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Reactivities of π-electron-rich phosphorus–nitrogen ligands toward Groups VIB and VIIB metal carbonyl complexes

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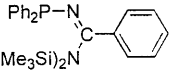
Abstract

The interaction of $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ (**L**^{1}) with one equivalent of $Mn(CO)_5Br$ afforded *cis*-$Mn(CO)_4Br\{(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]\}$ (**1**), which upon boiling in THF gave *fac*-$Mn(CO)_3Br[(Ph_2PNH)C(Ph)({=}NSiMe_3)]$ (**2**), and with one equivalent of $Re(CO)_5X$ (X = Br or Cl) gave *fac*-$Re(CO)_3X[(Ph_2PNH)C(Ph)({=}NH)]$ [X = Br (**3**) or Cl (**4**)] in good yield. Reaction of $1,4\text{-}C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2$ (**L**^{2}) with two equivalents of $Mn(CO)_5Br$ gave the symmetric dimer $[$*cis*-$Mn(CO)_4Br]_2\{(Ph_2PN{=})[N(SiMe_3)_2]C\}_2C_6H_4\text{-}1,4$ (**5**), and with two equivalents of $Re(CO)_5Br$ gave the cyclic dimer *cyclo*-[*fac*-$(Me_2NCHO)Re(CO)_3(\mu\text{-}Ph_2PO_2)]_2$ (**6**) upon recrystallization in DMF. Treatment of $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}\text{-}4$ (**L**^{3}) with one equivalent of $(nbd)M(CO)_4$ (M = Mo or Cr, nbd = norbornadiene) in THF produced *cis*-$M(CO)_4\{(NC_5H_4)\text{-}[(Ph_2PNH)C({=}NSiMe_3)]\text{-}4\}$ [M = Mo (**7**) or Cr (**8**)], and with excess $Mn(CO)_5Br$ led to the trinuclear complex *fac*-{*cis*-$Mn(CO)_4Br[(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}\text{-}4]\}_2Mn(CO)_3Br$ (**9**) in good yield. Compound **7**, in the presence of $CdCl_2$, hydrolyzed to *cis*-$Mo(CO)_4\{(NC_5H_4)[(Ph_2PNH)C({=}NH)]\text{-}4\}$ (**10**). Compound **8** reacted with half an equivalent of $Mn(CO)_5Br$ to give the trinuclear complex *fac*-[*cis*-$Cr(CO)_4\{(NC_5H_4)[(Ph_2PNH)C({=}NSiMe_3)]\text{-}4\}]_2Mn(CO)_3Br$ (**11**). All the new compounds were characterized by spectroscopic and analytical methods and the structures of compounds **1**, **3**, **6**, **9** and **10** were established by X-ray crystallography. © 2000 Elsevier Science B.V. All rights reserved.

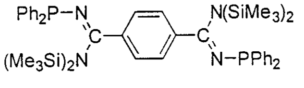
Keywords: Chromium; Molybdenum; Manganese; Rhenium; Carbonyl

1. Introduction

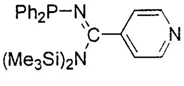
Phosphorus–nitrogen compounds are π-electron-rich compounds with unusual properties [1]. This has led to a considerable interest in their syntheses [2] and their coordination chemistry toward transition metals [3]. We have been interested in the preparation and the chemistry of P–N ligands as they are hemilabile ligands capable of exhibiting unusual coordination chemistry toward transition metals. Recently we have described the coordination chemistry of $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ (**L**^{1}), $C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2\text{-}1,4$ (**L**^{2}) and $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}\text{-}4$ (**L**^{3}) toward transition metal complexes and demonstrated that these ligands, depending on the reaction conditions, could behave as mono-, bi-, tri- and tetra-dentate ligands [4–7]. Herein we report the detail study of the reactions of **L**^{1}, **L**^{2} and **L**^{3} toward Groups 6 and 7 metal carbonyl complexes.



L^1



L^2



L^3

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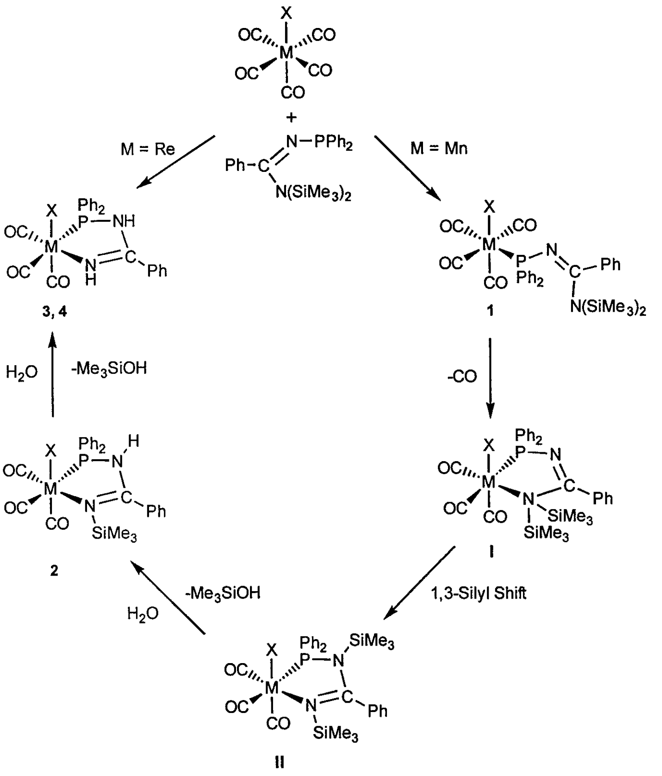


Scheme 1. **1**: M = Mn, X = Br; **2**: M = Mn, X = Br; **3**: M = Re, X = Br; **4**: M = Re, X = Cl.

2. Results and discussion

2.1. Reactions of $\mathbf{L^1}$ with $M(CO)_5X$ ($M = Mn, Re$)

When $Mn(CO)_5Br$ was allowed to react with one equivalent of $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ (**L**^{1}) in THF for 1 day, work-up gave red crystals of *cis*-$Mn(CO)_4Br\{(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]\}$ (**1**) in moderate yield (60%) after recrystallization from hexane (Scheme 1). In the terminal carbonyl region, compound **1** exhibited four absorptions at 2085s, 2000vs, 1956vs and 1921m (sh) cm^{-1} in the IR spectrum (KBr), and two doublets at δ 217.3 ($J_{P\text{–}CO} = 21.9$ Hz) and 212.9 ($J_{P\text{–}CO} = 12.2$ Hz) in the $^{13}C\{^1H\}$-NMR spectrum. These data are indicative of a *cis*-$Mn(CO)_4(L)Br$ compound. The $^{31}P\{^1H\}$-NMR spectrum of **1** exhibited a singlet at δ 73.6 for the PPh_2 group; and the $^{13}C\{^1H\}$-NMR spectrum displayed a doublet and a singlet at δ 171.4 ($J_{P\text{–}NC} = 7.3$ Hz) and 3.2 for the C=N and $SiMe_3$ carbon atoms, respectively.

Crystals of **1** suitable for an X-ray diffraction study were grown from its hexane solution. A perspective drawing is shown in Fig. 1. The solid-state structure is consistent with its spectroscopic data and reveals that **L**^{1} simply acts as a monodentate ligand with the phosphino group P(1) coordinated to the $MnBr(CO)_4$ moi-

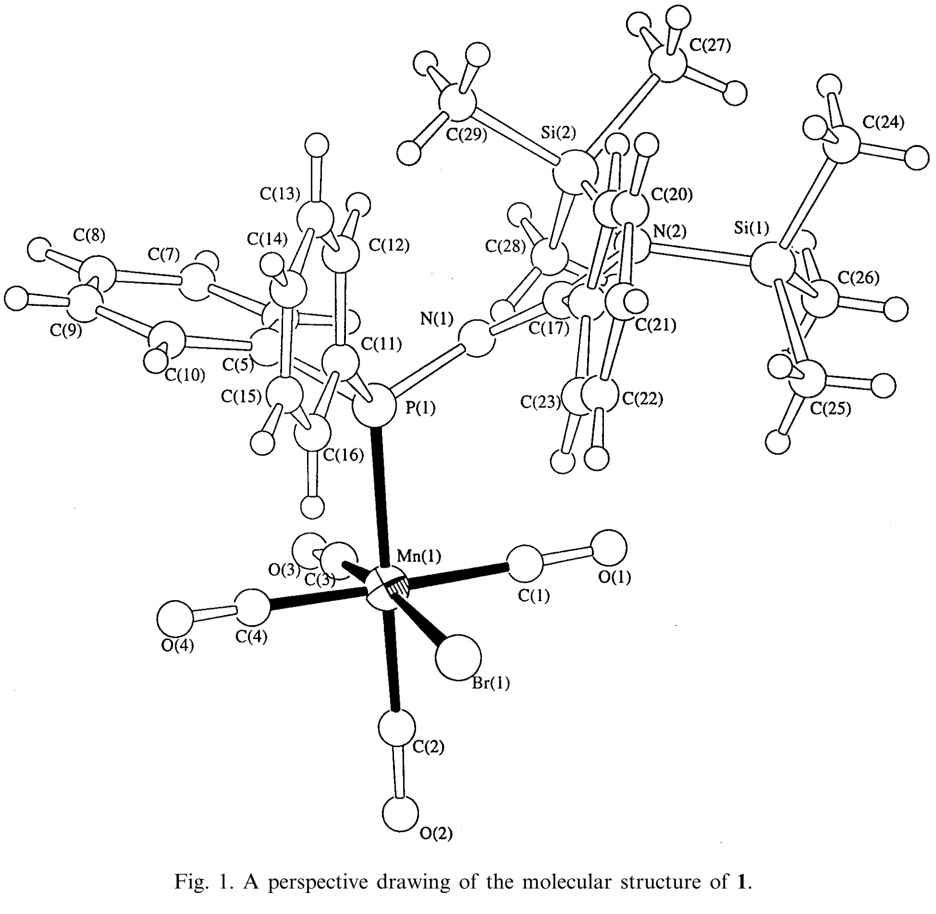


Fig. 1. A perspective drawing of the molecular structure of **1**.

