Hydride transfer reactions in dimolybdenum compounds: a simple route to the novel μ-$\eta^1:\eta^1$-tetrahydroboride complex [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-$BH_4)$]

Philippe Schollhammer,[a] Nolwenn Cabon,[a] François Y. Pétillon,*[a] Jean Talarmin[a] and Kenneth W. Muir*[b]

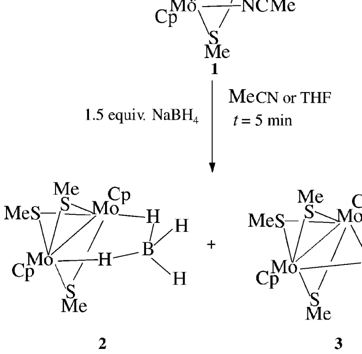
[a] *UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 809, 29285 Brest-Cedex, France. E-mail: francois.petillon@univ-brest.fr*
[b] *Chemistry Department, University of Glasgow, Glasgow, Scotland, UK G12 8QQ*

Received (in Cambridge, UK) 7th August 2000, Accepted 27th September 2000
First published as an Advance Article on the web

The reaction of $NaBH_4$ with the bis-nitrile compound [$Mo_2Cp_2(\mu$-SMe$)_3(MeCN)_2](BF_4)$ 1 unexpectedly gives rise to the rare, stable μ-(η^1-H):(η^1-H) tetrahydroborato complex [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-$BH_4)$] 2, in addition to the expected azavinylidene product [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-η^1-NCHMe)] 3.

The versatility shown by the tetrahydroborate anion in binding to transition metal ions is well known: it can bind *end-on* to a single metal atom through one, two or three hydrogen atoms [η^1-H, η^2-H,H or η^3-H,H,H modes] or *side-on via* an η^2-B,H interaction.[1,2] The same variable hapticity is observed in metal clusters: BH_4^- can link two metal atoms through μ-(η^3-H,H,H) : (η^3-H,H,H), μ-(η^2-H,H):(η^2-H,H), μ-(η^1-H) : (η^1-H) or μ-(η^2-H,H) : (η^1-H) bridges.[2] Of these four bridge types only the {$M_2(\mu$-$\eta^2:\eta^2$-$BH_4)$} core, which is a straightforward modification of the *end-on* η^2-H,H mode of coordination, is relatively common. The {$M_2(\mu$-$\eta^1:\eta^1$-$BH_4)$} bridge is particularly rare: we know only of single structurally characterized examples for three metals: Ir, Ru and Mn.[3–5] The three complexes involved each contain H^- as well as BH_4^- ligands and were obtained during studies of the synthesis and reactivity of polyhydride complexes in whose formation they are thought to be intermediate.[3,4]

We now report that $NaBH_4$ in acetonitrile reacts readily at room temperature with the bis-nitrile compound [$Mo_2Cp_2(\mu$-SMe$)_3(MeCN)_2](BF_4)$**1**[6] to afford a true μ-η^1-η^1-tetrahydroborate bridge in the novel, diamagnetic complex [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-$BH_4)$] **2**, together with the azavinylidene product [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-η^1-NCH(Me)] **3**. Formation of **2** involves substitution of the two acetonitrile ligands by BH_4^-, while the azavinylidene species **3** arises from the transfer of hydride to a coordinated acetonitrile (Scheme 1). Complexes **2** and **3** were obtained in different ratios which depend upon the solvent: **2**:**3** = 80:20 in MeCN but 20:80 in THF. They were separated by chromatography on a silica gel column using hexane–dichloromethane as eluent. Recrystallisation of **2** and **3** from diethyl ether afforded orange crystals.† **2** and **3** have been fully characterized by NMR and IR spectroscopy, microanalysis, and single crystal X-ray analysis.‡§



Scheme 1

The IR and $^{11}B\{^1H\}$ NMR spectra both revealed the presence of coordinated borohydride in **2**. In the $^{11}B\{^1H\}$ NMR spectrum a single broad resonance at δ −27.0 confirmed these assignments. The ^1H NMR spectrum displayed a broad high-field resonance at δ −15.79 (in $CDCl_3$) assignable to two equivalent Mo–H–B bridges. The detection of the two terminal hydrogens bound to the boron atom, at δ 2.32 and 1.28, required the recording of a ^1H spectrum with selective ^{11}B decoupling. The results of 2D ^1H–^1H and ^1H–^{11}B correlation NMR experiments are in accord with these assignments. A ^{11}B-decoupled ^1H–^1H 2D-experiment showed the two resonances at δ 2.32 and 1.28, to be coupled to each other and also to the peak at δ −15.79 (in toluene-d_8), and a ^1H–^{11}B inverse-correlation experiment confirmed that these protons are bound to the boron atom. The well resolved $^2J_{HH}$ couplings (*ca.* 18, 3 and 3 Hz) suggested significant deviations from regular tetrahedral coordination at the boron atom. Moreover, the observation of these couplings at room temperature and further variable temperature NMR experiments between 293 and 363 K implies that the commonly observed interchange of bridging and terminal hydrogens in BH_4 does not occur in **2** in this temperature range. The structure of **2** (Fig. 1)§ involves covalent interaction of the {$Mo_2Cp_2(\mu$-SMe$)_3$}$^+$ moiety with a BH_4^- anion through two bent 3c–2e Mo–H–B bonds [Mo–H_b 1.87(5), 1.84(5); B–H_b 1.19(5), 1.20(5) Å; Mo–H–B 121(3), 125(3)°]. The molecule contains a distorted tetrahedral μ-$\eta^1:\eta^1$-BH_4 ligand in which the bridging B–H_b bonds are somewhat longer than the terminal B–H_t bonds

