ligands of two $Mo(\mu-H)_2B$ groups. The Mo(1)-B(1) and Mo(1)-B(2) distances in 6 [2.468(2) and 2.481(2) Å, respectively] are very similar and lie at the longer end of the previously characterized molybdenum borohydride compounds: $[Mo^{0}(CO)_{4}(\eta^{2}-BH_{4})]^{-}$ [Mo-B2.41(2) Å],^[27a] trans-[Mo^{II}(PMe₃)₄H(η^2 -BH₄)] [Mo-B 2.468(12) Å],^[27b] [Mo⁰(η^7 , η^1 -C₇H₆-2-C₆H₄P*i*Pr₂)(η^2 -BH₄)] (Mo-B 2.358 Å), ^[27c] $[Mo^{0}(\eta-C_{7}H_{7})(PCy_{3})(\eta^{2}-BH_{4})]$ (Mo-B)2.379 Å)^[27d] and $[Mo^{V}(NAr)_{2}(PMe_{3})_{2}(\eta^{2}-BH_{4})]$ (1) [Mo-B2.461(3) Å].^[14] The Mo(1)-N(1)-C(7) linkage is approximately linear [176.7(1)°], which suggests that the ArN²⁻ ligand acts as a six-electron donor to the metal atom.^[16] The Mo=N bond of 1.7434(15) Å comes at the shorter end of (imido)Mo distances [range 1.745(4)–1.780(3) Å] in complexes featuring the same NAr substituent.^[28]

Complexes 6 and 7 turned out to be surprisingly robust. Like 3 and 5 they are inert towards a variety of Lewis bases. Thus, treatment with NEt₃ or PMe₃ did not show any significant reaction even upon heating up to 50 °C. Even more remarkably, no reaction was observed in the case of alcohols (ethanol and ethylene glycol) and water! Heating of compound 7 up to 100 °C in the presence of an excess amount of water gave only a slow decomposition of the complex by partial hydrolysis of the Mo=NAr bond and formation of ArNH₂.



Figure 4. Molecular structure of complex **6**. Hydrogen atoms except for the BH_4^- ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–N(1) 1.7434(15), Mo(1)–P(1) 2.4918(5), Mo(1)–P(2) 2.4905(5), Mo(1)–B(1) 2.468(2), Mo(1)–B(2) 2.481(2); P(1)–Mo(1)–P(2) 162.586(17), B(1)–Mo(1)–B(2) 124.07(9), B(1)–Mo(1)–P(1) 85.50(5), B(1)–Mo(1)–P(2) 87.06(5), B(2)–Mo(1)–P(1) 85.13(6), B(2)–Mo(1)–P(2) 86.05(6), N(1)–Mo(1)–B(1) 115.94(7), N(1)–Mo(1)–B(2) 119.99(8), N(1)–Mo(1)–P(1) 99.64(5), N(1)–Mo(1)–P(2) 97.77(5).

Conclusion

New imido bis(borohydride) complexes[(RN=)M(PMe₃)₂- $(\eta^2 - BH_4)_2$ [R = Ar, M = Ti (3); R = Ar, M = V (5); R = Ar, M = Mo (6); R = Ar', M = Mo (7); Ar = $2,6-iPr_2C_6H_3$, $Ar' = 2,6-Me_2C_6H_3$ can be easily prepared by treating the dichloride precursors with 2 equiv. of LiBH₄ in THF. X-ray studies of 3, 5, 6 and 7 showed mutual *trans* disposition of two borohydride groups and two phosphane ligands in all four structures. However, the geometry of **3** is different from the others in that one BH₂Ti unit is orthogonal to the other BH₂Ti unit. We attribute the difference to the overlap of an antiphase combination of B-H bonding orbitals with the empty d_{xy} orbital of the titanium atom. In contrast, d_{xy} is half-full or full in the other three compounds and is not available for bonding. Complexes 3, 6 and 7 are surprisingly stable and do not undergo abstraction of the BH₃ unit upon addition of phosphane.