ety. The Mn center adopts an approximately octahedral geometry with the phosphino group and bromide ligand arranged in a *cis* configuration. The Mn–C distances of the two mutually *trans*-carbonyls are 1.840(9) and 1.864(8) Å for Mn(1)–C(1) and Mn(1)–C(4), respectively, and are slightly longer than the Mn–C distances of 1.822(8) and 1.765(9) Å for the carbonyl *trans* to the phosphino [P(1)] group and the bromo [Br(1)] group, respectively. Within the monodentate ligand, the P(1)–N(1) bond length of 1.661(5) Å lies in the normal range for a phosphorus–nitrogen bond. The C(17)–N(1) (1.291(7) Å) and C(17)–N(2) (1.388(7) Å) bonds are intermediate between those for single (1.46 Å) and double (1.26 Å) bonds indicating some delocalization about the N–C–N framework. This is further supported by the geometry of N(2) of the $N(SiMe_3)_2$ group which is approximately trigonal planar with bond angles of 121.9(4), 121.7(3) and 115.5(4)° for Si(1)–N(2)–C(17), Si(1)–N(2)–Si(2) and Si(2)–N(2)–C(17), respectively. This suggests that the lone pair on N(2) is primarily of p character and has the correct symmetry to interact with the neighboring empty π^* orbital. This p–π^* interaction is reflected in the C(17)–N(2) distance (1.388(7) Å). Similar observation has been reported for the related molybdenum complex [6].

When **1** was allowed to reflux gently in THF for 4 h, work-up gave a yellow solid of stoichiometry $Mn(CO)_3Br(C_{22}H_{25}N_2SiP)\cdot 0.5H_2O$ (**2**$\cdot 0.5H_2O$) in high yield (90%). Likewise, the thermal reaction of $Mn(CO)_5Br$ with **L^1** also afforded compound **2**. In the IR spectrum, **2** exhibited three ν(CO) absorptions with a pattern characteristic of a *fac*-$Mn(CO)_3$ moiety. Comparing to **1**, these absorptions were shifted to lower frequencies which is characteristic of an increase in d–π back bonding from the metal to the carbonyl groups. The IR spectrum also showed an absorption at 3230s cm^{-1} indicating the presence of an NH group. The $^{31}P\{^1H\}$-NMR spectrum of **2** exhibited a singlet at δ 106.4 for the PPh_2 group. The large positive increase in chemical shift for the PPh_2 group from δ 73.6 to 106.4 is characteristic of chelating ring formation [8]. Other than the phenyl resonances, the ^1H-NMR spectrum of **2** also displayed two singlets of relative intensity 1:9 at δ 6.70 (br) and 0.13 for the NH and $SiMe_3$ protons, respectively; and the $^{13}C\{^1H\}$-NMR spectrum exhibited a singlet at δ 3.6 for the $SiMe_3$ carbon atoms. The mass spectrum of **2** exhibited the parent peak at *m*/*z* 595 [(M + 1) for ^{55}Mn and ^{79}Br]. The spectroscopic data are consistent with the formulation *fac*-$Mn(CO)_3Br$-[$(Ph_2PNH)C(Ph)(=NSiMe_3)$] for compound **2**. A related chromium complex has been isolated and structurally characterized [6].

The interaction of $Re(CO)_5X$ (X = Br or Cl) with one equivalent of **L^1** in refluxing THF gave white crystals of *fac*-$Re(CO)_3X[(Ph_2PNH)C(Ph)(=NH)]$ [X = Br (**3**); X = Cl (**4**)] in moderate yield. In the carbonyl region, the IR and $^{13}C\{^1H\}$-NMR spectral patterns of both **3** and **4** are characteristic of a *fac*-$Re(CO)_3$ configuration. The IR spectrum also exhibited two NH absorptions at 3408m and 3252m cm^{-1} for **3** and 3408m and 3245s cm^{-1} for **4**. A singlet at δ 75.0 and 77.5 was observed for the PPh_2 group in the $^{31}P\{^1H\}$-NMR spectra of **3** and **4**, respectively. The ^1H-NMR spectrum also showed two singlets of equal intensity for the two different NH protons at δ 6.58 and 7.76 for **3** and 6.67 and 7.86 for **4**. The mass spectrum gave the parent peak at *m*/*z* 653 [(M + 1) for ^{185}Re and ^{79}Br] for **3** and 608 [M for ^{185}Re and ^{35}Cl] for **4**.

Suitable crystals of compound **3** were grown from a CH_2Cl_2/hexane mixture. A perspective drawing is depicted in Fig. 2. The solid-state structure reveals that the $(Ph_2PNH)C(Ph)(=NH)$ group acts as a chelate with the imino group N(1) and phosphino group P(1) coordinated to the metal forming a five-membered ring. The geometry of the Re atom is approximately octahedral with a *fac*-$Re(CO)_3$ configuration. The Re–C distances are 1.98(2), 1.87(2) and 1.95(2) Å for Re–C(1), Re–C(2) and Re–C(3), respectively, which reflect the π-acidity of the ligands *trans* to the carbonyl groups. Delocalization about the N–C–N framework of the five-membered ring is also observed. The P(1)–N(2), C(4)–N(1) and C(4)–N(2) distances are 1.69(2), 1.40(1) and 1.25(2) Å, respectively; and the P(1)–N(2)–C(4) bond angle is 119.8(8)°.

A possible mechanism for the formation of compounds **1**–**4** is shown in Scheme 1. Following the reaction of $Mn(CO)_5Br$ with **L^1** to produce compound **1**, product **1** then underwent further substitution by replacing one of the mutually *trans*-carbonyls with the amino group of the P–N ligand forming a five-membered ring intermediate **I**. It is followed by a rapid 1,3-shift to give an intermediate **II**. Subsequent hydrolysis of **II** afforded compound **2**. A similar mechanism has been proposed for other related complexes [6]. With $Re(CO)_5X$, the compound underwent further hydrolysis to give compound **3** (X = Br) or **4** (X = Cl).

2.2. Reactions of **L^2** with $M(CO)_5X$ (M = Mn, Re)

When 1,4-$C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$ (**L^2**) was allowed to react with two equivalents of $Mn(CO)_5Br$ in THF for 1 day, a yellow solid of stoichiometry $[Mn(CO)_4Br]_2[C_{44}H_{60}N_4P_2Si_4]\cdot 0.5C_4H_8O$ (**5**$\cdot 0.5C_4H_8O$) was obtained in moderate yield (40%). Compound **5** has been characterized as a symmetric dimer [*cis*-$Mn(CO)_4Br]_2\{(Ph_2PN=)[N(SiMe_3)_2]C\}_2C_6H_4$-1,4 with **L^2** linking the two $Mn(CO)_4Br$ moieties together via the two phosphino groups leaving the two amino groups uncoordinated. The proposed structure for compound **5** is shown below. The $^{31}P\{^1H\}$-NMR spectrum of **5**

