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Journal of Organometallic Chemistry 655 (2002) 55–62

Journal of Organometallic Chemistry

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A comparison of the ligating properties of the mixed P/O- and P/S-donor ligands $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ and $Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$ with Group 6 and 7 carbonyls

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Received 14 February 2002; accepted 20 March 2002

Abstract

$[M(CO)_4(nbd)]$ ($M = Cr$ or Mo) react with L^1 ($Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$) to give the *trans*-$[Cr(CO)_4(L^1)]$ and *cis*-$[Mo(CO)_4(L^1)]$ respectively, both of which show coordination of L^1 through the P atoms only, giving 11-membered ring metallocyclic complexes. The crystal structure of $[Mo(CO)_4(L^1)]$ confirms the *cis*-geometry of the product. The *cis*-$[W(CO)_4(L^1)]$ is obtained similarly from $[W(CO)_4(TMPA)]$. Prolonged reaction of $[MnCl(CO)_5]$ with L^1 affords *mer*-*trans*-$[MnCl(CO)_3(L^1)]$, with L^1 functioning as a *trans* chelate via the phosphine functions. The kinetic product *fac*-$[MnCl(CO)_3(L^1)]$ is obtained when short reaction times are used. In contrast, $[ReBr(CO)_5]$ reacts with L^1 to give $[ReBr(CO)_3(L^1)]$ as a mixture of geometric isomers. Both 1:1 and 2:1 $M{:}L^2$ ($L^2 = Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$) may be obtained for $M = Mn(I)$ or Mo(0). The $[MnCl(CO)_3(L^2)]$ exists in solution as the *fac* isomer with L^2 functioning as a bidentate P,S-donor ligand giving a five-membered chelate ring and with the remaining thioether and phosphine functions uncoordinated. Addition of a further equivalent of $[MnCl(CO)_5]$ affords the binuclear *fac*-$[\{MnCl(CO)_3\}_2(\mu^2\text{-}L^2)]$, with symmetrical P,S-chelation to each metal centre. Similar behaviour is seen for Mo, thus *cis*-$[\{Mo(CO)_4\}_2(\mu^2\text{-}L^2)]$ involves P,S-chelation to each Mo(0) ion. The related 1:1 species *cis*-$[Mo(CO)_4(L^2)]$ exists as a mixture of two compounds each with bidentate L^2 coordination, the P_2-chelate (11-membered ring metallocycle) and P,S-coordinated (five-membered chelate ring) species. The new compounds are characterised by microanalyses, IR, ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$-, ^{55}Mn-NMR spectroscopy and mass spectrometry as appropriate. The different ligating properties of the related compounds L^1 and L^2 are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: P/O- and P/S-donor ligands; NMR spectroscopy; X-ray crystallography; Transition metal carbonyl complexes

1. Introduction

Interest in mixed phospha-thia and phospha-oxa ligands stems from their ability to bond to a wide range of metal ions, and the presence of the two different donor atom types leads to considerable coordinative flexibility for these ligands. In the ligands which we have been studying [1–6], the phosphine functions (good σ-donors) are specifically introduced at the termini to encourage coordination via the (soft) thioether or (hard) ether functions (both of which are much more modest σ-donors). For example, the crystal structure of the unusual Pt(II) species $[Pt(OH_2)\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\}]^{2+}$ shows Pt(II) coordinated to both phosphine functions, one water molecule and to one of the ether oxygens of the mixed P/O-donor ligand [7], while halogen oxidation of the square planar $[Pt(L^2)](PF_6)_2$ ($L^2 = Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$) gives the unusual Pt(IV) species, $[PtX_2(L^2)](PF_6)_2$ ($X = Cl$ or Br) with retention of the tetradentate L^2 coordination [2]. Alternatively, the thioether/ether groups may act as spacers between the phosphines as, for example, in $[Au(L)]PF_6$ ($L = L^1$ or L^2) [1,3,4] and $[NiI_2(L^1)]$ [8] in which L^2 behaves as a *trans* chelate via the P-functions, or $[Au_2(L^2)_2]Cl_2$ in which each Au(I) centre is coordinated to two phosphine functions from the bridging ligands, giving a helical metallocyclic structure with one of the Cl^- anions occupying the cavity [1].

