

Reactions of transition-metal nitrido compounds with $B(C_6F_5)_3$: crystal structure of $[Re\{NB(C_6F_5)_3\}(PMe_2Ph)(S_2CNMe_2)_2]$

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The transition-metal nitrido complexes $[Re(N)(PR_3)(S_2CNR'_2)]$ ($PR_3 = PMe_2Ph$, $R' = Me$; $PR_3 = PMePh_2$, $R' = Et$ **1**), $[Re(N)(Cl)(PMePh_2)_2(S_2CNMe_2)]$ **2**, $[Mo(N)(S_2CNR_2)_3]$ ($R = Me$ or Et) and $[NBu^*_4][Os(N)(1,2-S_2C_6H_4)_2]$ reacted with the strong Lewis acid $B(C_6F_5)_3$ to yield the adducts $[Re\{NB(C_6F_5)_3\}(PR_3)(S_2CNR'_2)]$ ($PR_3 = PMe_2Ph$, $R' = Me$ **3***; $PR_3 = PMePh_2$, $R' = Et$ **4**), $[Re\{NB(C_6F_5)_3\}(Cl)(PMePh_2)_2(S_2CNMe_2)]$ **5**, $[Mo\{NB(C_6F_5)_3\}(S_2CNR_2)_3]$ ($R = Me$ **6** or **7**) and $[NBu^*_4][Os\{NB(C_6F_5)_3\}(1,2-S_2C_6H_4)_2]$ **8** (* indicates that the compound has been structurally characterised). Reactions of **3**, **6** and **8** with competing strong Lewis bases have revealed differences in the stability of the $M\equiv N-B$ interaction depending on the steric crowding around the metal centre. Reaction of **8** with MeO_3SCF_3 causes the formation of $[Os\{NB(C_6F_5)_3\}\{1,2-(S)(SMe)C_6H_4\}(1,2-S_2C_6H_4)]$ **9**.

Recently we have been exploring the varied chemistry of the strong Lewis acid $B(C_6F_5)_3$ which is crystalline and easily synthesized. As well as mediating unusual and unexpected reactions,^{1,2} it has been shown to form relatively stable adducts with transition metal oxo complexes.^{3,4} Transition metal nitrido complexes are another class of nucleophiles that might be expected to react with strong Lewis acids; indeed reactions between rhenium nitrido compounds and boron trihalides have been reported.^{5,6} However, adducts with triarylboranes have only previously been demonstrated by indirect reaction⁷ and electrophilic attack at nitrido moieties bound to other metals has been confined to carbocationic Lewis acids.^{8,9} We here describe studies into the reactivity of $B(C_6F_5)_3$ with transition metal nitrido complexes.†

Results and discussion

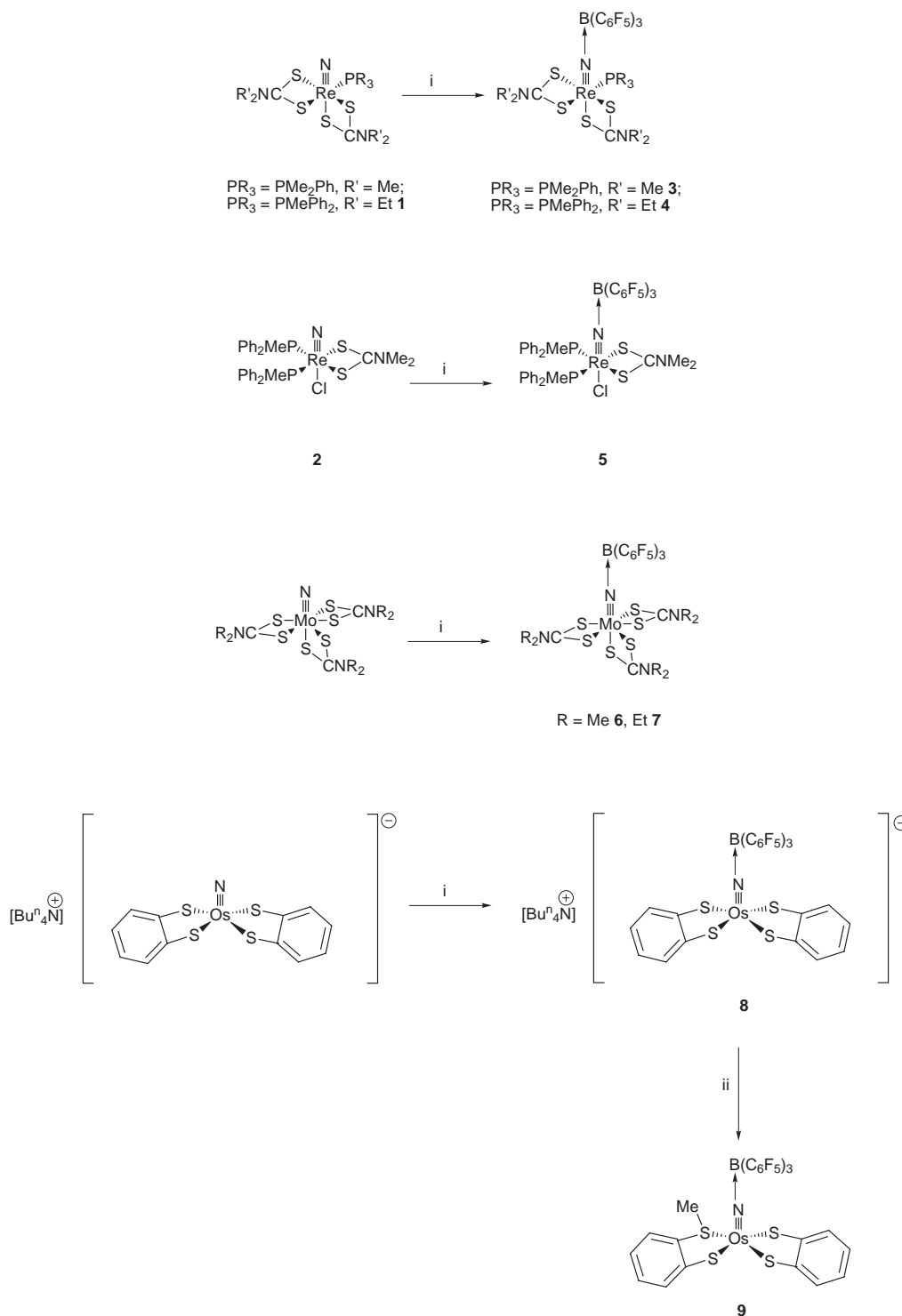
The new rhenium(v) nitrido complexes $[Re(N)(PMePh_2)(S_2CNEt_2)_2]$ **1** and $[Re(N)(Cl)(PMePh_2)_2(S_2CNMe_2)]$ **2** were prepared by reaction of $[Re(N)Cl_2(PMePh_2)_3]$ ¹¹ with 2 equivalents of $NaS_2CNET_2 \cdot 3H_2O$ and 1 equivalent of $NaS_2CNMe_2 \cdot H_2O$ respectively in refluxing methanol. The preparations used were analogous to those used by Ritter and Abram¹² to prepare $[Re(N)(PMe_2Ph)(S_2CNEt_2)_2]$ and $[Re(N)(Cl)(PMe_2Ph)_2(S_2CNMe_2)]$. Characterisation was undertaken by means of microanalysis and IR and NMR spectroscopies; these data are summarised in Table 1. Assignments were straightforward; the $Re\equiv N$ stretches in the IR spectra were assigned by analogy with those of previously reported complexes.