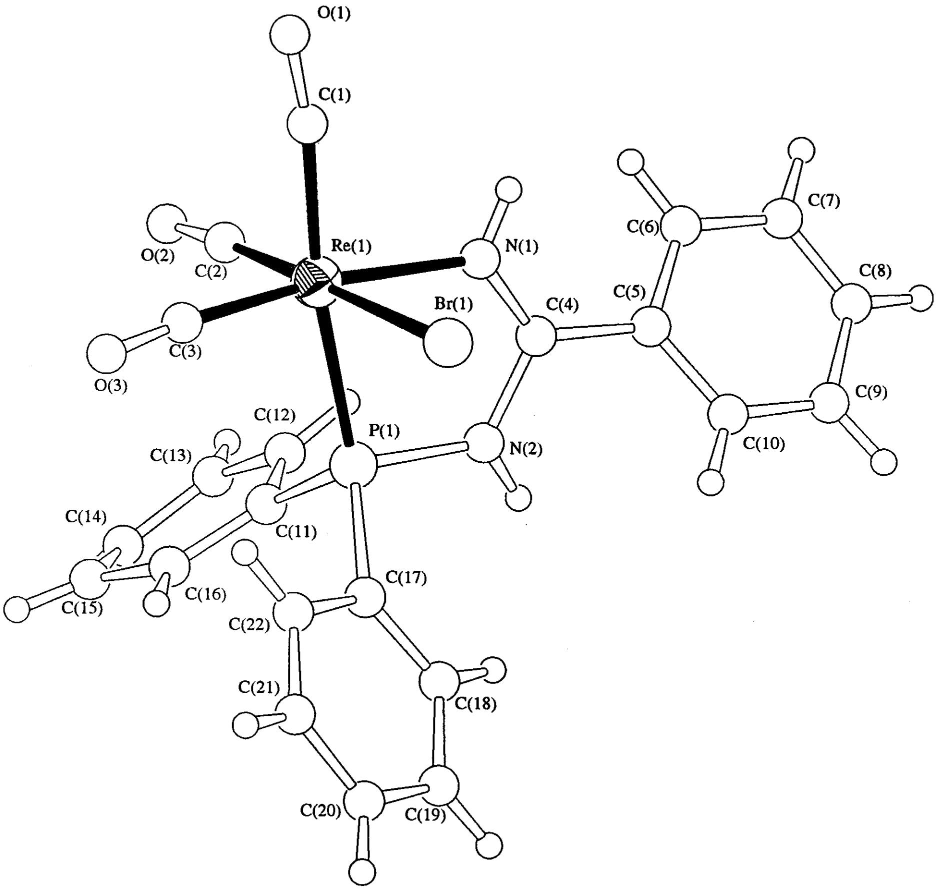
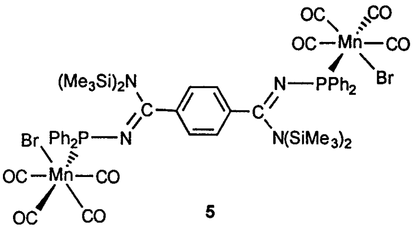


Fig. 2. A perspective drawing of the molecular structure of **3**.

showed only a singlet at δ 68.4, indicating the presence of two equivalent PPh_2 groups. The chemical shift of the PPh_2 groups is similar to that of **1** and much more upfield than that of **2** suggesting no chelate ring formation. Compound **5** also exhibited a singlet at δ 0.11 in the ^1H-NMR spectrum and a singlet at δ 3.1 in the $^{13}C\{^1H\}$-NMR spectrum for the trimethylsilyl groups.



5

Treatment of $Re(CO)_5Br$ with **L**^{2} under the same conditions led to the formation of a white solid, which was insoluble in common organic solvents. However, the solid dissolved in hot DMF and its color changed from white to yellow. Yellow crystals of stoichiometry $Re_2(CO)_6(C_{30}H_{34}N_2O_6P_2)$ (**6**) with two DMF solvate molecules were obtained in 40% yield after recrystallization from a hot DMF solution. The molecular structure of compound **6** was ascertained by an X-ray diffraction study to be consistent with the formulation *cyclo*-[*fac*-$(Me_2NCHO)Re(CO)_3(\mu\text{-}Ph_2PO_2)]_2$. A perspective drawing is shown in Fig. 3. Structural analysis revealed that the phosphorus atoms of the **L**^{2} ligand were oxidized to the $Ph_2PO_2^-$ fragments with concomitant cleavage of the P–N bonds. Compound **6** is centro-symmetric with the two rhenium atoms linked together via two μ-$Ph_2PO_2^-$ moieties through their two oxygen atoms forming an eight-membered $Re_2O_4P_2$ ring in a zig–zag conformation. The geometries of the two rhenium atoms are approximately octahedral with the three terminal carbonyl ligands adopting a *fac* configuration. The Re–C distances are 1.89(2), 1.88(2) and 1.93(2) Å for Re(1)–C(1), Re(1)–C(2) and Re(1)–C(3), respectively. The $Ph_2PO_2^-$ anion adopts a deformed tetrahedron with the O(5)–P(1)–O(6*) bond angle of 116.5(5)°. The P(1)–O(5) and P(1)–O(6*) distances of 1.503(9) and 1.521(9) Å, respectively, are slightly shorter than P–O single bond (~ 1.6 Å) and are nearly equal to each other, indicating delocalization about the O–P–O framework.

The spectroscopic data of **6** are consistent with its solid-state structure. The $^{31}P\{^1H\}$-NMR spectrum in

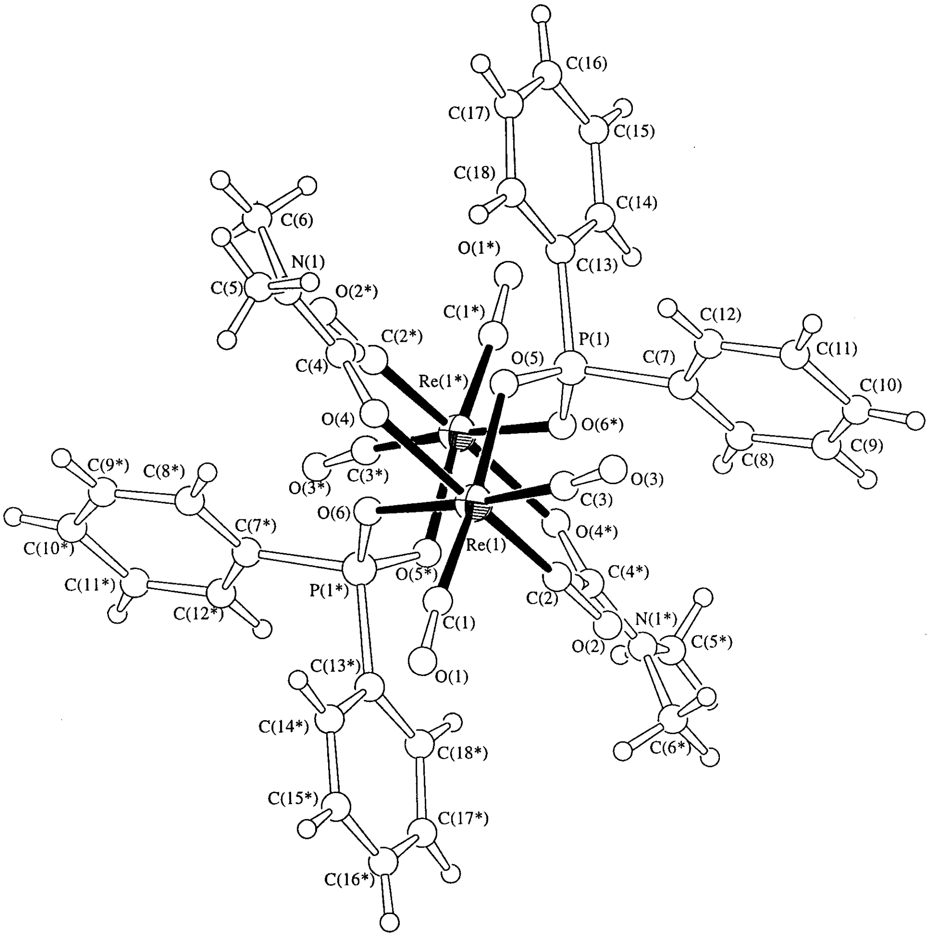


Fig. 3. A perspective drawing of the molecular structure of **6**.