Experimental Section

General: All manipulations were carried out by using conventional inert gas glovebox and Schlenk techniques. Dry solvents were obtained by using Grubbs-type purification columns. NMR spectra were obtained with Bruker DPX-300 and Bruker DPX-600 instruments (¹H: 300 and 600 MHz; ¹³C: 75.5 and 151 MHz; ²⁹Si: 59.6 and 119.2 MHz; ³¹P: 121.5 and 243 MHz, ¹¹B: 96.3 and 192.6 MHz). EPR spectra were collected by using a Bruker Elexsys E580 instrument operating in continuous-wave (cw) mode. The simulation of the EPR spectra were carried out by using Easy-

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Spin.^[29] IR spectra were measured with a Perkin–Elmer 1600 FTIR spectrometer. Elemental analyses were performed in "ANALEST" laboratories (University of Toronto) by using a Perkin–Elmer Model 2400II CHN analyzer with a Perkin–Elmer AD-6 autobalance or at the Service de Microanalyses du LCC-CNRS. PMe₃ was purchased from Strem, and C₆D₆ was from Cambridge Isotope Laboratories. All other chemicals were obtained from Aldrich. $\{V(NAr)Cl_2\}_n$ was prepared according to a known procedure.^[18]

Preparation of $[(ArN=)VCl_2(PMe_3)_2]$ (4): PMe₃ (0.192 mg, 2.524 mmol) was added to a solution of $\{V(NAr)Cl_2\}_n$ (0.250 g, 0.841 mmol) in toluene (1 mL). The solution was shaken for a few minutes and left at room temperature for 6 h for crystallization. The first crop of red crystals of 4 (0.125 g) was separated by filtration. Slow addition of pentane to the filtrate afforded a second crop of 4 (0.120 mg). The crystals were washed with pentane (3 × 2 mL) and dried under vacuum. The combined yield was 0.245 g (65%). EPR (toluene, 20 °C): g = 1.990, $A_{iso}(^{51}V) = 7.8$ mT, $A_{iso}(^{31}P) = 5.8$ mT. $C_{18}H_{35}Cl_2NP_2V$ (449.27): calcd. C 48.12, H 7.85, N 3.12; found C 48.30, H 7.96, N 3.17.

Preparation of [(ArN=)TiCl₂(PMe₃)₂] (2): This compound was prepared by using the same procedure as that described above for **4**, but starting from {Ti(NAr)Cl₂}_n^[30] (0.500 g) and PMe₃ (0.388 g, 3 equiv.). Yield 550 g (72%). ¹H NMR (C₆D₆, 300 MHz, 25 °C): δ = 7.01 (d, *J* = 7.5 Hz, 2 H, *m*-Ar), 6.86 (d, *J* = 7.6 Hz, 2 H, *p*-Ar), 4.63 (sept, *J* = 6.7 Hz, 2 H, *CHM*e₂), 1.44 (d, *J* = 6.9 Hz, 12 H, CHMe₂), 1.05 (app t, *J* = 3.6 Hz, 18 H, PMe₃) ppm. ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 25 °C): δ = -25.6 ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆, 23 °C): δ = 158.4 (*i*-*C*, ArN), 145.5 (*o*-*C*, ArN), 124.2 (*p*-*C*, ArN), 123.0 (*m*-*C*, ArN), 28.5 (*CH*, ArN), 24.8 (*CH*₃, ArN), 13.6 (*PMe*₃) ppm. C₁₈H₃₅Cl₂NP₂Ti (446.20): calcd. C 48.45, H 7.91, N 3.14; found C 48.48, H 7.95, N 3.26.

Preparation of $[(ArN=)Ti(PMe_3)_2(\eta^2-BH_4)_2]$ (3): Toluene (10 mL) was added to a dry mixture of [(ArN=)TiCl₂(PMe₃)₂] (0.100 g, 0.224 mmol) and LiBH₄ (0.224 g, 0.448 mmol). The colour changed to orange-yellow. The mixture was stirred overnight. The solution in toluene was filtered, and all volatiles were removed under vacuum to give a yellow-brown compound (0.065 g, 0.160 mmol, 72%). Recrystallization from diethyl ether afforded well-formed red crystals. ¹H NMR (C₆D₆, 300 MHz, 23 °C): δ = 6.98 (d, J = 7.5 Hz, 2 H, *m*-Ar), 6.85 (d, J = 7.5 Hz, 2 H, *p*-Ar), 4.34 (sept, J = 6.9 Hz, 2 H, CHMe₂), 1.33 (d, J = 6.9 Hz, 12 H, $CHMe_2$), 1.06 (d, J = 7.2 Hz, 18 H, PMe₃), 0.5–1.5 (BH₄) ppm. ³¹P NMR (C₆D₆, 121.5 MHz, 23 °C): $\delta = -21.0$ ppm. ¹¹B{¹H} NMR (C₆D₆, 96.3 MHz, 23 °C): δ = -11.4 (t, $J_{B,P}$ = 85.7 Hz) ppm. ¹³C NMR (C₆D₆, 23 °C): δ = 14.3 (d, ¹J_{C,P} = 16.6 Hz, PMe₃), 24.0 (s, CH₃, Ar), 27.4 (s, CH, Ar), 122.4 (s, m-Ar), 123.5 (s, p-Ar), 144.5 (s, o-Ar), 155.5 (s, i-C, Ar) ppm. IR (Nujol): v = 2469, 2401, 2370, 2249, 2116, 2042, 1951 (BH₄) cm⁻¹. $C_{18}H_{43}B_2NP_2Ti$ (404.982): calcd. C 53.38, H 10.7, N 3.46; found C 51.49, H 10.16, N 3.82.[31]