Treatment of each of the transition-metal nitrido complexes $[Re(N)(PR_3)(S_2CNR'_2)]$ ($PR_3 = PMe_2Ph$, $R' = Me$; $PR_3 = PMePh_2$, $R' = Et$ **1**), $[Re(N)(Cl)(PMePh_2)_2(S_2CNMe_2)]$ **2**, $[Mo(N)(S_2CNR_2)_3]$ ($R = Me$ or Et) and $[NBu^*_4][Os(N)(1,2-S_2C_6H_4)_2]$ with an excess of $B(C_6F_5)_3$ in dichloromethane at ambient temperature yields the nitridometal-Lewis acid adducts as purple $[Re\{NB(C_6F_5)_3\}(PR_3)(S_2CNR'_2)_2]$ ($PR_3 = PMe_2Ph$, $R' = Me$ **3**; $PR_3 = PMePh_2$, $R' = Et$ **4**), orange $[Re\{NB(C_6F_5)_3\}(Cl)(PMePh_2)_2(S_2CNMe_2)]$ **5**, cream and red-brown $[Mo\{NB(C_6F_5)_3\}(S_2CNR_2)_3]$ ($R = Me$ **6** or Et **7**) and olive-green $[NBu^*_4]-$

$[Os\{NB(C_6F_5)_3\}(1,2-S_2C_6H_4)_2]$ **8** respectively (Scheme 1). These compounds are all highly soluble in dichloromethane but virtually insoluble in hydrocarbon solvents and removal of the excess of borane by washing thoroughly with hexanes was generally sufficient to obtain analytically pure product. The compounds **3–8** are reasonably air- and moisture-tolerant in the solid state and can be stored indefinitely under an inert atmosphere without decomposition. Yields were generally quite high (ca. 60–90%).

Compounds **3–8** have been characterised by standard techniques, namely ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P NMR and IR spectroscopies, microanalysis and, in the case of **3**, **4** and **6**, FAB (Fast Atom Bombardment) mass spectrometry (Table 1). A single crystal determination of compound **3** has been carried out; crystals of **4** were also obtained but they proved to be of insufficient quality to obtain a properly refined structure although the connectivity between atoms could be verified. As expected, an upfield shift of the ¹¹B-¹H NMR spectroscopic resonance of $B(C_6F_5)_3$ (δ 51) to δ -3 to -6 is observed on adduct formation. This is consistent with the presence of a four-co-ordinate boron species and hence with the expected formation of an $M\equiv N-B$ dative bond. Infrared spectroscopy was in the main rather uninformative as regards the strength of the $M\equiv N-B$ interaction since pentafluorophenyl groups display strong absorptions in the range 900–1100 cm^{-1} , preventing unambiguous assignment of the $M\equiv N$ stretch. One might expect that the nitridometal complex-Lewis acid interaction would weaken the $M\equiv N$ bond, as is found to be the case with Lewis acid adducts of oxometal complexes.¹³ However, in practice, an increase in the $M\equiv N$ stretching frequency is usually observed, e.g. the $Re\equiv N$ stretch in $[AsPh_4][Re(N)Br_4]$ is observed to move from 1099 to 1170 cm^{-1} on addition of BBr_3 .¹⁴ This is often attributed to resonance between the $B-N$ and $M\equiv N$ stretches; however one of the referees has suggested an alternative explanation based on Molecular Orbital theory. The “nitrogen lone pair” MO in the parent nitrido compound has significant $M-N$ σ -antibonding character. Upon co-ordination of the Lewis acid this orbital gains some $B-N$ bonding character hence increasing the $M-N$ stretching frequency. In general, IR stretching frequencies are more sensitive to such changes in antibonding/bonding character than are bond distances. Tentative assignments of the $M\equiv N$ stretch in compounds **3** to **8**, based on the premise that they increase upon borane co-

† During the revision of this manuscript a report of work demonstrating different reactivity between arylborane species and osmium nitrido compounds was published.¹⁰



Scheme 1 Reagents and conditions: (i) excess of $\text{B}(\text{C}_6\text{F}_5)_3$ in CH_2Cl_2 ; (ii) excess of MeO_3CF_3 in CH_2Cl_2 .

ordination, are given in Table 1. The C_6F_5 regions of the $^{13}\text{C}\{-^1\text{H}\}$ and ^{19}F NMR spectra of compounds **3** to **9** have been assigned by analogy with those of $\text{B}(\text{C}_6\text{F}_5)_3$ ¹⁵ and also with those of other published adducts.¹⁶ For compounds **3** to **5**, the phenyl resonances in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were assigned by examination of the magnitude of $^nJ_{\text{PC}}$; for compound **4**, a $^{13}\text{C}\{-^1\text{H}\}$ correlation experiment was performed to assign the downfield region of the ^1H NMR spectrum. Other assignments are straightforward and are not discussed further.

The molecular structure of compound **3** is shown in Fig. 1; principal bond distances and angles are given in Table 2. The rhenium centre has an octahedral co-ordination environment with the nitride-borane unit occupying an axial site and the phosphine *cis* to it. The starting nitrido complex has not been

structurally characterised, however a single crystal X-ray study has been performed on the closely related compound $[\text{Re}(\text{N})(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNET}_2)_2]$.¹² Comparison of the two structures reveals the expected features, namely an extremely small increase in Re–N bond distance on Lewis acid co-ordination [from 1.666(6) to 1.700(4) Å], an almost linear Re≡N–B moiety [$170.9(3)^\circ$] and a significant diminishing of the *trans* influence of the nitrido ligand (reduction in the difference between the Re–S_{*trans*} and Re–S_{*cis*} distances from *ca.* 0.35 to *ca.* 0.25 Å). Table 3 shows the structurally characterised borane adducts of octahedral rhenium nitrido complexes found in the literature and demonstrates the generality of all three of these features. Crystallographically characterised starting metal nitrido compounds are included for comparison purposes.