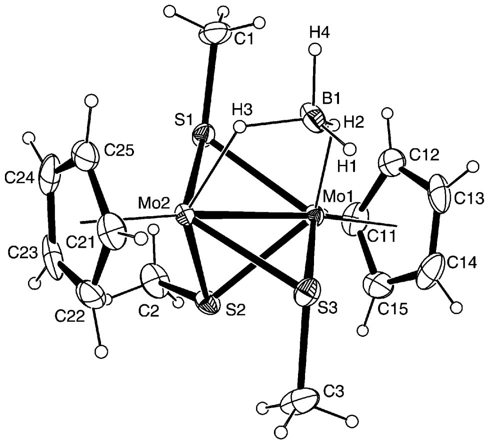


Fig. 1 An ORTEP drawing (20% thermal ellipsoids) of the complex [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-$BH_4)$] **2**. Selected bond lengths (Å) and angles (°): Mo1–Mo2 2.653(1), Mo1–S1 2.4544(12), Mo1–S2 2.4313(12), Mo1–S3 2.4499(12), Mo2–S1 2.4513(11), Mo2–S2 2.4280(12), Mo2–S3 2.4531(12); Mo2–S1–Mo1 65.48(3); Mo2–S2–Mo1 66.18(3), Mo2–S3–Mo1 65.52(3); Mo1–H2 1.87(5), Mo2–H3 1.84(5), B1–H2 1.19(5), B1–H3 1.20(5), B1–H1 1.08(5), B1–H4 1.11(5); H2–B1–H4 96(3), H3–B1–H4 98(3), H1–B1–H2 118(4), H1–B1–H3 115(4), H2–B1–H3 110(3), H1–B1–H4 116(4), Mo1–H2–B1 125(3), Mo2–H3–B1 121(3). Minor disorder sites of the bridging ligands [occupancy 5.6(2)%] are not shown.

DOI: 10.1039/b006457m

[B–H$_t$ 1.08(5), 1.11(5) Å]. The Mo–B distances [2.681(6), 2.711(6) Å] are nearly equal and their length suggests that there is little or no direct Mo–B bonding. Indeed, they are longer than the single Mo–Mo bond [2.653(1) Å]. In all other {$M_2(\mu$-$\eta^1:\eta^1$-$BH_4)$} bridge systems the M–B distances are shorter than the M–M bond length. Thus, in the diiridium complex [$Ir_2(C_5Me_5)_2H_3(\mu$-$BH_4)$] the Ir–B distances are 2.214(4) Å, compared with an Ir–Ir bond length of 2.823(1) Å. In this case it has been suggested that the two bridging hydrogen atoms of the BH_4^- ligand are almost completely transfered to the iridium atoms and that the BH_4^- coordination should be described as μ-(η^2-B,H):(η^2-B,H) rather than μ-($\eta^1:\eta^1$-BH_4).[3] In the dimanganese species [$Mn_2(\mu$-H)(μ-BH_4)$(CO)_6$(μ-$Ph_2PCH_2PPh_2$)][5,7] the Mn–B distances [2.557(3), 2.607(4) Å] are again shorter than the Mn–Mn bond length [2.989(1) Å] and may indicate some direct Mn–B bonding. The Mn–H bond lengths [1.65(4), 1.68(4) Å] are slightly shorter than the Mo–H distances in **2**. The B–H$_b$ [1.24(4), 1.18(4) Å] and B–H$_t$ [1.08(4), 1.09(4) Å] distances are comparable with those in **2** indicate that hydrogen transfer from boron to the metal atoms is small compared with the Ir$_2$ complex. The third example of a μ-($\eta^1:\eta^1$-BH_4) ligand is found in [$Ru_2(C_5Me_5)_2H_3(\mu$-$BH_4)$].[4] The Ru–B distances [2.406(4) Å] are consistent with closed 3c–2e Ru–H–B interactions though they are again shorter than the Ru–Ru bond [2.895(1) Å].[8] Two features of complex **2** appear therefore to be unprecedented: (i) the presence of a μ-$\eta^1:\eta^1$-tetrahydroborate bridge which involves very weak or no direct interaction between boron and the metal atoms and (ii) the stability of this bridge which does not depend on the presence of H$^-$, as is the case with the Ir, Mn and Ru species.