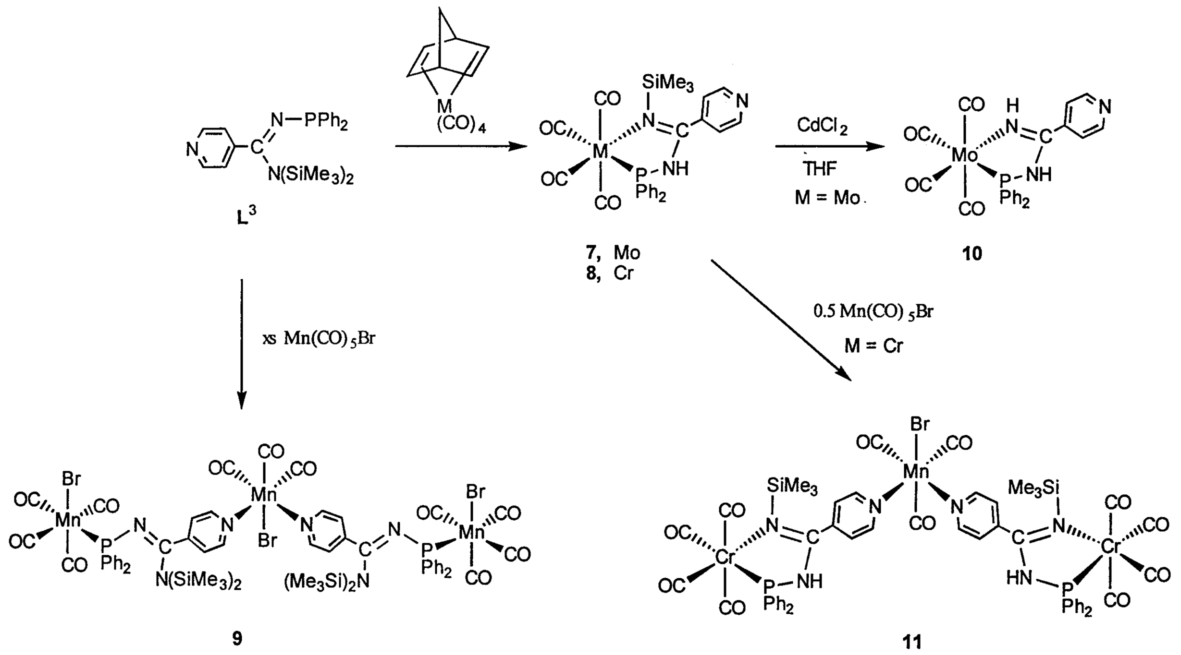
d_7-DMF exhibited a singlet at δ 35.4 for the two μ-diphenylphosphate groups. The IR spectrum (KBr) exhibited four absorptions at 2019s, 1905vs, 1889vs and 1875vs cm^{-1} for the terminal carbonyls of the two *fac*-Re(CO)$_3$ moieties and an absorption at 1647s cm^{-1} for the C=O group of the coordinated DMF molecules. The mass spectral parent peak at m/z 1047 (M for ^{185}Re) also agrees well with its formulation.

2.3. Reactions of $\boldsymbol{L^3}$ with (nbd)M(CO)$_4$ (M = Cr, Mo) or Mn(CO)$_5$Br

When (nbd)M(CO)$_4$ (M = Cr or Mo) was allowed to react with one equivalent of (NC$_5$H$_4$){(Ph$_2$PN=)-C[N(SiMe$_3$)$_2$]}-4 (**L**^{3}) in THF for 1 day, yellow crystals of stoichiometry M(CO)$_4$(C$_{21}$H$_{24}$N$_3$SiP) [M = Mo (**7**); M = Cr (**8**)] were isolated in moderate yields (Scheme 2). Compounds **7** and **8** exhibited similar ν(CO) absorption patterns in their IR spectra, which are indicative of a *cis*-M(CO)$_4$LL′ complex. An NH absorption was also evident at 3449w for **7** and 3448w cm^{-1} for **8**. The ^{31}P{^{1}H}-NMR chemical shifts at δ 89.9 (**7**) and 112.3 (**8**) are characteristic of chelating ring formation [8]. The ^{1}H-NMR spectrum of each complex also displayed resonances of relative intensity 1:9 for the NH and Me$_3$Si protons; and their ^{13}C{^{1}H}-NMR spectrum a singlet at δ 3.6 for the SiMe$_3$ carbon atoms. The mass spectrum showed the parent peak at m/z 587 [(M + 1) for ^{98}Mo] for **7** and 541 (M for ^{55}Cr) for **8**. Compounds **7** and **8** can satisfactorily be formulated as *cis*-M(CO)$_4${(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NSiMe$_3$)]-4}. The structure of **7** was also confirmed by an X-ray diffraction study [9].

When Mn(CO)$_5$Br was allowed to react with **L**^{3} in a 3:2 molar ratio, red crystals of a trinuclear complex *fac*-{*cis*-Mn(CO)$_4$Br[(NC$_5$H$_4$){(Ph$_2$PN=)C[N(SiMe$_3$)$_2$]}-4]}$_2$Mn(CO)$_3$Br (**9**) were obtained in good yield (58%) after recrystallization from a hexane solution. The ^{31}P{^{1}H}-NMR spectrum of **9** exhibited a singlet at δ 73.6 for the PPh$_2$ group. The chemical shift is similar to that of **1**. Compound **9** also showed a singlet at δ 0.17 in the ^{1}H-NMR spectrum and a singlet at δ 3.2 in the ^{13}C{^{1}H}-NMR spectrum for the SiMe$_3$ groups. Good quality crystals of **9** were grown from a hexane solution and the molecular structure is shown in Fig. 4. The three Mn centers are linked together via two **L**^{3} ligands, which behave as bridging ligands. All three Mn centers adopt an approximately octahedral geometry with the two pyridyl nitrogen atoms N(1) and N(4) coordinating to the central metal Mn(1) in a *cis* configuration and the two phosphino groups coordinating to the terminal metal centers *cis* to the bromine atoms. For the bridging ligand, the geometry of N(3) of the $N(SiMe_3)_2$ group is approximately trigonal planar with bond angles of 114(1), 120(1) and 124(1)° for Si(2)-N(3)-C(17), Si(1)-N(3)-Si(2) and Si(1)-N(3)-C(17), respectively. Similar to **1**, this indicates that the lone pair on N(4) has primarily p character and the correct symmetry to interact with the neighboring empty π^* orbital, as revealed by the C(17)–N(3) distance (1.32(3) Å). A similar geometry is also observed on N(6) of the $N(SiMe_3)_2$ moiety with bond angles of 116(1), 120(1) and 122(1)° for Si(3)–N(6)–C(41), Si(4)–N(6)–C(41) and Si(3)–N(6)–Si(4), respectively.

Further attempts to react compound **7** with half an equivalent of $CdCl_2$ in THF for 1 day at ambient temperature did not afford any Cd-containing product.



Scheme 2.

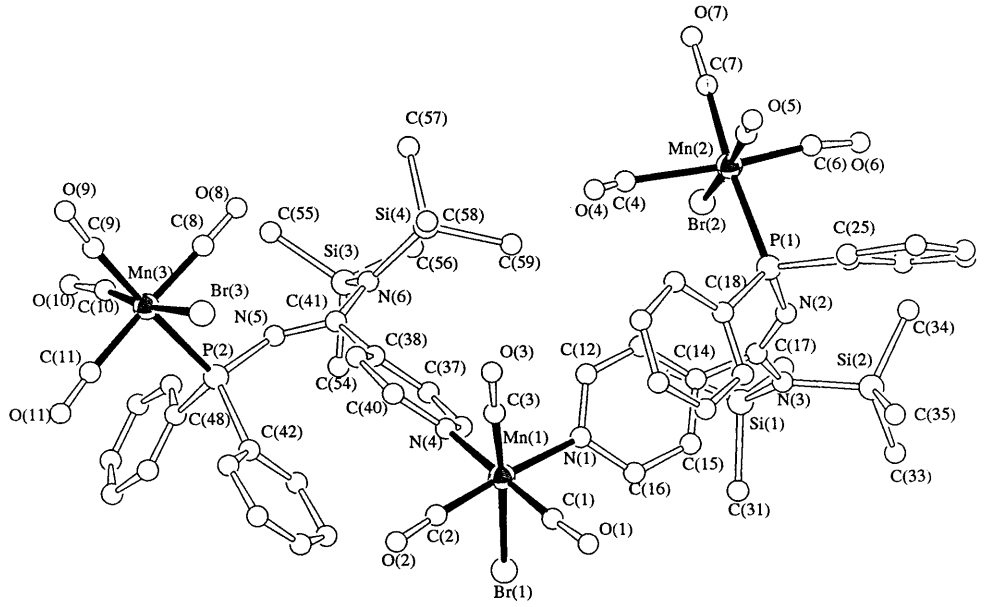


Fig. 4. A perspective drawing of the molecular structure of **9**. Hydrogen atoms are omitted for clarity.