Table 1 Analytical and spectroscopic data for compounds 1–9

Compound ^a	NMR Data ^b
1 [Re(N)(PMePh ₂)(S ₂ CNEt ₂) ₂] Orange-brown C, 40.2 (39.6); H, 4.7 (4.8); N, 5.8 (6.0); P, 4.6 (4.4) IR: 1358s, 1302s, 1273s, 1212s, 1146s, 1096s, 1076s, 1054s [ν(Re–N)], 914s, 888s	¹ H: 1.04 (dd, 6 H, ³ J _{HH} = 7.1, 7.2, NCH ₂ CH ₃), 1.36 (dd, 6 H, ³ J _{HH} = 7.2, 7.2, NCH ₂ CH ₃), 2.31 (d, 3 H, ² J _{PH} = 8.8, PCH ₃), 3.36, 3.58, 3.71 and 3.87 (m, 2 H each, NCH ₂ CH ₃), 7.3–7.8 (m, 10 H, PC ₆ H ₅) ¹³ C- ¹ H: 12.45 and 12.84 (s, NCH ₂ CH ₃), 18.02 (d, ¹ J _{CP} = 36.7, PCH ₃), 45.14 and 46.03 (s, NCH ₂ CH ₃), 128.38 (d, ² J _{CP} = 11.2, PC ₆ H ₅ , C _o), 131.56 (s, PC ₆ H ₅ , C _p), 134.04 (d, ¹ J _{CP} = 48.5, PC ₆ H ₅ , C _{ipso}), 135.17 (d, ³ J _{CP} = 8.9, PC ₆ H ₅ , C _m), 202.66 and 223.87 (s, S ₂ CNEt ₂) ³¹ P- ¹ H: –5.05 (s)
2 [Re(N)(Cl)(PMePh ₂)(S ₂ CNMe ₂) ₂] Yellow-brown C, 46.5 (46.1); H, 4.1 (4.3); N, 4.0 (3.7) IR: 1261s, 1094s, 1060s [ν(Re–N)], 1020s, 800s	¹ H: 2.13 (d, 6 H, ² J _{PH} = 8.9, PCH ₃), 3.24 (s, 6 H, NCH ₃), 7.1–7.7 (m, 20 H, PC ₆ H ₅) ³¹ P- ¹ H: –10.77 (s)
3 [Re{NB(C ₆ F ₅) ₃ }(PMe ₂ Ph)(S ₂ CNMe ₂) ₂] Lavender C, 35.4 (35.2); H, 2.1 (2.1); B, 0.7 (1.0); N, 3.2 (3.85) Mass: 579, [M – B(C ₆ F ₅) ₃] ⁺ IR: 2727s, 1304s, 1281s, 1156s, 1092s [ν(Re–N)] ^d	¹ H: 1.81 and 1.97 (d, 3 H each, ² J _{PH} = 9.6, PCH ₃), 2.67, 2.98, 3.28 and 3.35 (s, 3 H each, NCH ₃), 7.3–7.4 (m, 5 H, PC ₆ H ₅) ¹¹ B- ¹ H: –3.9 (s) ¹³ C- ¹ H: 15.82 (d, ¹ J _{CP} = 33.6, PCH ₃), 16.04 (d, ¹ J _{CP} = 39.3, PCH ₃), 39.07, 39.17 and 39.71 (s, NCH ₃), 117.5 (br s, BC ₆ F ₅ , C _{ipso}), 127.32 (d, ² J _{CP} = 9.7, PC ₆ H ₅ , C _o), 130.03 (s, PC ₆ H ₅ , C _p), 131.37 (d, ³ J _{CP} = 8.3, PC ₆ H ₅ , C _m), 134.28 (d, ¹ J _{CP} = 53.1, PC ₆ H ₅ , C _{ipso}), 136.89 (d, ¹ J _{CF} = 257, BC ₆ F ₅ , C _m), 139.42 (d, ¹ J _{CF} = 247, BC ₆ F ₅ , C _p), 147.77 (d, ¹ J _{CF} = 241, BC ₆ F ₅ , C _o), 201.75 and 228.20 (s, S ₂ CNMe ₂) ³¹ P- ¹ H: –26.57 (s)
4 [Re{NB(C ₆ F ₅) ₃ }(PMePh ₂)(S ₂ CNEt ₂) ₂] ^c Purple C, 41.3 (41.2); H, 3.05 (3.0); B, 0.85 (0.9); N, 3.4 (3.4); P, 2.6 (2.5) Mass: 1209, M ⁺ ; 1042, [M – C ₆ F ₅] ⁺ ; 842, [M – PMePh ₂ – C ₆ F ₅] ⁺ ; 697, [M – B(C ₆ F ₅) ₃] ⁺ ; 581, [M – B(C ₆ F ₅) ₃ – 4Et] ⁺ ; 549, [M – B(C ₆ F ₅) ₃ – S ₂ CNEt ₂] ⁺ ; 497, [M – B(C ₆ F ₅) ₃ – PMePh ₂] ⁺ ; 399, [M – B(C ₆ F ₅) ₃ – 2S ₂ CNEt ₂] ⁺ IR: 1303m, 1276m, 1147m, 1089m [ν(Re–N)], ^d 978s	¹ H: 0.86 [d, 3 H, ³ J _{HH} = 6.5 (CH ₃) ₂ CHOH], 0.94, 1.10, 1.25 and 1.37 (dd, 3 H each, ³ J _{HH} = 7.0, 7.0, NCH ₂ CH ₃), 2.20 (d, 3 H, ² J _{PH} = 9.0, PCH ₃), 3.22, 3.29, 3.42, 3.52, 3.59, 3.72, 3.78 and 3.81 (m, 1 H each, NCH ₂ CH ₃), 3.73 [m, 0.5 H, (CH ₃) ₂ CHOH], 7.22 (dd, 2 H, ³ J _{PH} = 8.5, ³ J _{HH} = 8.5, PC ₆ H ₅ , H _o), 7.29 (t, 1 H, ³ J _{HH} = 8.5, PC ₆ H ₅ , H _p), 7.36 (dd, 2 H, ³ J _{HH} = 8.5, 8.5, PC ₆ H ₅ , H _m), 7.42 (m, 2 H, PC ₆ H ₅ , H _o), 7.43 (m, 1 H, PC ₆ H ₅ , H _p), 7.65 (dd, 2 H, ³ J _{HH} = 8.5, 8.5, PC ₆ H ₅ , H _m) ¹¹ B- ¹ H: –3.4 (s) ¹³ C- ¹ H: 1.10 [s, (CH ₃) ₂ CHOH], 12.01, 12.43, 12.58 and 12.67 (s, NCH ₂ CH ₃), 17.22, (d, ¹ J _{CP} = 36.8, PCH ₃), 22.68 [s, (CH ₃) ₂ CHOH], 44.72, 44.96, 45.00 and 45.98 (s, NCH ₂ CH ₃), 119.0 (br s, BC ₆ F ₅ , C _{ipso}), 128.02 and 128.38 (d, ² J _{CP} = 11.0, PC ₆ H ₅ , C _o), 130.23 and 130.93 (s, PC ₆ H ₅ , C _p), 132.2 and 133.40 (d, ³ J _{CP} = 9.2, PC ₆ H ₅ , C _m), 133.7 and 136.88 (d, ¹ J _{CP} = 49.2, PC ₆ H ₅ , C _{ipso}), 136.81 (d, ¹ J _{CF} = 271, BC ₆ F ₅ , C _m), 139.52 (d, ¹ J _{CF} = 245, BC ₆ F ₅ , C _p), 148.02 (d, ¹ J _{CF} = 241, BC ₆ F ₅ , C _o), 199.95 and 229.78 (s, S ₂ CNEt ₂) ¹⁹ F: –168.79 (dd, 6 F, ³ J _{FF} = 22.6, 20.7, BC ₆ F ₅ , F _m), –163.90 (t, 3 F, ³ J _{FF} = 20.7, BC ₆ F ₅ , F _p), –133.80 (d, 6 F, ³ J _{FF} = 22.6, BC ₆ F ₅ , F _o) ³¹ P- ¹ H: –12.86 (s)