Preparation of $[(ArN=)V(PMe_3)_2(\eta^2-BH_4)_2]$ (5): A 2 M solution of LiBH₄ in THF (0.23 mL, 0.464 mmol) was added to a solution of $[(ArN=)VCl_2(PMe_3)_2]$ (0.122 g, 0.232 mmol) in diethyl ether (20 mL) precooled to 0 °C. The pale-brown mixture was stirred for 40 min and warmed to room temperature. The solution was filtered, and the precipitate was washed with diethyl ether (5 mL). Volatiles were removed from combined fractions, and the residue was extracted with hexane (7 mL). Keeping the solution at -30 °C produced crystals. The cold solution was decanted, and the crystals were dried under vacuum (0.0183 g, 0.045 mmol, 19%). Hexane was removed under vacuum, and the residue was dissolved in diethyl ether cooled to -30 °C to give crystals suitable for X-ray analysis. IR (Nujol): $\tilde{v} = 2401$, 2388, 2362, 2231, 2168, 2110 (BH₄)

cm $^{-1}.$ $C_{18}H_{43}B_2NP_2V$ (408.057): calcd. C 52.98, H 10.62, N 3.43; found C 48.2, H 8.04, N 3.95. $^{[31]}$

Preparation of $[(ArN=)Mo(PMe_3)_2(\eta^2-BH_4)_2]$ (6): A solution of LiBH₄ in THF (2.0 M, 4.2 mL, 8.4 mmol) was added at room temperature to a solution of [(ArN=)Mo(Cl)₂(PMe₃)₃] (2.38 g, 4.2 mmol) in THF (100 mL). The reaction mixture was stirred overnight. During this time the colour changed from green to brown. All volatiles were removed under vacuum, and the residue was extracted with hexanes (150 mL). The solvent was removed under reduced pressure to give a fine yellow powder (1.07 g, 51%). ¹H NMR (300 MHz, [D₈]toluene, 25 °C): $\delta = -0.02$ (br. s, η^2 -BH₄), 1.16 (d, ${}^{3}J_{H,H}$ = 6.9 Hz, 12 H, 4 CH₃, ArN), 1.33 (vt, ${}^{2}J_{H,P}$ = 7.8 Hz, 18 H, 2 PMe₃), 3.91 (sept, ${}^{3}J_{H,H} = 6.9$ Hz, 2 H, 2 CH, ArN), 6.88 (d, ${}^{3}J_{H,H}$ = 7.8 Hz, 2 H, *m*-H, ArN), 7.00 (t, ${}^{3}J_{H,H}$ = 6.9 Hz, 1 H, p-H, ArN) ppm. ¹H NMR (600 MHz, [D₈]toluene, -44 °C): $\delta = -5.43$ (br. s, 2 H, Mo-H-B), -1.16 (br. s, 2 H, Mo-H-B), 3.60 (br. s, 4 H, BH₂) ppm. ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, [D₈]toluene, 25 °C): $\delta = 1.1$ (s, 2 *P*Me₃) ppm. ¹³C NMR (75.5 MHz, $[D_8]$ toluene, 25 °C): $\delta = 16.0$ (vt, ${}^1J_{C,P} = 24.9$ Hz, PMe₃), 23.4 (s, 2 CH₃, ArN), 27.8 (s, 2 CH, ArN), 123.7 (s, m-C, ArN), 127.1 (s, p-C, ArN), 146.4 (s, o-C, ArN), 153.1 (s, i-C, ArN) ppm. ¹¹B NMR (192.6 MHz, [D₈]toluene, 22 °C): $\delta = -15.84$ (quint, ${}^{1}J_{B,H} =$ 80.9 Hz, 2 BH₄) ppm. IR (Nujol): $\tilde{v} = 1950$ (weak), 1969 (w), 2013 (w), 2102 (m), 2266 (m), 2378 (s), 2405 (s) cm⁻¹. C₁₈H₄₃B₂MoNP₂ (453.050): calcd. C 47.72, H 9.57, N 3.09; found C 47.82, H 9.78, N 2.95