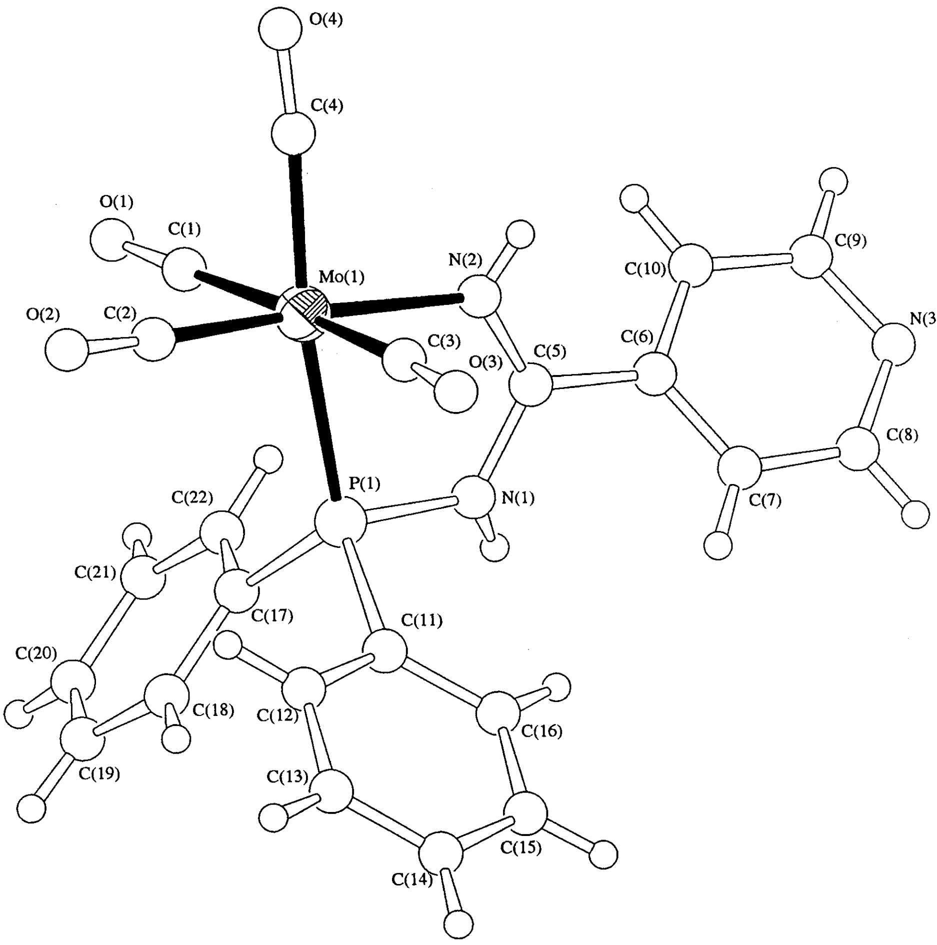


Fig. 5. A perspective drawing of the molecular structure of **10**.

Instead, a yellow solid of *cis*-$Mo(CO)_4\{(NC_5H_4)$-$[(Ph_2PNH)C$-$(=NH)]$-4} (**10**) was obtained in 50% yield. The IR spectrum (KBr) of **10** exhibited the characteristic absorption pattern of a *cis*-$M(CO)_4LL'$ complex in the carbonyl region, and an NH absorption at 3368s cm^{-1}. The $^{31}P\{^1H\}$-NMR spectrum exhibited a singlet at δ 98.8 for its PPh_2 group. The ^1H-NMR spectrum also exhibited two broad multiplets of relative intensity 1:1 for the NH protons at δ 6.24 and 7.56. The mass spectrum exhibited the parent peak at m/z 515 (M for ^{98}Mo). The structure of **10** was established by X-ray crystallography.

Yellow crystals of **10** were grown from a dichloromethane–hexane mixture. A perspective drawing of **10** is shown in Fig. 5. Structural analysis revealed that the $SiMe_3$ group had undergone hydrolysis to give a chelate ligand $(HN{=})C(4$-$C_5H_4N)(NHPPh_2)$ with the imino group N(1) and the phosphino group P(1) coordinated to the $Mo(CO)_4$ moiety. The geometry of Mo is approximately octahedral adopting a *cis*-$Mo(CO)_4LL'$ configuration. The Mo–C distances of the two mutually *trans*-carbonyls are 2.021(6) and 2.017(7) Å for Mo(1)–C(1) and Mo(1)–C(3), respectively, and are slightly longer than the Mo–C distances of 1.962(6) and 2.000(6) Å for the carbonyl *trans* to the imino N(1) and phosphino P(1) groups, respectively. Within the bidentate iminophosphine ligand, the P(1)–N(1), C(5)–N(1) and C(5)–N(2) distances are 1.711(4), 1.369(6) and 1.276(6) Å, respectively, and the P(1)–N(1)–C(5) bond angle is 119.8(3)°.

Another new compound *fac*-[*cis*-$Cr(CO)_4\{(NC_5H_4)$-$[(Ph_2PNH)C(=NSiMe_3)]$-$4\}]_2Mn(CO)_3Br$ (**11**) was formed upon the reaction between $Mn(CO)_5Br$ and two equivalents of **8** and compound **11** was isolated as a yellow solid in good yield (81%). The presence of NH groups was shown by an IR absorption at 3347w cm^{-1}. The $^{31}P\{^1H\}$-NMR spectrum of **11** displayed a singlet at δ 114.5 for the PPh_2 groups and showed no significant change in the chemical shift as compared with **8**. The ^1H-NMR spectrum of **11** in CD_2Cl_2 exhibited two singlets of relative intensity 1:9 at δ 6.75 and 0.12 for the NH and $SiMe_3$ protons, respectively. Also in the ^1H-NMR spectrum, the α- and β-H of the pyridyl group of **11** appeared at δ 8.89 and 7.26, respectively, corresponding to a shift of ca. 0.17 and 0.03 ppm as compared with the α- (δ 8.66) and β-H (δ 7.23) of the pyridyl group of **8**, indicating Mn–N bond formation.

3. Experimental

3.1. General procedures

All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. $Mn(CO)_5Br$ and $Re(CO)_5X$ (X = Br or Cl) were purchased from Strem Chemicals Inc. The compounds $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ [6], $C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 [6], $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 [7], and $M(CO)_4(nbd)$ (M = Cr, Mo) [10] were prepared according to literature methods. Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Infrared spectra (KBr pellets) were recorded on a Nicolet Nagna-IR 550 spectrometer, NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of ^1H and $^{13}C\{^1H\}$-NMR spectra were referenced to internal deuterated solvents and then recalculated to $SiMe_4$ (δ 0.00), those of $^{31}P\{^1H\}$-NMR spectra were referenced to external 85% H_3PO_4. Low-resolution mass spectra (LRMS) were obtained on a Finnigan MAT SSQ-710 spectrometer in FAB (positive-ion) mode and are reported as *m/z*.

3.2. Preparation of *cis*-$Mn(CO)_4Br\{(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]\}$ (**1**)

A solution of $\mathbf{L^1}$ (0.70 g, 1.50 mmol) in THF (10 cm^3) was added to a stirring solution of $Mn(CO)_5Br$ (0.40 g, 1.50 mmol) in THF (20 cm^3) at −78°C. The reaction mixture was allowed to warm to room temperature (r.t.) slowly and stirred for 1 day to give a golden yellow solution. The resulting solution was pumped to dryness and then extracted with hexane (2×10 cm^3) to give a red solution after filtration. The filtrate was concentrated to ca. 10 cm^3 and cooled to −20°C to give red crystals, which were filtered off and dried in vacuo. Yield: 0.63 g, 60%, m.p. 119–121°C (dec.) (Anal. Found: C, 50.1; H, 4.9; N, 4.0. Calc. for $C_{29}H_{33}BrMnN_2O_4PSi_2$: C, 50.1; H, 4.8; N, 4.0%). IR (cm^{-1}, in KBr): 2085s, 2000vs, 1956vs, 1921m (sh) ν(CO). NMR (C_6D_6): $^{31}P\{^1H\}$, δ 73.6 (br, s). $^{13}C\{^1H\}$, carbonyl, δ 217.3 (br, d, $J = 21.9$ Hz) and 212.8 (br, d, $J = 12.2$ Hz); C=N, 171.4 (d, $J = 7.3$ Hz); phenyl, 139.5 (d, $J = 4.9$ Hz), 137.1 (s), 137.1 (d, $J = 43.9$ Hz), 132.7 (d, $J = 9.8$ Hz), 130.1 (d, $J = 2.4$ Hz), 129.7, 128.4, 127.8 and 127.6; $N(SiMe_3)_2$, 3.2 (s). ^1H, phenyl, δ 7.64 (4H, m), 7.39 (3H, m), 6.87 (6H, m) and 6.69 (2H, m); $N(SiMe_3)_2$, 0.21 (18H, br, s). LRMS *m/z*: 615 (M − Br), 582 (M − 4CO), 557 (M − Br − 2CO) and 501 (M − Br − 4CO) for ^{55}Mn and ^{79}Br.

3.3. Preparation of *fac*-$\{[Mn(CO)_3Br][(Ph_2PNH)C(Ph)({=}NSiMe_3)]\}$ (**2**)

A solution of **1** (0.10 g, 0.14 mmol) in THF (10 cm^3) was heated to reflux for 4 h. After cooling to r.t., the resulting yellow solution was evaporated to dryness to give a yellow powder, which was washed with hexane (2×5 cm^3) and dried in vacuo. Yield: 78 mg, 90%, m.p. 161–163°C (dec.) (Anal. Found: C, 49.8; H, 4.3; N, 4.5. Calc. for $C_{25}H_{25}BrMnN_2O_3PSi{\cdot}0.5H_2O$: C, 49.7; H, 4.3; N, 4.6%). IR (cm^{-1}, in KBr): 3230s ν(NH), 2021vs, 1940vs, 1906vs ν(CO). NMR (C_6D_6): $^{31}P\{^1H\}$, δ 106.4 (br, s). $^{13}C\{^1H\}$, carbonyl, δ 224.4 (br, m); C=N, 173.7 (d, $J = 17.1$ Hz); phenyl, 137.6 (s), 137.0 (d, $J = 23.2$ Hz), 133.8 (d, $J = 11.0$ Hz), 132.0 (s), 131.4 (d, $J = 9.8$ Hz), 130.7 (s), 130.1 (d, $J = 12.2$ Hz), 129.5 (d, $J = 9.8$ Hz), 128.8 (d, $J = 9.8$ Hz) and 126.6 (br, s). ^1H, phenyl, δ 7.90–7.84 (2H, m) and 7.61–7.45 (13H, m); NH, 6.70 (1H, br, s); $N(SiMe_3)$, 0.13 (9H, s). LRMS *m/z*: 595 (M + 1), 510 (M − 3CO) and 431 (M − Br − 3CO) for ^{55}Mn and ^{79}Br.