5 [Re{NB(C ₆ F ₅) ₃ }(Cl)(PMePh ₂)(S ₂ CNMe ₂) ₂] Orange C, 44.5 (44.5); H, 3.3 (2.5); N, 1.9 (2.2) IR: 1099w [ν(Re–N)], ^d 970w, 895m, 722m	¹ H: 1.79 (d, 6 H, ² J _{PH} = 9.5, PCH ₃), 3.16 (s, 6 H, NCH ₃), 7.0–7.8 (m, 20 H, PC ₆ H ₅) ¹¹ B- ¹ H: –2.7 (s) ¹³ C- ¹ H: 15.31 (d, ¹ J _{CP} = 36.6, PCH ₃), 19.17 (d, ¹ J _{CP} = 38.3, PCH ₃), 38.58 and 39.65 (s, NCH ₃), 120.1 (br s, BC ₆ F ₅ , C _{ipso}), 127.84, 128.39, 129.01, 130.17, 130.92, 131.28, 132.18, 132.62 and 133.32 (PC ₆ H ₅), 134.37 (d, ¹ J _{CP} = 59.6, PC ₆ H ₅ , C _{ipso}), 135.82 (d, ¹ J _{CP} = 58.9, PC ₆ H ₅ , C _{ipso}), 136.68 (d, ¹ J _{CF} = 252, BC ₆ F ₅ , C _m), 139.27 (d, ¹ J _{CF} = 263, BC ₆ F ₅ , C _p), 148.03 (d, ¹ J _{CF} = 253, BC ₆ F ₅ , C _o), 191.15 (s, S ₂ CNMe ₂) ³¹ P- ¹ H: –16.73 (s)
6 [Mo{NB(C ₆ F ₅) ₃ }(S ₂ CNMe ₂) ₂] Cream C, 33.6 (33.0); H, 1.9 (1.85); B, 1.0 (1.1); N, 4.9 (5.7) Mass: 984, M ⁺ ; 773, [M – C ₆ F ₅ – MNe ₂] ⁺ ; 697, [M – C ₆ F ₅ – S ₂ CNMe ₂] ⁺ ; 472, [M – B(C ₆ F ₅) ₃] ⁺ ; 352, [M – B(C ₆ F ₅) ₃ – S ₂ CNMe ₂] ⁺ IR: 1645w, 1559m, 1514m, 1305m, 1156m, 1082m (br) [ν(Re–N)], ^d 979m (br)	¹ H: 3.19 (s, 3 H, NCH ₃), 3.25 (s, 6 H, NCH ₃), 3.34 (s, 6 H, NCH ₃), 3.38 (s, 3 H, NCH ₃) ¹¹ B- ¹ H: –6.5 (s) ¹³ C- ¹ H: 35.63, 37.36, 40.68 and 41.10 (s, NCH ₃), ^f 119.0 (br s, BC ₆ F ₅ , C _{ipso}), 136.86 (d, ¹ J _{CF} = 241, BC ₆ F ₅ , C _m), 139.28 (d, ¹ J _{CF} = 247, BC ₆ F ₅ , C _p), 147.81 (d, ¹ J _{CF} = 239, BC ₆ F ₅ , C _o), 200.78 and 203.62 (s, S ₂ CNMe ₂) ^g ¹⁹ F: –168.98 (m, 6 F, BC ₆ F ₅ , F _m), –163.87 (t, 3 F, ³ J _{FF} = 26.3, BC ₆ F ₅ , F _p), –134.17 (d, 6 F, ³ J _{FF} = 18.8, BC ₆ F ₅ , F _o)
7 [Mo{NB(C ₆ F ₅) ₃ }(S ₂ CNEt ₂) ₂] Red-brown C, 38.7 (37.2); H, 3.1 (2.8); B, 1.0 (1.0); N, 4.6 (5.25) IR: 1302s, 1262s, 1209m, 1152m, 1089m [ν(Re–N)], ^d 976s	¹ H: 1.11–1.46 (m, 18 H, NCH ₂ CH ₃), 3.61–3.81 (m, 12 H, NCH ₂ CH ₃) ¹¹ B- ¹ H: –6.6 (s) ¹³ C- ¹ H: 11.77, 12.23, 12.36 and 12.48 (2, NCH ₂ CH ₃), ^f 43.31, 44.46, 45.58 and 46.64 (s, NCH ₂ CH ₃), ^f 119.8 (br s, BC ₆ F ₅ , C _{ipso}), 136.87 (d, ¹ J _{CF} = 255, BC ₆ F ₅ , C _m), 139.24 (d, ¹ J _{CF} = 248, BC ₆ F ₅ , C _p), 147.81 (d, ¹ J _{CF} = 240, BC ₆ F ₅ , C _o), 199.39 and 202.38 (s, S ₂ CNEt ₂) ^g
8 [NBu ₄][Os{NB(C ₆ F ₅) ₃ }(1,2-S ₂ C ₆ H ₄) ₂] Olive-green C, 44.9 (44.6); H, 3.25 (3.6); B, 1.2 (0.9); N, 2.0 (2.3) IR: 1644m, 1515s, 1283m, 1275m, 1097s, 979s, 794m	¹ H: 0.90 [t, 12 H, ³ J _{HH} = 7.1, N(CH ₂) ₃ CH ₃], 1.26 [m, 8 H, N(CH ₂) ₂ CH ₂ CH ₃], 1.37 (m, 8 H, NCH ₂ CH ₂ CH ₂ CH ₃), 2.63 [m, 8 H, NCH ₂ (CH ₂) ₂ CH ₃], 7.03 and 7.68 (m, AA'BB' spin system, 8 H, S ₂ C ₆ H ₄) ¹¹ B- ¹ H: –3.7 (s) ¹³ C- ¹ H: 13.32 [s, N(CH ₂) ₃ CH ₃], 19.72 [s, N(CH ₂) ₂ CH ₂ CH ₃], 23.68 (s, NCH ₂ CH ₂ CH ₂ CH ₃), 58.98 [s, NCH ₂ (CH ₂) ₂ CH ₃], 114.0 (br s, BC ₆ F ₅ , C _{ipso}), 124.69 and 127.90 (s, S ₂ C ₆ H ₄), 136.67 (d, ¹ J _{CF} = 238, BC ₆ F ₅ , C _m), 139.56 (d, ¹ J _{CF} = 228, BC ₆ F ₅ , C _p), 147.56 (d, ¹ J _{CF} = 246, BC ₆ F ₅ , C _o), 149.77 (s, S ₂ C ₆ H ₄ , C _{ipso}) ¹⁹ F: –168.80 (m, 6 F, BC ₆ F ₅ , F _m), –162.99 (t, 3 F, ³ J _{FF} = 20.7, BC ₆ F ₅ , F _p), –134.72 (d, 6 F, ³ J _{FF} = 24.0, BC ₆ F ₅ , F _o)
9 [Os{NB(C ₆ F ₅) ₃ }{1,2-(S)(SMe)C ₆ H ₄ }(1,2-S ₂ C ₆ H ₄)] Dark green oil ^h	¹ H: 3.06 (s, SCH ₃), 7.0–7.8 (br, C ₆ H ₄) ¹¹ B- ¹ H: –2.3 (s) ¹³ C- ¹ H: 33.5 (br s, SCH ₃), 118.7 (br s, BC ₆ F ₅ , C _{ipso}), 122.17, 127.01, 128.36, 128.97, 130.47 and 132.27 [br s, S ₂ C ₆ H ₄ and (S)(SCH ₃)C ₆ H ₄], 136.90, (d, ¹ J _{CF} = 246, BC ₆ F ₅ , C _m), 140.30 (d, ¹ J _{CF} = 267, BC ₆ F ₅ , C _p), 148.12 (d, ¹ J _{CF} = 240, BC ₆ F ₅ , C _o)