Preparation of $[(Ar'N=)Mo(PMe_3)_2(\eta^2-BH_4)_2]$ (7): A solution of LiBH₄ (2.5 mL, 2.0 m) in THF was added at room temperature to a solution of [(Ar'N=)Mo(Cl)₂(PMe₃)₃] (0.300 g, 0.58 mmol) and PMe₃ (0.12 mL, 1.17 mmol) in THF (50 mL). After addition of LiBH₄, the colour of the reaction mixture turned from green to yellow-green and then, after 30 min of stirring, to yellow. The reaction mixture was stirred for an additional 4 h. All volatiles were pumped off, and the residue was extracted with toluene (50 mL). The solvent was removed under reduced pressure to give a yellow solid, which was then recrystallized at -30 °C from a solution in diethyl ether (0.155 g, 67%). ¹H NMR (300 MHz, [D₈]toluene, 24 °C): $\delta = -0.03$ (br. s, η^2 -BH₄), 1.27 (vt, ²J_{H,P} = 7.5 Hz, 18 H, 2 PMe₃), 2.23 (s, 6 H, 2 CH₃, Ar'N), 6.54 (m, 2 H, m-H, Ar'N), 6.80 (m, 1 H, p-H, Ar'N) ppm. ¹H NMR (600.2 MHz, [D₈]toluene, 22 °C): $\delta = -0.01$ (br. s, η^2 -BH₄), 1.27 (vt, ${}^2J_{\text{H,P}} = 7.5$ Hz, 18 H, 2 PMe_3), 2.23 (s, 6 H, 2 CH_3 , Ar'N), 6.71 (d, ${}^{3}J_{H,H} = 7.5$ Hz, 2 H, *m*-*H*, *Ar'*N), 6.80 (t, ${}^{3}J_{H,H} = 7.5$ Hz, 1 H, *p*-*H*, *Ar'*N) ppm. ¹H NMR (600.2 MHz, [D₈]toluene, -79 °C): $\delta = -5.38$ (br. s, 2 H, η^2 -BH₄, bridge), -1.10 (br. s, 2 H, η²-BH₄, bridge), 1.16 (br. s, 18 H, 2 PMe₃), 2.30 (br. s, 6 H, 2 CH₃, Ar'N), 3.60 (br. s, 2 H, 2 BH, term.), 3.79 (br. s, 2 H, 2 BH, term.), 6.62 (m, 2 H, m-H, Ar'N), 6.80 (m, 1 H, *p*-H, Ar'N) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆, 24 °C): $\delta = 1.9$ (s, *PMe*₃) ppm. ³¹P{¹H} NMR (243 MHz, [D₈]toluene, 22 °C): $\delta = 2.1$ (s, *PMe*₃) ppm. ¹¹B NMR (96.3 MHz, C_6D_6 , 22 °C): $\delta = -15.8$ (br. m, 2 η^2 -BH₄) ppm. ¹¹B NMR (96.3 MHz, [D₈]toluene, -78 °C): δ = -16.4 (br. s, 2 η^2 -*B*H₄) ppm. ¹³C NMR (75.5 MHz, [D₈]toluene, 24 °C): $\delta = 16.2$ (vt, ¹ $J_{CP} =$ 24.2 Hz, 2 PMe₃), 19.6 (s, 2 CH₃, Ar'N), 126.0 (s, p-C, Ar'N), 128.8 (s, m-C, Ar'N), 136.1 (s, o-C, Ar'N), 156.0 (s, i-C, Ar'N) ppm. ¹³C NMR (151 MHz, [D₈]toluene, -80 °C): $\delta = 15.3$ (vt, ${}^{1}J_{C,P} =$ 24.1 Hz, 2 PMe₃), 20.1 (s, 2 CH₃, Ar'N), 126.0 (s, p-C, Ar'N), 129.1 (s, m-C, Ar'N), 136.0 (s, o-C, Ar'N), 155.7 (s, i-C, Ar'N) ppm. IR (Nujol): $\tilde{v} = 2111$ (m), 2189 (w), 2269 (m), 2371 (s), 2395 (s) cm⁻¹. C14H35B2MoNP2 (396.944): calcd. C 42.36, H 8.89, N 3.53; found C 42.42, H 9.27, N 3.43.