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PII: S0022-328X(02)01413-4

Few studies have been conducted on transition metal carbonyl systems involving these or related ligands, although Gray and co-workers have investigated in detail the coordination of various P_2O_x-donor ligands ($x = 3-5$) with molybdenum carbonyl to give *cis*-[Mo(CO)$_4$(L)] and have shown that the resulting metallocyclic cavities can in certain cases host alkali metal ions. They have also shown that under UV irradiation or in the presence of $HgCl_2$ these Mo(0) species isomerise to the corresponding *trans* isomers [9,10].

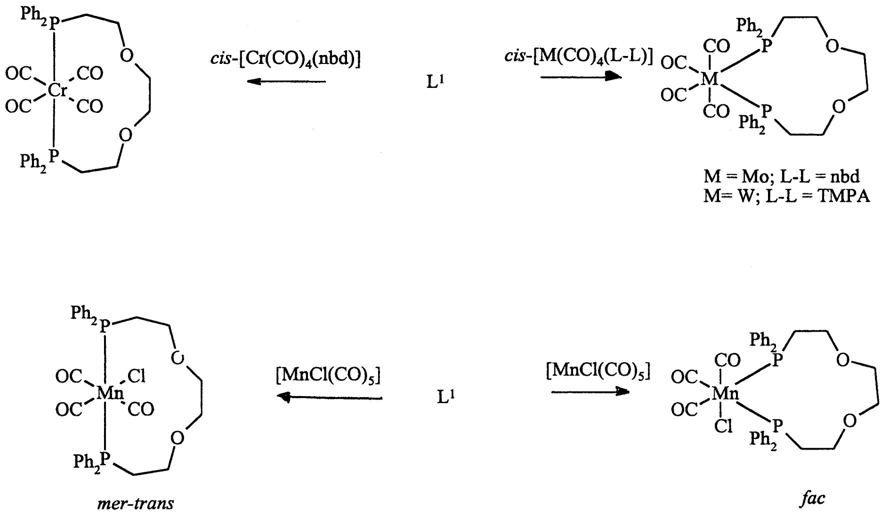
In this paper we describe the preparation and characterisation of a series of new Group 6 and 7 metal carbonyl complexes incorporating the mixed P/O- and P/S-donor ligands L^1 and L^2, including the crystal structure of [Mo(CO)$_4$(L^1)], which illustrate the quite different ligating properties of L^1 and L^2.

2. Results and discussion

2.1. Complexes of L^1

A summary of the products obtained from reaction of various Group 6 and 7 carbonyl species with L^1 is given in Scheme 1.