3.4. Preparation of *fac*-$Re(CO)_3Br[(Ph_2PNH)C(Ph)({=}NH)]$ (**3**)

A mixture of $Re(CO)_5Br$ (0.10 g, 0.24 mmol) and $\mathbf{L^1}$ (0.11 g, 0.24 mmol) in THF (12 cm^3) was refluxed for 2 h. The resulting pale yellow solution was allowed to cool down to r.t. and then pumped to dryness. The residue was washed with hexane (2×5 cm^3) and then recrystallized from a dichloromethane–hexane mixture to give white crystals, which were filtered and dried in vacuo. Yield: 0.09 g, 60%, m.p. 202–204°C (dec.) (Anal. Found: C, 39.7; H, 2.5; N, 4.1. Calc. for $C_{22}H_{17}BrN_2O_3PRe{\cdot}0.25CH_2Cl_2$: C, 39.5; H, 2.6; N, 4.2%). IR (cm^{-1}, in KBr): 3408m, 3252m ν(NH), 2028vs, 1943vs, 1871vs ν(CO). NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 75.0 (s). $^{13}C\{^1H\}$, carbonyl, δ 194.3, 191.5, 190.4 and 188.5 (d, $J = 7.3$ Hz); C=N, 173.3 (d, $J = 14.6$ Hz); phenyl, 133.2, 132.9 (d, $J = 6.1$ Hz), 132.0, 131.5, 130.6 (d, $J = 13.4$ Hz), 129.6, 128.9 (dd, $J = 11$ Hz, $J = 19.5$ Hz) and 126.6. ^1H, phenyl, 7.83–7.47 (15H, m); NH, 7.76 (1H, br, s) and 6.58 (1H, br, s). LRMS *m/z*: 653 (M + 1), 624 (M − CO), 573 (M − Br), 545 (M − Br − CO) and 489 (M − Br − 3CO) for ^{185}Re and ^{79}Br.

3.5. Preparation of *fac*-$Re(CO)_3Cl[(Ph_2PNH)C(Ph)({=}NH)]$ (**4**)

This compound was prepared as described for **3**. $Re(CO)_5Cl$ (0.20 g, 0.54 mmol) and $\mathbf{L^1}$ (0.24 g, 0.54 mmol) were used. White crystals of **4** were obtained from a dichloromethane–hexane mixture. Yield: 0.23 g, 70%, m.p. 185–187°C (dec.) (Anal. Found: C, 41.4; H, 3.1; N, 4.0. Calc. for $C_{22}H_{17}ClN_2O_3PRe{\cdot}1.5H_2O$: C, 41.5; H, 3.1; N, 4.4%). IR (cm^{-1}, in KBr): 3408m, 3245s ν(NH), 2030vs, 1940vs, 1870vs ν(CO). NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 77.5 (s). $^{13}C\{^1H\}$, carbonyl, δ 195.5 (d, $J = 4.7$ Hz), 191.1 (d, $J = 78.0$ Hz) and 188.9 (d, $J = 8.5$ Hz); C=N, 173.5 (d, $J = 15.9$ Hz); phenyl, 135.0 (d, $J = 52.4$ Hz), 133.2 (d, $J = 12.1$ Hz), 132.9, 132.1, 131.5, 130.6 (d, $J = 12.2$ Hz), 129.6, 128.9 (t, $J = 11$ Hz) and 126.7. ^1H, phenyl, 7.84–7.77 (2H, m) and 7.66–7.47 (13H, m); NH, 7.86 (1H, br, s) and 6.67 (1H, br, s); LRMS m/z: 608 (M), 573 (M − Cl), 545 (M − CO − Cl), 524 (M − 3CO) and 489 (M − 3CO − Cl) for ^{187}Re and ^{35}Cl.

3.6. Preparation of[cis-$Mn(CO)_4Br]_2\{(Ph_2PN=)$-$[(Me_3Si\ )_2N]C\}_2C_6H_4$-1,4 (**5**)

A solution of $\mathbf{L^2}$ (0.62 g, 0.76 mmol) in THF (10 cm^3) was added to a stirring solution of $Mn(CO)_5Br$ (0.41 g, 1.50 mmol) in THF (30 cm^3) at −78°C. After stirring at −78°C for 30 min, the solution was allowed to warm to r.t. and stirred for 1 day to give a golden yellow solution. The resultant solution was filtered and concentrated to ca. 5 cm^3. Hexane (5 cm^3) was subsequently added to the concentrate to give a yellow–orange precipitate which was washed with diethyl ether (2 × 5 cm^3) and then dried in vacuo. Yield: 0.43 g, 43%, m.p. 124–126°C (dec.) (Anal. Found: C, 48.0; H, 4.8; N, 4.2. Calc. for $C_{52}H_{60}Br_2Mn_2N_4O_8P_2Si_4 \cdot 5C_4H_8O$: C, 48.1; H, 4.7; N, 4.2%). IR (cm^{-1}, in KBr): 2085s, 2015vs, 2000vs, 1956s, 1912m ν(CO). NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 68.4 (s). $^{13}C\{^1H\}$, carbonyl, δ 211.5 (m) and 207.2; C=N, 169.4 (d, $J = 7.3$ Hz); phenylene and phenyl, 140.6, 138.0, 137.3, 132.0 (d, $J = 9.7$ Hz), 130.4 (d, $J = 7.3$ Hz) and 128.0 (d, $J = 9.7$ Hz); $SiMe_3$, 3.1 (br, s). ^1H, phenylene and phenyl, δ 7.50–7.40 (24H, m); $SiMe_3$, 0.11 (36H, br, s). LRMS m/z: 1088 (M − 8CO), 1009 (M − 8CO − Br), 955 (M − CO − Br − Mn), 929 (M − CO − 2Br) and 873 (M − 8CO − 2Br − Mn) for ^{55}Mn and ^{79}Br.

3.7. Preparation of cyclo-[fac-$(Me_2NCHO)Re(CO)_3(\mu$-$Ph_2PO_2)]_2$ (**6**)

$Re(CO)_5Br$ (0.10 g, 0.24 mmol) and $\mathbf{L^2}$ (0.10 g, 0.12 mmol) in THF (10 cm^3) were stirred under reflux for 1 day. The suspension was filtered off to give a white solid, which was washed with THF (5 cm^3), dried in vacuo, redissolved in hot DMF and filtered to give a yellow solution. After the solution was cooled down to ambient temperature, yellow block crystals were obtained. Yield: 0.10 g, 40%, m.p. 172–174°C (dec.) (Anal. Found: C, 39.9; H, 3.8; N, 4.3. Calc. for $C_{36}H_{34}N_2O_{12}P_2Re_2 \cdot 2C_3H_7NO$: C, 39.8; H, 3.8; N, 4.4%). IR (cm^{-1}, in KBr): 2019s, 1905vs, 1889vs, 1875vs ν(CO). NMR (d_7-DMF): $^{31}P\{^1H\}$, δ 35.4 (s). LRMS m/z: 1047 (M + 2 − DMF), 974 (M + 2 − 2DMF), 918 (M + 2 − 2DMF − 2CO), 834 (M + 2 − 2DMF − 5CO) and 806 (M + 2 − 2DMF − 6CO) for ^{185}Re.

3.8. Preparation of cis-$Mo(CO)_4\{(NC_5H_4)[(Ph_2PNH)C(=NSiMe_3)]-4\}$ (**7**)

A solution of $(nbd)Mo(CO)_4$ (0.39 g, 1.28 mmol) in THF (20 cm^3) was added to a stirring solution of $\mathbf{L^3}$ (0.58 g, 1.28 mmol) in THF (15 cm^3) at 0°C. The resulting solution was allowed to warm to r.t. slowly and stirred for 1 day to give a red solution. The solution was filtered and pumped to dryness to give an orange–red residue. The residue was washed with a 1:1 diethyl ether–hexane mixture (3 × 5 cm^3), redissolved in dichloromethane (5 cm^3) and filtered. A layer of hexane was then laid over the filtrate. Yellow block crystals were obtained after standing for 2 days at r.t. The crystals were filtered and dried in vacuo. Yield: 0.28 g, 37%, m.p. 140–142°C (dec.) (Anal. Found: C, 50.9; H, 4.1; N, 6.9. Calc. for $C_{25}H_{24}MoN_3O_4PSi$: C, 51.1; H, 4.1; N, 7.2%). IR (cm^{-1}, in KBr): 3449w ν(NH), 2018s, 1902vs, 1879vs, 1846vs ν(CO). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, δ 89.9 (s). $^{13}C\{^1H\}$, carbonyl, δ 220.9 (d, $J = 8.5$ Hz), 216.8 (d, $J = 36.5$ Hz), 216.6 and 208.0 (d, $J = 9.8$ Hz); C=N, 167.1 (d, $J = 18.2$ Hz); pyridyl, 150.9 ($C_{2,6}$), 131.1 (C_4) and 121.8 ($C_{3,5}$); phenyl, 145.2 (d, $J = 6.1$ Hz), 137.3 (d, $J = 39.0$ Hz), 130.9 (d, $J = 15.6$ Hz) and 129.3 (d, $J = 11.0$ Hz); $N(SiMe_3)$, 3.6 (br, s). ^1H, pyridyl, δ 8.71 ($2H_{2,6}$, d, $J = 5.9$ Hz) and 7.23 ($2H_{2,3}$, m); phenyl, 7.56–7.44 (10H, m), NH, 6.28 (1H, br, m), $N(SiMe_3)$, 0.09 (9H, br, s). LRMS m/z: 587 (M), 559 (M − CO), 531 (M − 2CO) and 475 (M − 4CO) for ^{98}Mo.