X-ray Diffraction Analysis: Single crystals of 3, 5, 6 and 7 were grown from solutions in Et_2O by cooling to -30 °C. The crystals

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Table 1. Crysta	l and structure	refinement	data	for	3,	5, 6	and 7.	
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	3	5	6	7	
Empirical formula	C ₁₈ H ₄₃ B ₂ NP ₂ Ti	$C_{18}H_{43}B_2NP_2V$	$C_{18}H_{43}B_2MoNP_2$	C ₁₄ H ₃₅ B ₂ MoNP ₂	
Formula mass	404.99	408.3	453.03	396.93	
<i>T</i> [K]	123(2)	123(2)	123(2)	120(2)	
λ[Å]	0.71073	0.71073	0.71073	0.71073	
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	
Space group	Pnma	Pnma	<i>P</i> 2(1)2(1)2(1)	P12(1)/n1	
<i>a</i> [Å]	19.1641(8)	18.8898(19)	11.6885(3)	8.192(4)	
b [Å]	13.8042(6)	13.9170(14)	12.1854(3)	19.071(8)	
c [Å]	9.4761(4)	9.5429(10)	18.0303(4)	13.840(6)	
β [°]	90	90	90	92.615(10)	
V [Å ³]	2506.86(18)	2508.7(4)	2568.04(11)	2159.9(17)	
Ζ	4	4	4	4	
$\rho_{\rm calcd.} [\rm g cm^{-3}]$	1.073	1.080	1.172	1.221	
$\mu \text{ [mm^{-1}]}$	0.470	0.524	0.637	0.747	
F(000)	880	884	960	832	
Crystal size [mm]	$0.38 \times 0.32 \times 0.26$	$0.38 \times 0.34 \times 0.24$	$0.34 \times 0.28 \times 0.22$	$0.22 \times 0.12 \times 0.04$	
θ range collected data [°]	2.13 to 29.98	2.16 to29.00	2.02 to 29.97	1.82 to 27.00	
Index ranges [°]	$-24 \le h \le 26$	$-25 \le h \le 25$	$-15 \le h \le 16$	$-10 \le h \le 10$	
	$-19 \le k \le 19$	$-18 \le k \le 18$	$-14 \le k \le 16$	$-22 \leq k \leq 24$	
	$-12 \le l \le 13$	$-13 \le l \le 13$	$-24 \leq l \leq 24$	$-17 \le l \le 17$	
Reflections collected	21671	24791	25298	11303	
Independent reflections	3790 [R(int) = 0.0325]	3457 [R(int) = 0.0460]	7044 [R(int) = 0.0374]	4698 [R(int) = 0.1311]	
Absorption correction	multiscan	multiscan	multiscan	multiscan	
Max. transmission	0.8875	0.8845	0.8726	0.9707	
Min. transmission	0.8416	0.8257	0.8127	0.8528	
Data/restraints/parameters	3790/0/153	3457/0/153	7044/0/389	4698/0/198	
Goodness-of-fit on F^2	1.024	0.980	1.022	0.887	
Final R indices $[I \ge 2\sigma(I)]$	<i>R</i> 1: 0.0306,	<i>R</i> 1: 0.0358,	<i>R</i> 1: 0.0240,	<i>R</i> 1: 0.0950,	
	wR2: 0.0811	wR2: 0.1068	wR2:0.0474	wR2: 0.2081	
R indices (all data)	<i>R</i> 1: 0.0432,	<i>R</i> 1: 0.0483,	<i>R</i> 1: 0.0287,	<i>R</i> 1: 0.1721,	
	wR2: 0.0856	wR2: 0.1147	wR2:0.0485	wR2: 0.2425	
Absolute structure parameter	_	_	0.00(2)	-	
Largest difference peak/hole [eÅ ⁻³]	0.384/-0.434	0.444/-0.386	0.562/-0.247	5.045/-1.268	

were coated with perfluorated oil and mounted on a Bruker SMART diffractometer. Data collection by using an ω -scan technique was performed. Data reduction was carried out by using SAINT software.^[32] Absorption correction based on measurements of equivalent reflections was applied.^[33] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 (Table 1).^[34] CCDC-909414 (3), -909415 (5), -909416 (6) and -909417 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Molecular structure and selected bond lengths and distances of complex **7**.

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FULL PAPER



Treatment of (imido)Ti, -V and -Mo dichloride complexes with $LiBH_4$ gives imido bis(borohydride) complexes, which have been studied by NMR and EPR spectroscopy, and X-ray diffraction.

Borohydrides

A. Y. Khalimon, E. Peterson, C. Lorber, L. G. Kuzmina, J. A. K. Howard, A. van der Est, G. I. Nikonov* 1–8

Imido-Supported Borohydrides of Titanium, Vanadium and Molybdenum

Keywords: Borohydrides / Imides / Titanium / Vanadium / Molybdenum