The hydride transfer from BH_4^- to the dimolybdenum site is stopped at a very early stage in **2**. The reaction can also continue to completion, with hydride adding to one acetonitrile ligand, as is shown by the isolation and characterization of **3**.‡ In the IR spectrum of **3** a C=N bond was revealed by a typical band at 1624 cm^{-1}. In the ^{1}H NMR spectrum a quadruplet at δ 7.69 and a doublet at δ 1.82 (J_{HH} 4.6 Hz) indicate that a hydride has been transferred to one of the acetonitrile ligands. The structure of **3** was confirmed by X-ray analysis (Fig. 2).§ It was found to consist of a typical [$Mo^{III}_2Cp_2(\mu$-SMe$)_3$] unit[6] bridged by the nitrogen atom of the azavinylidene N=C(H)Me ligand.

The reaction of BH_4^- with transition metal halides is a standard route to the borohydride complexes which are thought to be intermediates in the conversion of metal halides to metal hydrides.[2a] The simultaneous formation of **2** and **3** reveals a competition between the incomplete transfer of hydride to the bimetallic site and the reduction of one acetonitrile ligand (MeC≡N) into an azavinylidene group (MeCH=N), this latter transformation being favored in THF rather than in acetonitrile. Finally, the four known structural examples of $M_2(\mu$-$BH_4)$ system may represent different stages in the double σ-activation of an XH$_4$ entity at a bimetallic site: in **2** and in the Mn complex the H atoms bridge M and B atoms which do not interact directly; in the Ir complex H transfer is nearly complete and the Ir–B distance is close to the value expected for a single bond; an intermediate stage between these extremes is illustrated by the Ru complex. Further experiments to convert **2** into dimolybdenum hydride and dimolybdenum borane complexes of higher nuclearity are now under investigation.

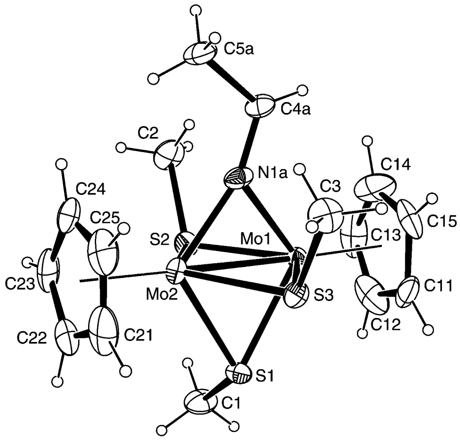


Fig. 2 An ORTEP drawing (20% thermal ellipsoids) of the complex [$Mo_2Cp_2(\mu$-SMe$)_3(\mu$-η^1-N=CHCH$_3$)] **3**. Selected bond lengths (Å) and angles (°): Mo1–Mo2 2.564(1), Mo1–S1 2.446(2), Mo1–S2 2.450(2), Mo1–S3 2.467(2), Mo2–S1 2.448(2), Mo2–S2 2.456(2), Mo2–S3 2.472(2), Mo1–N1A 2.089(8), Mo2–N1A 2.067(8), N1A–C4A 1.38(2), C4A–C5A 1.58(3); Mo1–S1–Mo2 63.18(5), Mo1–S2–Mo2 63.01(5), Mo1–S3–Mo2 62.54(5), Mo1–N1A–Mo2 76.2(2). Random disorder of the azavinylidene C atoms over two sites is not shown.

Notes and references

† *Experimental procedure:* A solution of **1** (0.2 g, 0.32 mmol) in acetonitrile (10 mL) [or a suspension of **1** in thf (10mL)] was treated with NaBH$_4$ (20 mg, 0.53 mmol) at room temperature. The red solution turned readily to orange. After stirring for 5 min the solvent was removed under vacuum and the residue was extracted with diethyl ether. This extract was chromatographed on a silica gel column and elution with hexane–dichloromethane gave two orange bands of **2** and **3**. Recrystallisation from diethyl ether of the two fractions afforded orange crystals of **2** (92 mg, 60%, in MeCN) and **3** (8 mg, 5%, in MeCN). Anal. for $C_{13}H_{23}BMo_2S_3$ **2**. Calc.: C, 32.6; H, 4.8; B, 2.3. Found: C, 32.4; H, 4.8; B, 2.0%. Anal. for $C_{15}H_{23}NMo_2S_3$ **3**. Calc.: C, 35.6; H, 4.6; N, 2.8. Found: C, 35.9; H, 4.7; N, 2.8%.