^a Analytical data given as found (calculated) in %. Mass spectral data (Fast Atom Bombardment) given as *m/z* (assignment), selected IR data (cm^{–1}) as Nujol mulls. ^b At probe temperature. Data given as: chemical shift (δ) (multiplicity, relative intensity, *J* in Hz, assignment). All obtained in CD₂Cl₂. ^c Two coincident resonances. ^d Tentative assignment, see text. ^e Crystallised with 0.5 molecule of Pr³OH. ^f Resonances in 2:2:1:1 intensity ratio. ^g Resonances in 2:1 intensity ratio. ^h Oil too sensitive to obtain microanalytical data.

The NMR spectra of compounds **3–5** reveal that there is a lowering of symmetry upon co-ordination of the Lewis acid. For instance, compound **1** displays 2 methyl and 4 methylene resonances in its ^1H NMR spectrum whereas 4 and 8 signals respectively are observed for the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct **4**. This may be attributed to restriction of free rotation about the $\text{Re}-\text{P}$ bond upon addition of the bulky triarylborane. A further point of interest is provided by compound **5** where there is apparently only one dithiocarbamate methyl environment and one phosphine methyl environment in the ^1H NMR spectrum but two distinct resonances for each in the $^{13}\text{C}-\{^1\text{H}\}$ NMR spectrum. This has been attributed to the different timescales involved in ^1H and $^{13}\text{C}-\{^1\text{H}\}$ NMR spectroscopy. The adducts **6** and **7** display 4 distinct dithiocarbamate resonances in their ^1H and $^{13}\text{C}-\{^1\text{H}\}$ NMR spectra with intensity ratios 1:2:2:1; this is in agreement with published data for the compound $[\text{Mo}(\text{NCPh}_3)(\text{S}_2\text{CNMe}_2)_3][\text{BF}_4]$.⁸ The NMR spectra of compound **8** are similar to those of the parent nitrido complex and are not discussed further.

In order to test the strength of the $\text{M}=\text{N}-\text{B}$ interaction, the reactions of compounds **3**, **6** and **8** with a series of competing Lewis bases were attempted. The bases used were NEt_3 , PMe_3

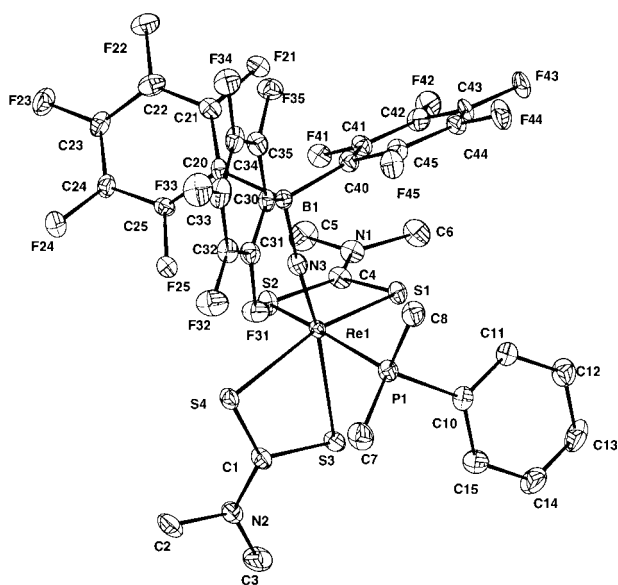


Fig. 1 Molecular structure of $[\text{Re}\{\text{NB}(\text{C}_6\text{F}_5)_3\}(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2]$ **3** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances (\AA) and angles ($^\circ$) for compound **3**

$\text{B}(1)-\text{N}(3)$	1.548(7)	$\text{B}(1)-\text{N}(3)-\text{Re}$	170.9(3)
$\text{Re}-\text{N}(3)$	1.700(4)	$\text{C}(20)-\text{B}(1)-\text{C}(30)$	103.3(4)
$\text{Re}-\text{S}(1)$	2.3769(12)	$\text{C}(30)-\text{B}(1)-\text{C}(40)$	114.5(4)
$\text{Re}-\text{S}(2)$	2.4350(15)	$\text{C}(20)-\text{B}(1)-\text{C}(40)$	114.7(4)
$\text{Re}-\text{S}(3)$	2.6090(12)	$\text{C}(20)-\text{B}(1)-\text{N}(3)$	109.0(4)
$\text{Re}-\text{S}(4)$	2.4608(13)	$\text{C}(30)-\text{B}(1)-\text{N}(3)$	115.2(4)
$\text{Re}-\text{P}(1)$	2.4154(15)	$\text{C}(40)-\text{B}(1)-\text{N}(3)$	100.4(4)