Treatment of *cis*-[M(CO)$_4$(nbd)] (M = Cr or Mo) or *cis*-[W(CO)$_4$(TMPA)] (nbd = 2,5-norbornadiene = bicyclo[2.2.1]-hepta-2,5-diene; TMPA = *N*,*N*,*N*′,*N*′-tetramethyl-propylendiamine) with L^1 in a 1:1 molar ratio in toluene (or chloroform for W) gave yellow solutions. The reactions were monitored by solution IR spectroscopy, until the ν(CO) absorptions due to the starting material had disappeared. The products were isolated by evaporation to dryness, dissolution in CH_2Cl_2 and precipitation with hexane. While the electrospray mass (MeCN) spectra of the Mo and W complexes showed clusters of peaks with the correct isotopic patterns consistent with $[Mo(CO)_2(L^1)]^+$ and $[Mo(CO)(L^1)]^+$ or $[W(CO)_2(L^1)]^+$ and $[W(L^1)]^+$, the mass spectrum of the chromium species gave no useful information. These data and ^{1}H-NMR spectroscopic data are consistent with the formulation [Mo(CO)$_4$(L^1)] or [W(CO)$_4$(L^1)] for the products. The solution IR spectrum (CH_2Cl_2) of the Mo product shows four peaks associated with ν(CO), consistent with retention of the *cis*-tetracarbonyl arrangement (C_{2v}, theory: $2a_1+b_1+b_2$). For the tungsten complex only three bands are seen, probably due to accidental coincidence of two peaks at 1883 cm^{-1}. *Cis*-[Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_3$CH$_2$CH$_2$PPh$_2$}] [9] shows ν(CO) at 2022, 1920, 1905 and 1885 cm^{-1}. The ^{13}C{^{1}H}-NMR spectra of the Mo and W complexes of L^1 each show resonances associated with coordinated L^1, together with a (poorly resolved) triplet and doublet of doublets due to CO *trans* CO and CO *trans* P, respectively. However, the ^{13}C{^{1}H}-NMR spectrum of the Cr species shows only one poorly resolved triplet in the CO region, while the IR spectrum shows a single, strong ν(CO) absorption at 1877 cm^{-1}, both of which are indicative of the presence of only the *trans*-[Cr(CO)$_4$(L^1)] isomer. The ^{31}P{^{1}H}-NMR spectrum of this Cr(0) compound shows a singlet at +56.5 ppm. The ready formation of the *trans* isomer under these mild reaction conditions contrasts with the report from Gray and co-workers for related molybdenum species where UV irradiation or $HgCl_2$ catalysis are required to convert the *cis*-[Mo(CO)$_4$(L)] (L = P_2O_x-donor ligands) into the corresponding *trans* species [10]. We also note that a ^{31}P{^{1}H}-NMR spectrum of the reaction mixture at an earlier stage in the reaction showed a further singlet at δ 28.8 (together with a resonance corresponding to ‘free’ L^1 and the +56.5 ppm resonance associated with the *trans* isomer above) which we tentatively assign to an intermediate *cis* isomer involving P_2-coordination from L^1.



Scheme 1. Complexes of L^1 (L^1 = $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$).

The $^{31}P\{^{1}H\}$-NMR spectra of the *cis*-[$Mo(CO)_4(L^1)$] and *cis*-[$W(CO)_4(L^1)$] each show a singlet at 17.8 and 3.9 ppm, respectively with ^{183}W satellites on the latter ($^{1}J(^{183}W-^{31}P)$ 225 Hz). This trend in $\delta(^{31}P)$ with Group 6 element is as expected, and the resonances are all to high frequency of L^1 itself (−21 ppm), indicative of κ^2-coordination through P, although the shifts are not sufficiently high to suggest that the phosphines are part of a five-membered chelate ring [11].

The crystal structure of [$Mo(CO)_4(L^1)$] confirms (Fig. 1, Table 1) that L^1 acts as a *cis*-chelate to Mo via the two P-donor atoms at the termini, with four CO ligands completing the distorted octahedral coordination at Mo(0). The P–Mo–P angle within the large 11-membered metallocyclic ring is 95.41(4)°, with the O-atoms remaining uncoordinated. This structure is similar to that reported by Gray and co-workers for *cis*-[$Mo(CO)_4\{Ph_2P((CH_2)_2O)_3(CH_2)_2PPh_2\}$] which shows Mo–P bond lengths of 2.5444(7), 2.5608(7) Å and Mo–C bond lengths in the range 1.976(3)–2.036(3) Å [9]. The P–Mo–P angle in this larger ring metallocyclic compound is smaller (93.78(2)°) than in *cis*-[$Mo(CO)_4(L^1)$].