3.9. Preparation of cis-$Cr(CO)_4\{(NC_5H_4)[(Ph_2PNH)C(=NSiMe_3)]-4\}$ (**8**)

This compound was prepared as described for **7**. $(nbd)Cr(CO)_4$ (0.22 g, 0.86 mmol) and $\mathbf{L^3}$ (0.58 g, 1.28 mmol) were used. Yellow block crystals were obtained. Yield: 0.29 g, 62%, m.p. 173–175°C (dec.) (Anal. Found: C, 55.1; H, 4.4; N, 7.5. Calc. for $C_{25}H_{24}CrN_3O_4PSi$: C, 55.4; H, 4.4; N, 7.8%). IR (cm^{-1}, in KBr): 3448w ν(NH), 2009s, 1904vs, 1875vs, 1842vs ν(CO). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, δ 112.3 (s). $^{13}C\{^1H\}$, carbonyl, δ 228.7 (d, $J = 13.4$ Hz), 227.4 (d, $J = 4.1$ Hz) and 219.2 (d, $J = 15.9$ Hz); C=N, 166.9 (d, $J = 20.7$ Hz); pyridyl, 150.8 ($C_{2,6}$), 131.1 (C_4) and 121.9 ($C_{3,5}$); phenyl, 145.2 (d, $J = 4.9$ Hz), 137.3 (d, $J = 39.0$ Hz), 130.9 (d, $J = 13.4$ Hz) and 129.2 (d, $J = 9.7$ Hz); $N(SiMe_3)$, 3.6 (br, s). ^1H: pyridyl, δ 8.66 ($2H_{2,6}$, d, $^3J = 4.6$ Hz) and 7.23 ($2H_{3,5}$, d, $^3J = 2.4$ Hz); phenyl, 7.61 (4H, m) and 7.23 (6H, m); NH, 6.85 (1H, br, m); $N(SiMe_3)$, 0.11 (9H, br, s). LRMS m/z: 541 (M), 513 (M − CO), 457 (M − 3CO) and 429 (M − 4CO) for ^{52}Cr.

Table 1
Selected bond lengths (Å) and angles (°) for compounds **1**, **3**, **6**, **9** and **10**

Compound ***1***					
Mn(1)–P(1)	2.382(2)	Mn(1)–Br(1)	2.517(1)	Mn(1)–C(1)	1.840(9)
Mn(1)–C(2)	1.822(8)	Mn(1)–C(3)	1.765(9)	Mn(1)–C(4)	1.864(8)
P(1)–N(1)	1.661(5)	N(1)–C(17)	1.291(7)	N(2)–C(17)	1.388(7)
N(2)–Si(1)	1.779(5)	N(2)–Si(2)	1.777(5)		
P(1)–Mn(1)–Br(1)	98.64(5)	P(1)–Mn(1)–C(1)	87.7(2)	P(1)–Mn(1)–C(2)	178.4(2)
P(1)–Mn(1)–C(3)	90.7(2)	P(1)–Mn(1)–C(4)	88.8(2)	P(1)–N(1)–C(17)	133.7(4)
N(1)–C(17)–N(2)	119.2(5)	Si(1)–N(2)–Si(2)	121.7(3)	Si(1)–N(2)–C(17)	121.9(4)
Si(2)–N(2)–C(17)	115.5(4)				
Compound ***3***					
Re(1)–Br(1)	2.642(2)	Re(1)–P(1)	2.412(3)	Re(1)–N(1)	2.176(10)
Re(1)–C(1)	1.98(2)	Re(1)–C(2)	1.87(2)	Re(1)–C(3)	1.95(2)
P(1)–N(2)	1.69(2)	N(2)–C(4)	1.25(2)	N(1)–C(4)	1.40(1)
P(1)–N(2)–N(1)	76.3(3)	P(1)–Re(1)–Br(1)	88.96(8)	P(1)–Re(1)–C(1)	171.4(4)
P(1)–Re(1)–C(2)	178.6(5)	P(1)–Re(1)–C(3)	89.6(5)	P(1)–N(2)–C(4)	119.8(8)
Re(1)–N(1)–C(4)	125.4(8)	N(1)–C(4)–N(2)	117(1)	Re(1)–P(1)–N(2)	101.0(4)
Compound ***6***					
Re(1)–O(4)	2.182(10)	Re(1)–O(5)	2.167(8)	Re(1)–O(6)	2.149(8)
Re(1)–C(1)	1.89(2)	Re(1)–C(2)	1.88(2)	Re(1)–C(3)	1.93(2)
P(1)–O(5)	1.503(9)	P(1)–O(6*)	1.521(9)		
O(4)–Re(1)–O(5)	80.4(3)	O(4)–Re(1)–O(6)	78.4(3)	O(4)–Re(1)–C(1)	93.8(5)
O(4)–Re(1)–C(2)	175.7(5)	O(4)–Re(1)–C(3)	97.4(5)	Re(1)–O(5)–P(1)	130.4(6)
O(5)–P(1)–O(6*)	116.5(5)	Re(1)–O(6)–P(1*)	130.5(5)	O(5)–Re(1)–O(6)	81.2(3)
O(5)–P(1)–C(7)	111.2(6)	O(5)–P(1)–C(13)	104.6(6)	O(6*)–P(1)–C(7)	106.6(6)
O(6*)–P(1)–C(13)	111.7(6)				
Compound ***9***					
Mn(1)–Br(1)	2.534(5)	Mn(2)–Br(2)	2.494(6)	Mn(3)–Br(3)	2.533(6)
Mn(1)–N(1)	2.07(2)	Mn(2)–P(1)	2.372(7)	Mn(3)–P(2)	2.340(8)
Mn(1)–N(4)	2.07(2)	Mn(2)–C(4)	2.18(3)	Mn(3)–C(8)	1.74(6)
Mn(1)–C(1)	1.74(3)	Mn(2)–C(5)	1.90(4)	Mn(3)–C(9)	1.88(4)
Mn(1)–C(2)	1.80(3)	Mn(2)–C(6)	1.83(4)	Mn(3)–C(10)	1.75(3)
Mn(1)–C(3)	1.79(3)	Mn(2)–C(7)	1.82(3)	Mn(3)–C(11)	1.88(3)
P(1)–N(2)	1.66(2)	P(2)–N(5)	1.68(2)	N(2)–C(17)	1.27(3)
N(5)–C(41)	1.33(3)	N(3)–C(17)	1.32(3)	N(6)–C(41)	1.36(3)
N(1)–Mn(1)–N(4)	85.7(7)	P(1)–N(2)–C(17)	136(1)	P(2)–N(5)–C(41)	135(1)
N(2)–C(17)–N(3)	123(3)	N(5)–C(41)–N(6)	119(1)	Si(1)–N(3)–Si(2)	120(1)
Si(1)–N(3)–C(17)	124(1)	Si(2)–N(6)–C(41)	114(1)	Si(3)–N(6)–Si(4)	122(1)
Si(3)–N(6)–C(41)	116(1)	Si(4)–N(6)–C(41)	120(1)		
Compound ***10***					
Mo(1)–P(1)	2.483(1)	Mo(1)–N(2)	2.246(4)	Mo(1)–C(1)	2.021(6)
Mo(1)–C(2)	1.962(6)	Mo(1)–C(3)	2.017(7)	Mo(1)–C(4)	2.000(6)
P(1)–N(1)	1.711(4)	N(1)–C(5)	1.369(6)	N(2)–C(5)	1.276(6)
P(1)–Mo(1)–N(2)	74.51(1)	P(1)–Mo(1)–C(1)	91.7(2)	P(1)–Mo(1)–C(2)	102.7(2)
P(1)–Mo(1)–C(3)	89.8(2)	P(1)–Mo(1)–C(4)	167.9(2)	Mo(1)–P(1)–N(1)	101.6(1)
Mo(1)–N(2)–C(5)	124.6(3)	N(1)–C(5)–N(2)	119.2(4)	C(5)–N(1)–P(1)	119.8(3)