Table 3 Comparison of *cis* and *trans* metal–ligand distances and $\text{Re}-\text{N}-\text{B}$ bond angles for some octahedral rhenium(v) nitrido complexes and their Lewis acid adducts

Compound	$\text{Re}-\text{L}_{\text{trans}}/\text{\AA}$	$\text{Re}-\text{L}_{\text{cis}}/\text{\AA}$	$\text{B}-\text{N}-\text{Re}/^\circ$	$\text{Re}-\text{N}/\text{\AA}$
3 $[\text{Re}\{\text{NB}(\text{C}_6\text{F}_5)_3\}(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2]$	2.6090	2.3769(12)–2.4608(13)	170.9(3)	1.700(4)
$[\text{Re}(\text{N})(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNEt}_2)_2]^{12}$	2.793(2)	2.396(1)–2.449(1)	<i>a</i>	1.666(6)
$[\text{Re}(\text{N}(\text{BCl}_3)(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNEt}_2)_2]^{16}$	2.565(2)	2.376(2)–2.455(2)	170.5(3)	1.704(3)
$[\text{Re}(\text{N}(\text{BPh}_3)(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNEt}_2)_2]^{17}$	2.579(4)	2.362(4)–2.431(4)	170.9(9)	1.653(12)
$[\text{Re}(\text{N})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]^{17}$	2.633(2)	2.442(2) ^b	<i>a</i>	1.660(8)
$[\text{Re}(\text{N}(\text{BCl}_3)\text{Cl}_2(\text{PMe}_2\text{Ph}))_3]^{18}$	2.439(3)	2.394(3) ^b	176.5(6)	1.728(7)

^a Not applicable. ^b $\text{Re}-\text{Cl}_{\text{cis}}$ distance.

and THF and in all cases an excess of base was added to a dichloromethane solution of the adduct and after 1 h stirring the reaction residues were analysed by NMR spectroscopy. Tetrahydrofuran was shown to cause no alteration to either the ^1H or $^{11}\text{B}-\{^1\text{H}\}$ NMR spectra of all 3 compounds, however NEt_3 and PMe_3 had differing effects depending on the metal centre. For the rhenium complex **3** no effect was observed on Lewis base addition, whereas for the osmium compound **8**, addition of L ($\text{L} = \text{PMe}_3$ or NEt_3) caused quantitative formation of the parent nitrido compound and $\text{L}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ within 1 h. The molybdenum compound **6** displayed intermediate stability with approximately 50% displacement of the parent nitrido complex by the competing Lewis base over 1 h. The difference in stability of these 3 metal nitrido complex–Lewis acid adducts is probably due to steric factors since the $\text{Re}=\text{N}-\text{B}$ moiety in **3** is protected by the bulky *cis* tertiary phosphine and the $\text{Os}=\text{N}-\text{B}$ linkage in **8** is exposed by the ‘tied back’ dithiolate ligands. Compound **6** displays intermediate steric hindrance.

Following the work of Sellmann *et al.*⁹ who demonstrated the presence of two nucleophilic sites on the compound $[\text{NBu}^n_4][\text{Os}(\text{N})(1,2-\text{S}_2\text{C}_6\text{H}_4)_2]$, the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct of this metal nitrido complex was treated with 2 competing Lewis acids, namely $[\text{Ph}_3\text{C}][\text{BF}_4]$ and MeO_3SCF_3 . As expected, the bulky trityl cation displaced the borane at the less hindered nitrido moiety to yield the known compound $[\text{Os}(\text{N}(\text{CPh}_3)(1,2-\text{S}_2\text{C}_6\text{H}_4)_2)]$.⁹ However, reaction of $[\text{NBu}^n_4][\text{Os}\{\text{NB}(\text{C}_6\text{F}_5)_3\}(1,2-\text{S}_2\text{C}_6\text{H}_4)_2]$ **8** with an excess of methyl triflate in dichloromethane yields, after extraction into toluene, the olive-green oil $[\text{Os}\{\text{NB}(\text{C}_6\text{F}_5)_3\}(1,2-\text{S})(\text{SMe})\text{C}_6\text{H}_4\}(1,2-\text{S}_2\text{C}_6\text{H}_4)]$ **9** in which Lewis acids are co-ordinated to both nucleophilic sites. This adduct has been characterised by NMR spectroscopy only since the oil was too sensitive to obtain meaningful microanalytical data. This indicates that the methyl group is relatively mobile and can move between the 4 sulfur donors.

In conclusion, we have demonstrated that the nitrido group in transition metal nitrido complexes is sufficiently nucleophilic to form a dative bond with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. These adducts are the first reported from direct reactions between a triarylborane and a transition metal nitrido complex. The $\text{M}=\text{N}-\text{B}$ interaction is reasonably strong as demonstrated by the relative stability of the adducts towards atmospheric oxygen and moisture, although stability towards competing strong Lewis bases seems to vary from metal to metal and is probably a function of steric crowding.

Experimental

All preparations and manipulations of air and/or moisture sensitive materials were carried out under an atmosphere of dinitrogen using standard Schlenk line techniques or in an inert-atmosphere glove-box containing dinitrogen. Dinitrogen was purified before use by passage through a drying column filled with activated molecular sieves (4 \AA) and a deoxygenating column filled with either manganese(II) oxide suspended on vermiculite (Schlenk line) or BASF catalyst (glove-box). Solvents were predried over activated 4 \AA molecular sieves and then distilled from sodium (toluene), sodium–potassium alloy

[pentane and light petroleum (bp 40–60 °C)], potassium (THF) or calcium hydride (dichloromethane) under a slow continuous stream of dinitrogen. The Analar solvents methanol and PrⁱOH were used as supplied without drying and degassed by bubbling dinitrogen through them for 15 min. Deuteriated dichloromethane for NMR spectroscopy was dried over calcium hydride and deoxygenated by three freeze–pump–thaw cycles. Deuteriochloroform was used as supplied.