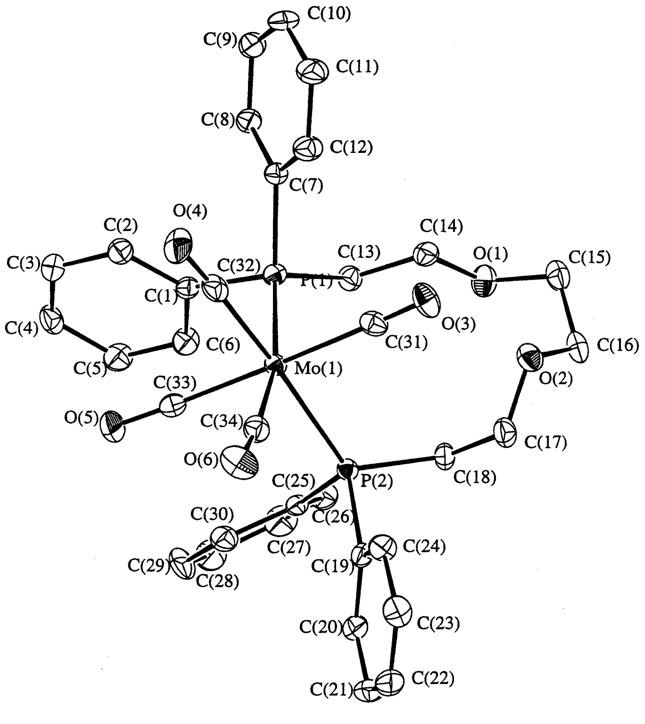


Fig. 1. View of the structure of *cis*-[$Mo(CO)_4(L^1)$] with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for *cis*-[$Mo(CO)_4(L^1)$]

Bond lengths			
Mo(1)–P(1)	2.539(1)		
Mo(1)–P(2)	2.573(1)		
Mo(1)–C(31)	2.041(5)		
Mo(1)–C(32)	1.982(5)		
Mo(1)–C(33)	2.033(5)		
Mo(1)–C(34)	2.004(5)		
Bond angles			
P(1)–Mo(1)–P(2)	95.41(4)	P(1)–Mo(1)–C(31)	95.6(1)
P(1)–Mo(1)–C(32)	86.7(1)	P(1)–Mo(1)–C(33)	88.4(1)
P(1)–Mo(1)–C(34)	169.7(1)	P(2)–Mo(1)–C(31)	91.9(1)
P(2)–Mo(1)–C(32)	176.7(1)	P(2)–Mo(1)–C(33)	91.5(1)
P(2)–Mo(1)–C(34)	92.6(1)	C(31)–Mo(1)–C(32)	90.5(2)
C(31)–Mo(1)–C(33)	174.5(2)	C(31)–Mo(1)–C(34)	90.7(2)
C(32)–Mo(1)–C(33)	85.9(2)	C(32)–Mo(1)–C(34)	85.1(2)
C(33)–Mo(1)–C(34)	84.9(2)		

For the Group 7 carbonyl complexes we employed [$MnCl(CO)_5$] and [$ReBr(CO)_5$] as the precursors, both of which readily undergo substitution of two CO ligands on addition of e.g. a diphosphine. In a preliminary reaction [$MnCl(CO)_5$] was treated with L^1 in a 1:1 molar ratio in chloroform to give a yellow solution. The reaction was monitored by solution IR, until the peaks due to the starting material disappeared completely, by which stage they had been replaced by peaks at 2095, 2026, 2010 and 1958 cm^{-1}. The appearance of four ν(CO) bands of different intensities suggested the presence of more than one geometric isomer. Several isomeric forms are possible for [$MnCl(CO)_3(\kappa^2-L^1)$], however, if we consider only P-coordination (coordination to the soft Mn(I) centre via the ether functions is unlikely and does not occur—see below) the possibilities are *fac*, *mer-cis* and *mer-trans*, each of which should lead to three CO stretching vibrations, although the intensities and positions of the bands are expected to vary. In the solid state IR spectrum (CsI) five bands were observed in the CO region, attributed (on the basis of these data and the NMR data) to the presence of a mixture of the *fac* and the *mer-trans* isomers—see below. The electrospray mass spectrum showed peaks corresponding to [$Mn(CO)_3(L^1)]^+$ as well as several fragment ions at lower *m*/*z*, due to loss of CO. The $^{31}P\{^{1}H\}$-NMR spectrum of this product showed two resonances at 44.0 and 29.9 ppm of different intensities. Repeating the reaction with refluxing for a longer period (18 h) gave a yellow solid. The IR spectrum of this product shows three ν(CO) bands at 2045, 1949 and 1909 cm^{-1}, while the $^{31}P\{^{1}H\}$-NMR spectrum shows only one resonance at 44 ppm. The presence of only one resonance eliminates the *mer-cis* isomer and this, together with the IR data suggest that the product isolated under these conditions is the *mer-trans* isomer. In this species L^1 is therefore behaving as a *trans* chelate through the phosphine units. The $^{13}C\{^{1}H\}$-NMR spectrum shows resonances associated with coordinated L^1 as well as δ(CO) at 212 ppm which is broadened significantly by the directly bonded ^{55}Mn quadrupolar nucleus and therefore the different CO environments are poorly resolved. Similar observations have been made for other Mn(I) carbonyl complexes with phosphine co-ligands [12]. The ^{55}Mn-NMR spectrum shows a very broad resonance at -1300 ppm ($w_{1/2} = 19{,}000$ Hz), consistent with coordination of L^1 to the Mn(I) centre via the phosphines only, giving *mer-trans*-[MnCl(CO)$_3$(L^1)]. The low symmetry of this isomer leads to the very large line-width.