‡ *Selected spectroscopic data*: for **2**: IR (KBr pellet, cm^{-1}): ν(BH)$_t$: 2449s, 2375s, 2245w; ν(BH)$_b$: 1871. ^{1}H{^{11}B} NMR (toluene-d$_8$), δ 4.94 (s, 10H, C_5H_5), 2.32 [td, J_{HH} 18.3, J_{HH} 3.0 Hz, 1H, $Mo_2(\mu$-$H)_2B\mathit{H}_2$], 1.89 (s, 3H, SCH$_3$), 1.65 (s, 3H, SCH$_3$), 1.42 (s, 3H, SCH$_3$), 1.28 [br m, 1H, $Mo_2(\mu$-$H)_2BH_2$], −15.53 [dd, J_{HH} 18.3, J_{HH} 3.0 Hz, 2H, $Mo_2(\mu$-$\mathit{H})_2BH_2$]. ^{11}B NMR (CDCl$_3$), δ −27.0 (br s, $Mo_2(\mu$-$H)_2BH_2$]. For **3**: IR (KBr pellet, cm^{-1}): ν(C=N), 1624. ^{1}H NMR (CDCl$_3$), δ 7.69 (q, J_{HH} 4.6 Hz, 1H, Mo$_2$-μ-N=C*H*CH$_3$), 5.41 (s, 5H, C_5H_5), 5.23 (s, 5H, C_5H_5), 1.82 (d, J_{HH} 4.6 Hz, 3H, CH$_3$), 1.72 (s, 3H, SCH$_3$), 1.26 (s, 3H, SCH$_3$), 1.22 (s, 3H, SCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$), δ 167.7 (br s, Mo$_2$-μ-N=*C*HCH$_3$), 93.0 (C_5H_5), 91.1 (C_5H_5), 29.7, 23.4 15.4 (N=CH*C*H$_3$ + SCH$_3$).

§ *Crystal data*: for **2**: $C_{13}H_{23}BMo_2S_3$, M = 478.18, monoclinic, space group $P2_1/n$, a = 11.7445(13), b = 10.4279(7), c = 14.196(2) Å, β = 100.77(1)°, U = 1707.9(3) Å^3, Z = 4, D_c = 1.860 Mg m^{-3}, μ = 1.819 mm^{-1}, F(000) = 952. 8632 reflections measured, 3366 unique (R_{int} = 0.011) used in refinement. $R1[2373$ with $I > 2\sigma(I)]$ = 0.027, $wR2$(all data) = 0.070. For **3**: $C_{15}H_{23}Mo_2NS_3$, M = 505.40, orthorhombic, space group $P2_12_12_1$, a = 10.1071(12), b = 13.1712(17), c = 14.0181(18) Å, U = 1866.1(4) Å^3, Z = 4, D_c = 1.779 Mg m^{-3}, μ = 1.672 mm^{-1}, F(000) = 1008. 4219 reflections measured, 3961 unique (R_{int} = 0.051) used in refinement. $R1[3296$ with $I > 2\sigma(I)]$ = 0.057, $wR2$(all data) = 0.16. Flack absolute structure parameter x = 0.21(12).[9]

CCDC 182/1791. See http://www.rsc.org/suppdata/cc/b0/b006457m/ for crystallographic files in .cif format.

1 R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789; M. Brookhart, M. L. H. Green and L. L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

2 (*a*) T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263; (*b*) Z. Xu and Z. Lin, *Coord. Chem. Rev.*, 1996, **156**, 139.

3 T. M. Gilbert, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 3508.

4 M. Jahncke, G. Mester, G. Rheiwald, H. Stoekli-Evans and G. Suss-Fink, *Organometallics*, 1997, **16**, 1137.

5 R. Carreno, V. Riera, M. A. Ruiz, Y. Jeannin and M. Philoche-Levisalles, *J. Chem. Soc., Chem. Commun.*, 1990, 15.

6 F. Barrière, Y. Le Mest, F. Y. Pétillon, S. Poder-Guillou, P. Schollhammer and J. Talarmin, *J. Chem. Soc., Dalton Trans.*, 1996, 3967.

7 R. Carreno, V. Riera, M. A. Ruiz, C. Bois and Y. Jeannin, *Organometallics*, 1993, **12**, 1946.

8 R. W. Parry and G. Kodama, *Coord. Chem. Rev.*, 1993, **128**, 245; R. Bau, R. G. Teller, S. W. Kirtley and T. F. Koetzle, *Acc. Chem. Res.*, 1979, **12**, 176; J. E. McMurry and T. Lectka, *J. Am. Chem. Soc.*, 1993, **115**, 10 167.

9 Programs used: SHELX97—Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998; WinGX—A Windows Program for Crystal Structure Analysis, L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.