The NMR spectra were recorded on either a Varian Unity-Plus 500 (¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P at 499.87, 160.38, 123.70, 470.28 and 202.35 MHz respectively) or a Bruker AM300 spectrometer (¹H, ¹¹B, ¹³C and ³¹P at 300.13, 96.25, 75.5 and 121.6 MHz respectively). They were referenced internally using the residual protio-solvent (¹H) and solvent (¹³C) resonances and measured relative to tetramethylsilane (δ 0), or referenced externally to BF₃·Et₂O (¹¹B, δ 0), CFCl₃ (¹⁹F, δ 0) or 85% H₃PO₄ (³¹P, δ 0). Chemical shifts are quoted in δ (ppm); a positive sign indicates a downfield shift relative to the standard. Fast atom bombardment mass spectra were obtained by the EPSRC Mass Spectrometry Service at the University College of Swansea under the supervision of Dr J. A. Ballantine; infrared spectra as Nujol mulls between NaCl plates on a Perkin-Elmer 1710 FTIR spectrometer in the range 400 to 4000 cm⁻¹. Elemental analyses were obtained by the microanalytical department of the Inorganic Chemistry Laboratory.

The compounds [Re(N)Cl₂(PMePh₂)₃],¹¹ [Re(N)(PMe₂Ph)(S₂CNMe₂)₂],¹² [Mo(N)(S₂CNR₂)₃] (R = Me or Et),¹⁹ [N-Buⁿ][Os(N)(1,2-S₂C₆H₄)₂]⁹ and B(C₆F₅)₃^{1,20} were prepared by literature methods.

Preparations

[Re(N)(PMePh₂)(S₂CNEt₂)₂] 1. To a stirred solution of [Re(N)Cl₂(PMePh₂)₃] (0.300 g, 0.34 mmol) in methanol (30 cm³), Na₂CNEt₂·3H₂O (0.233 g, 1.03 mmol) in methanol (15 cm³) was added. The reaction mixture, which immediately changed from yellow to orange, was heated to reflux for 1 h before being allowed to cool to room temperature. The solvent was removed *in vacuo* and the resulting, rather oily, orange solid washed with PrⁱOH (20 cm³). Recrystallisation from PrⁱOH and dichloromethane (15 cm³ of a 1 : 1 mixture) at –80 °C afforded complex **1** analytically pure. Yield: 0.116 g (48%).

[Re(N)(Cl)(PMePh₂)₂(S₂CNMe₂)] 2. The complex [Re(N)Cl₂(PMePh₂)₃] (0.436 g, 0.500 mmol) was dissolved in methanol (20 cm³) and a solution of Na₂CNMe₂·H₂O (72 mg, 0.500 mmol) in methanol (15 cm³) was added causing immediate darkening of the reaction mixture. The mixture was heated to reflux for 1 h after which time it was cooled to ambient temperature and concentrated to half volume. This led to precipitation of the product which was isolated analytically pure by filtration and washing with PrⁱOH (2 × 10 cm³). Yield: 0.201 g (53%).

[Re{NB(C₆F₅)₃}(PMe₂Ph)(S₂CNMe₂)₂] 3. To a stirred solution of [Re(N)(PMe₂Ph)(S₂CNMe₂)₂] (0.289 g, 0.500 mmol) in dichloromethane (20 cm³) was added B(C₆F₅)₃ (0.280 g, 0.547 mmol) in dichloromethane (15 cm³). Upon stirring overnight the solution darkened somewhat and the solvent was removed under vacuum to yield a grey oily solid. The product was afforded analytically pure by trituration with pentane (2 × 15 cm³) and drying overnight *in vacuo*. Single crystals suitable for analysis by X-ray diffraction were grown by slow vapour diffusion of pentane into a dichloromethane (20 cm³) solution of complex **3** (*ca.* 20 mg). Yield: 0.300 g (55%).

[Re{NB(C₆F₅)₃}(PMePh₂)(S₂CNEt₂)₂] 4. To a stirred solution of [Re(N)(PMePh₂)(S₂CNEt₂)₂] **1** (90 mg, 0.129 mmol) in dichloromethane (15 cm³), B(C₆F₅)₃ (72 mg, 0.140 mmol) in dichloromethane (5 cm³) was added. An immediate change

from yellow to violet was observed. After 1 h of stirring, light petroleum (30 cm³) was added but no solid precipitated overnight. Hence the volatiles were removed under vacuum and the resulting oily solid triturated with light petroleum (20 cm³) to yield the product as a lavender powder. Crystallisation by slow evaporation of a solution of the product in PrⁱOH and dichloromethane (10 cm³ of a 1 : 1 mixture) led to its isolation as purple single crystals which proved to be of insufficient quality for analysis by X-ray diffraction. Microanalysis and NMR spectroscopy identified this product as pure complex **4**·0.5 PrⁱOH. Yield: 0.104 g (65%).

[Re{NB(C₆F₅)₃}(Cl)(PMePh₂)₂(S₂CNMe₂)] 5. To a stirred solution of [Re(N)(Cl)(PMePh₂)₂(S₂CNMe₂)] **2** (0.180 g, 0.238 mmol) in dichloromethane (15 cm³) a solution of B(C₆F₅)₃ (0.144 g, 0.281 mmol) in dichloromethane (5 cm³) was added dropwise. An immediate change from yellow to orange-red was observed. Stirring was maintained for 3 h after which time the solvent was removed under vacuum and the resulting red oily solid triturated with pentane (20 cm³). This afforded the product as a dark orange powder which was dried *in vacuo* overnight and shown to be pure by microanalysis. Yield: 0.199 g (66%).

[Mo{NB(C₆F₅)₃}(S₂CNMe₂)₃] 6. To a stirred suspension of [Mo(N)(S₂CNMe₂)₃] (0.200 g, 0.425 mmol) in dichloromethane (30 cm³) a solution of B(C₆F₅)₃ (0.250 g, 0.488 mmol) in dichloromethane (15 cm³) was slowly added. Stirring was maintained for 48 h after which time all solid material had dissolved and the solution had changed from orange to red. Volatiles were removed *in vacuo* to yield a brown oily solid which was rendered as an orange powder by trituration with pentane (40 cm³). The yellow microcrystalline solid was obtained analytically pure by cooling a solution in dichloromethane (15 cm³) to –80 °C. Yield: 0.251 g (60%).

[Mo{NB(C₆F₅)₃}(S₂CNEt₂)₃] 7. To a stirred suspension of [Mo(N)(S₂CNEt₂)₃] (0.250 g, 0.451 mmol) in dichloromethane (30 cm³) a solution of B(C₆F₅)₃ (0.245 g, 0.479 mmol) in dichloromethane (15 cm³) was slowly added. Stirring was maintained for 48 h after which time all solid material had dissolved and the solution had changed from brown to red. Volatiles were removed *in vacuo* to yield a brown-red oil. This failed to crystallise from a solution in dichloromethane–pentane (30 cm³ of a 1 : 4 mixture) and was rendered as a solid by sonication for 15 min in pentane (30 cm³). The red-brown foamy solid product was isolated by filtration and dried overnight *in vacuo*. Yield: 0.101 g (21%).