Repeating this reaction at room temperature with stirring for only ca. 2 h results in incomplete consumption of the [MnCl(CO)$_5$] precursor, however, IR and NMR spectroscopic studies indicate that the major product is the *fac*-[MnCl(CO)$_3$(L^1)] with P$_2$-coordination of L^1 (δ^{31}P 29.9). The ν(CO) bands at 2027, 1957, 1910 cm^{-1} are in accord with those in other *fac*-[MnCl(CO)$_3$(diphosphine)] compounds [12]. It is interesting to note the ease with which this complex undergoes isomerisation to the *mer-trans* form compared to species such as *fac*-[MnCl(CO)$_3$(L)$_2$], L = PPh$_2$H or PPhH$_2$. In the case of [MnCl(CO)$_3$(L^1)] this isomerisation may relieve strain in the large 11-membered chelate ring present in the *fac* isomer.

We also obtained [ReBr(CO)$_3$(L^1)] in good yield, although even after 24 h at reflux in CHCl$_3$, the IR spectrum shows bands associated with both *fac* and *mer* species and the ^{31}P-NMR spectrum shows the presence of two resonances of unequal intensities at -12.9 and -13.5 ppm. These data suggest that two isomers are present, probably *fac* and *mer-trans* like in the Mn(I) system above. Varying the reaction time leads to changes in the relative quantities of the two species, but prolonged reflux (intended to encourage formation of the *mer-trans* species) led to decomposition, while short reaction times (intended to favour the *fac* isomer) gave a significant amount of unreacted [ReBr(CO)$_5$] and still showed a mixture of isomers. This behaviour is consistent with the low spin Re(I) ion being much more inert to substitution than the corresponding Mn(I)—the need for long reaction times and refluxing solvent to effect substitution also promotes some isomerisation. The mass spectrum of the solid isolated shows clusters of peaks with the correct isotope pattern for [Re(CO)$_3$(L^1)]$^+$ and fragments corresponding to successive loss of CO.

Microanalytical data suggest that the isolated complexes of L^1 (and L^2 below) have a tendency to associate solvent and there is evidence for CH$_2$Cl$_2$ in the ^{1}H- (5.3 ppm) and ^{13}C{^{1}H}-NMR spectra (54.1 ppm) of the complexes even after drying in vacuo.