3.10. Preparation of *fac*-{*cis*-$Mn(CO)_4Br[(NC_5H_4)$-$\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4]}$_2Mn(CO)_3Br$ (**9**)

A solution of $\mathbf{L}^{\mathbf{3}}$ (0.90 g, 2.0 mmol) in dichloromethane (15 cm^3) was added to a solution of $Mn(CO)_5Br$ (1.65 g, 6 mmol) in THF (20 cm^3) at ambient temperature and the solution mixture was allowed to react overnight to give a red solution. The solution was filtered, pumped to dryness and then extracted with hexane (10 cm^3) to give a red solution after filtration. The filtrate was then cooled to -20°C to give red crystals, which were filtered off and dried in vacuo. Yield: 0.67 g, 58%, m.p. 155–157°C (dec.) (Anal. Found: C, 44.9; H, 4.4; N, 5.5. Calc. for $C_{59}H_{64}Br_3Mn_3N_6O_{11}P_2Si_4{\cdot}0.5C_6H_{14}$: C, 45.0; H, 4.3; N, 5.1%). IR (cm^{-1}, in KBr): 2087vs, 2027vs, 1999vs, 1945vs, 1906vs ν(CO). NMR (C_6D_6): $^{31}P\{^1H\}$, δ 78.1 (br, s). $^{13}C\{^1H\}$, C=N, δ 167.6 (d, $J = 8.5$ Hz); pyridyl and phenyl, 154.6 (d, $J = 4.9$ Hz), 147.1 (d, $J = 4.8$ Hz), 132.0–131.3 (m) and 124.5 (s); $N(SiMe_3)_2$, 3.2 (s). ^1H, pyridyl and phenyl, δ 8.27 (2H, br, s), 7.44 (6H, br, s) and 6.91 (20H, m); $N(SiMe_3)_2$, 0.17 (36H, s). LRMS m/z: 616 [(**1** + 1) − Br] and 583 [(**1** + 1) − 4CO] for ^{55}Mn and ^{79}Br.

3.11. Preparation of *cis-Mo(CO)$_4${(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NH)]-4}* (**10**)

Compound **7** (0.24 g, 0.4 mmol) and $CdCl_2$ (36 mg, 0.20 mmol) in THF (20 cm^3) were stirred at ambient temperature for 1 day. The resulting brown yellow solution was filtered and pumped to dryness to give a yellow residue. The residue was washed with diethyl ether (2 × 6 cm^3), dissolved in dichloromethane and filtered. The filtrate was then covered with a layer of hexane. A yellow precipitate was obtained after standing for 3 days. After filtering off the yellow residue, the yellow filtrate was cooled at −5°C for 2 days to give yellow crystals, which were filtered and dried in vacuo. Yield: 0.19 g, 50%, m.p. 180–182°C (dec.) (Anal. Found: C, 51.5; H, 3.1; N, 8.1. Calc. for $C_{22}H_{16}MoN_3O_4P$: C, 51.5; H, 3.1; N, 8.2%). IR (cm^{-1}, in KBr): 3368s ν(NH), 2016vs, 1918vs, 1911vs, 1891vs, 1838vs, 1816vs ν(CO). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, δ 98.8 (s). ^1H, phenyl, δ 7.57–7.48 (4H, m) and 7.44–7.41 (6H, m); pyridyl, 8.74 ($2H_{2,6}$, d, $J = 5.9$ Hz) and 7.36 ($2H_{3,5}$, d, $J = 6.2$ Hz); NH, 7.56 (1H, br, m) and 6.24 (1H, br, m). LRMS (FAB: positive mode) m/z: 515 (M) and 403 (M − 4CO) for ^{98}Mo.

3.12. Preparation of *fac-[cis-Cr(CO)$_4${(NC$_5$H$_4$)-[(Ph$_2$PNH)C(=NSiMe$_3$)]-4}]$_2$Mn(CO)$_3$Br* (**11**)

A solution of $Mn(CO)_5Br$ (0.10 g, 0.34 mmol) in THF (10 cm^3) was added to a stirring solution of **8** (0.19 g, 0.34 mmol) in THF (10 cm^3) at 0°C. The mixture was then allowed to warm to r.t. Upon stirring overnight, the resulting red solution was pumped to dryness and washed with diethyl ether (3 × 2 cm^3) to give a yellow residue, which was redissolved in dichloromethane (5 cm^3) and filtered. A layer of diethyl ether was then laid over the filtrate. Yellow crystals were obtained after standing for 2 days. The crystals were filtered and dried in vacuo. Yield: 0.18 g, 81%, m.p. 145–147°C (dec.) (Anal. Found: C, 47.9; H, 3.6; Br, 6.4; N, 6.3. Calc. for $C_{53}H_{48}BrCr_2MnN_6O_{11}P_2Si_2 \cdot 0.5CH_2Cl_2$: C, 47.8; H, 3.7; Br, 6.0; N, 6.3%). IR (cm^{-1}, in KBr): 3347w ν(NH), 2032s, 2013s, 1951s, 1904vs, 1882vs, 1836vs ν(CO). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, δ 114.5 (s). ^1H, pyridyl, δ 8.89 ($4H_{2,6}$, br, s) and 7.27 ($4H_{3,5}$, br, s); phenyl, 7.58–7.51 (20H, m); NH, 6.75 (2H, br, s); $N(SiMe_3)$, 0.12 (18H, br, s). LRMS m/z: 992 (M − 11CO) and 911 (M − 11CO − Br) for ^{52}Cr, ^{55}Mn and ^{79}Br.

Table 2
Summary of crystal data for compounds **1**, **3**, **6**, **9** and **10**

	1	**3**	**6**	**9**	**10**
Empirical formula	$C_{29}H_{33}BrMnN_2O_4PSi_2$	$C_{22}H_{17}BrN_2O_4PRe$	$C_{42}H_{48}N_4O_{14}P_2Re_2$	$C_{59}H_{64}Br_3Mn_3N_6O_{11}P_2Si_4$	$C_{22}H_{16}MoN_3O_4P$
Formula weight	695.58	670.47	1267.22	1612.00	513.30
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 4)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/a$ (no. 14)
a (Å)	10.632(1)	9.976(1)	12.216(2)	16.865(1)	11.866(1)
b (Å)	21.139(1)	11.519(1)	12.167(7)	22.989(1)	13.902(1)
c (Å)	15.342(1)	12.823(1)	17.342(5)	25.158(1)	13.376(1)
α (°)		88.20(2)			
β (°)	101.3(2)	68.06(2)	108.19(2)	98.76(1)	98.41(1)
γ (°)		81.83(2)			
U (Å^3)	3378.2(9)	1352.5(3)	2448 (1)	9640.2(8)	2182.8(3)
Z	4	2	2	4	4
μ (Mo–K$_\alpha$) (cm^{-1})	17.29	60.61	50.71	17.59	7.07
Temperature (K)	298	298	298	298	298
Reflections collected	13 319	11 413	2691	19 026	18 136
Independent reflections (R_{int})	4351 (0.053)	4659 (0.065)	2545 (0.026)	9662 (0.071)	4158 (0.042)
Observed reflections	2904 [$I > 1.50\sigma(I)$]	4147 [$I > 1.50\sigma(I)$]	1931 [$I > 1.50\sigma(I)$]	5073 [$I > 1.50\sigma(I)$]	2534 [$I > 3.00\sigma(I)$]
R [a]	0.054	0.052	0.041	0.117	0.039
R_w [b]	0.052	0.098	0.049	0.136	0.045

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

4. Crystallography

Selected bond lengths and angles of compounds **1**, **3**, **6**, **9** and **10** are given in Table 1. All pertinent crystallographic data and other experimental details are summarized in Table 2. Intensity data of **1**, **3**, **9** and **10** were collected on a MAR research image plate scanner, and **6** on a Rigaku AFC7R diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects. For **1**, **3**, **9** and **10**, absorption corrections were applied by inter-image scaling whereas semi-empirical ψ-scan method was used for **6**. The structures were solved by a combination of direct methods (SIR-92) [11] and Fourier difference techniques. The structure solutions were refined by full-matrix least-squares analysis on F until convergence was reached. Except for **9**, all non-hydrogen atoms were refined anisotropically. Because of the poorly diffracting nature of the crystal sample of **9**, only the Mn, Br, P and Si atoms were assigned with anisotropic displacement parameters to maintain a reasonable data-to-parameter ratio. Hydrogen atoms on the nitrogen were located from difference Fourier synthesis using low angle data ($2\theta < 30°$) while other hydrogen atoms on the organic moieties were generated at their ideal positions (C–H 0.95 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned with appropriate isotropic thermal parameters and included in the structure factor calculations but were not refined. All calculations were performed on a Silicon Graphics workstation using the TEXSAN software package [12].

5. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis have been deposited with the Cambridge Crystallographic Centre (deposition nos. 143059–143063). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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