[NBuⁿ][Os{NB(C₆F₅)₃}(1,2-S₂C₆H₄)₂] 8. To a stirred solution of [NBuⁿ][Os(N)(1,2-S₂C₆H₄)₂] (0.450 g, 0.619 mmol) in dichloromethane (40 cm³), B(C₆F₅)₃ (0.450 g, 0.879 mmol) in dichloromethane (20 cm³) was added. An immediate change from yellow to deep red was observed and after 1 h of stirring the volatiles were removed under vacuum. The resulting oily green solid was triturated with pentane (20 cm³) to yield the product. It was isolated analytically pure as an olive-green powder by filtration and drying under vacuum. Yield: 0.675 g (88%).

[Os{NB(C₆F₅)₃}(1,2-(S)(SMe)C₆H₄)(1,2-S₂C₆H₄)] 9. The complex [NBuⁿ][Os{NB(C₆F₅)₃}(1,2-S₂C₆H₄)₂] **8** (200 mg, 0.160 mmol) and MeO₃SCF₃ (50 mg, 0.305 mmol) were combined in a dry-box and dissolved in dichloromethane (15 cm³). The reaction mixture was stirred for 1 h without any obvious colour change and then the volatiles were removed under vacuum. Extraction of the oily residues with toluene yielded a red solution. Removal of the solvent from this afforded the product as an olive-green oil. Vigorous washing with pentane (30 cm³) failed to yield a solid so the product was characterised

by NMR spectroscopy. It was too air-sensitive to allow satisfactory microanalytical data to be obtained.

Reactions with L = THF, NEt₃ or PMe₃

[Re{NB(C₆F₅)₃}(PMe₂Ph)(S₂CNMe₂)₂] 3. To a solution of [Re{NB(C₆F₅)₃}(PMe₂Ph)(S₂CNMe₂)₂] **3** (20 mg, 0.018 mmol) in dichloromethane (10 cm³) was added an excess of Lewis base; either THF (3 drops), NEt₃ (3 drops) or PMe₃ (1 cm³ of a 0.105 M solution in light petroleum, 0.105 mmol). No immediate colour change was observed and the reactions were allowed to proceed for 1 h. Volatiles were then removed *in vacuo* and the residues dried for 2 h. The products were analysed by ¹H and ¹¹B-¹H NMR spectroscopy in CDCl₃ and this showed that in all three experiments no reaction of compound **3** had occurred.

[Mo{NB(C₆F₅)₃}(S₂CNMe₂)₃] 6. To a solution of [Mo{NB(C₆F₅)₃}(S₂CNMe₂)₃] **6** (20 mg, 0.020 mmol) in dichloromethane (10 cm³) an excess of Lewis base was added as above. Little immediate colour change was observed and the reactions were allowed to proceed for 1 h. Further treatment and NMR analysis as above showed that in the case where L = THF no decomposition of compound **6** had occurred whereas when L = NEt₃ or PMe₃ the residue consisted of *ca.* 50% **6** and 50% [Mo(N)(S₂CNMe₂)₃] plus B(C₆F₅)₃·L. NMR data (CDCl₃, 298 K): B(C₆F₅)₃·NEt₃, ¹H, δ 1.46 (m, 9 H, NCH₂CH₃) and 3.60 (m, 6 H, NCH₂CH₃); ¹¹B-¹H, δ -4.2 (s); B(C₆F₅)₃·PMe₃, ¹H, δ 1.79 (d, ²J_{PH} = 13.1 Hz, PCH₃); ¹¹B-¹H, δ -4.4 (s)

[NBuⁿ]₄[Os{NB(C₆F₅)₃}(1,2-S₂C₆H₄)₂] 8. To a solution of [NBuⁿ]₄[Os{NB(C₆F₅)₃}(1,2-S₂C₆H₄)₂] **8** (20 mg, 0.016 mmol) in dichloromethane (10 cm³) an excess of Lewis base was added as above. Little immediate colour change was observed and the reactions were allowed to proceed for 1 h. Further treatment and NMR analysis as above showed that in the case where L = THF no decomposition of compound **8** had occurred whereas when L = NEt₃ or PMe₃ the residue consisted entirely of [NBuⁿ]₄[Os(N)(1,2-S₂C₆H₄)₂]⁹ and B(C₆F₅)₃·L (NMR spectroscopic data as above).

Reaction of [NBuⁿ]₄[Os{NB(C₆F₅)₃}(1,2-S₂C₆H₄)₂] **8** with [Ph₃C][BF₄]

Complex **8** (50 mg, 0.040 mmol) and [Ph₃C][BF₄] (50 mg, 0.151 mmol) were combined as solids and dissolved in dichloromethane (15 cm³). The mixture was stirred for 30 min after which it appeared to have darkened slightly. The volatiles were removed *in vacuo* and the whole of the reaction residues analysed by ¹H, ¹¹B-¹H and ¹³C-¹H NMR spectroscopy in CDCl₃. This confirmed the formation of the known compound [Os(NCPh₃)(1,2-S₂C₆H₄)₂]⁹, B(C₆F₅)₃ and [NBuⁿ]₄[BF₄].

Crystallography

Single crystals of complex **3** suitable for analysis by X-ray crystallography were grown by slow vapour diffusion of pentane into a solution of **3** in dichloromethane at 298 K. A plate-shaped crystal was selected for diffraction, covered with paratone-N oil under an inert atmosphere and mounted on the end of a glass fibre.

Crystal data. C₃₂H₂₃BF₁₅N₃PrSe₄ **3**, *M* = 1090.75, triclinic, space group *P* $\bar{1}$, *a* = 8.871(5), *b* = 13.233(1), *c* = 16.7220(13) Å, *a* = 80.73(4), *β* = 77.13(5), *γ* = 86.05(5)°, *V* = 1887.6 Å³, *Z* = 2, *D*_c = 1.92 g cm⁻³, *μ* = 3.62 mm⁻¹, purple crystals, crystal dimensions 0.25 × 0.05 × 0.05 mm.

Data collection and processing. Data were collected at 125 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å).

11663 Reflections were measured (1 < θ < 26°, ±*h*, ±*k*, +*l*, 6103 unique giving 5408 with *I* > 3σ(*I*). The images were processed with the DENZO and SCALEPACK programs.²¹

Structure solution and refinement. All solution, refinement and graphical calculations were performed using the CRYSTALS²² and CAMERON²³ software packages. The structure was solved by direct methods using the SIR 92 program²⁴ and refined by a full-matrix least squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme with the parameters 2.84, 0.362 and 2.06 was applied as well as an empirical absorption correction.²⁵ This yielded *R* = 0.042 and *R*' = 0.051 with maximum residual electron density of 1.61 e Å⁻³.

CCDC reference number 186/1188.

See <http://www.rsc.org/suppdata/dt/1998/3941/> for crystallographic files in .cif format.

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