2.2. Complexes of L^2

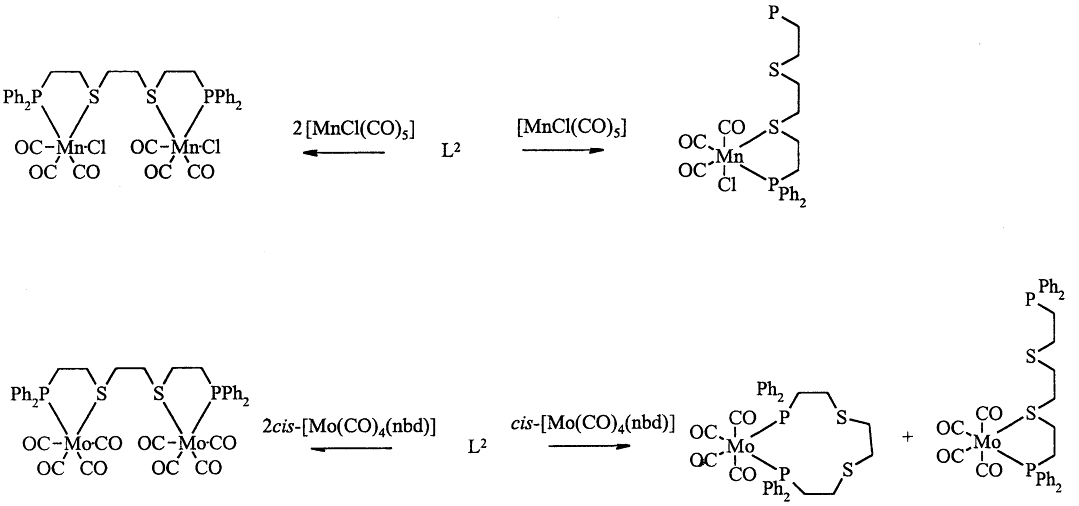
The products obtained from reaction of Mn(I) and Mo(0) carbonyls with L^2 are illustrated in Scheme 2.

[Mo(CO)$_4$(nbd)] reacts with 1 M equivalent of L^2 in CH$_2$Cl$_2$ to give a mixture of two products which, on the basis of IR and ^{13}C{^{1}H}-NMR spectroscopy, both appear to be *cis*-tetracarbonyl species. The ^{31}P{^{1}H}-NMR spectrum of this mixture shows three singlet resonances; a 1:1 pair at 52.9 and -16.6 ppm associated with a bidentate P,S chelated L^2 on Mo (the resonance at 52.9 ppm corresponds to a coordination shift ($\delta_{\text{complex}} - \delta_{\text{free ligand}}$) of +68 ppm, strongly suggesting that the P atom is contained within a five-membered chelate ring [11], whereas the low frequency resonance is very close to 'free' L^2, suggesting that this P centre is uncoordinated in the complex) and a third resonance at 26.1 ppm, which is of higher intensity and is attributed to a complex involving P$_2$-coordination by L^2. The ^{13}C{^{1}H}-NMR spectrum of this mixture is complex, however, the CO region is clearly consistent with the assignment of the products as *cis*-tetracarbonyl Mo(0) complexes, one of which shows P,S-chelation (three doublets in a 1:1:2 ratio) and the other of which shows P$_2$-chelation of L^2 (doublet of doublets and triplet).

A similar reaction of L^2 with 2 M equivalents of [Mo(CO)$_4$(nbd)] leads to the formation of a single species assigned as *cis*-[{Mo(CO)$_4$}$_2$(μ^2-L^2)] (IR ν(CO) = 2024, 1919, 1910sh, 1872 cm^{-1}). The ^{31}P{^{1}H}-NMR spectrum of this product reveals only one singlet at 53.0 ppm, very similar to the chemical shift for the P,S-chelate complex in the 1:1 Mo–L^2 species above. As expected, the ^{13}C{^{1}H}-NMR spectrum of this species shows three doublet CO resonances corresponding to CO *trans* S, CO *trans* P and CO *trans* CO. The CH$_2$ region of the spectrum is also consistent with symmetrical coordination of L^2, giving three CH$_2$ environments.

Reaction of [MnCl(CO)$_5$] with 1 M equivalent of L^2 in CH$_2$Cl$_2$ gives a yellow solid. IR spectrum shows three strong CO stretching vibrations associated with the *fac* isomer. The ^{31}P-NMR spectrum of this species shows two resonances of equal intensity at 70.0 and -16.6 ppm. The low frequency resonance is essentially unshifted from L^2 itself (-16 ppm), while the high frequency resonance corresponds to a coordination shift of 86 ppm, strongly suggesting that this P centre is part of a five-membered chelate ring [11]. Thus, these data suggest that L^2 coordinates to Mn(I) via chelation through one P atom and an adjacent S atom. The other P and S atoms remain uncoordinated. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra are also consistent with this assignment, both of which show more resonances than expected for a symmetrically bound L^2. The ^{55}Mn-NMR spectrum reveals a very broad resonance at ca. -700 ppm, intermediate between the chemical shifts for *fac*-[MnCl(CO)$_3${MeS(CH$_2$)$_2$SMe}] and *fac*-[MnCl(CO)$_3$(dppe)] (dppe = Ph$_2$P(CH$_2$)$_2$PPh$_2$) and consistent with P,S-chelation by L^2 at Mn(I) [12,13].

Reaction of L^2 with 2 M equivalents of [MnCl(CO)$_5$] leads to the binuclear species *fac*-[{MnCl(CO)$_3$}$_2$(μ^2-L^2)] in which L^2 functions as a bidentate (P,S) chelate to each Mn(I) centre. This is confirmed by microanalyses



Scheme 2. Complexes of L^2 (L^2 = $Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$).

and spectroscopic studies. The IR spectrum shows three strong ν(CO) bands (2033, 1958, 1921 cm^{-1}), consistent with the *fac*-tricarbonyl unit, while the ^{31}P-NMR spectrum of this compound shows a single resonance at 70.6 ppm. As in the case for the 1:1 Mn–L^2 complex above, the coordination shift of 86.6 ppm here is significantly greater than for *fac*-[$MnCl(CO)_3(L^1)$] above (50 ppm) which has no five-membered chelate ring. No resonance was observed by ^{55}Mn-NMR for this compound, possibly due to slow tumbling of the large dimer molecules.

2.3. Comparisons and conclusions

These results show that a range of carbonyl complexes involving Group 6 and 7 elements may be obtained upon reaction with the related P_2O_2- and P_2S_2-donor ligands L^1 or L^2. While all of the complexes isolated involve phosphine coordination, the structures of the products are very dependent on the nature of the other donor atoms present in the ligand.

For L^1 we have obtained a new series of mononuclear products with coordination of L^1 occurring through the phosphine functions. In the low valent complexes the ethers essentially act as spacers, thus L^1 behaves as a long chain diphosphine ligand. With the 3d metals, Cr(0) and Mn(I), the thermodynamic products appear to be the *trans* (or *mer-trans* for Mn(I)) isomers. This illustrates the propensity for L^1 to function as a *trans* chelate and is consistent with earlier observations on a variety of other transition metal complexes e.g. with Ni(II) [8], Ag(I) and Au(I) [4,6] where *trans* L^1 coordination also occurs. With Mo(0) and W(0) *cis* P$_2$-coordination of L^1 is observed, giving rise to 11-membered ring metallocyclic products. These species probably represent kinetic products.

In contrast, L^2 readily forms both mono- and dinuclear complexes with Mn(I) and Mo(0). This is because both the phosphines and the thioethers can coordinate to the metal ion. Thus, the 1:1 Mn–L^2 species exists as a five-membered ring P,S-chelate complex (with the other S and P atoms uncoordinated), while the 1:1 Mo–L^2 species occurs as a mixture of the 11-membered ring P$_2$-chelate complex (with the thioethers uncoordinated) and the five-membered ring P,S-chelate. Formation of the P,S-chelate complexes with L^2 may be accounted for by the availability of the soft thioethers (compared to the hard ethers in L^1 which are not compatible with the soft metal ions) adjacent to the phosphines, both of which are suitable for coordination to the low valent metal centres, together with the extra stability associated with the five-membered chelate ring. Addition of a further equivalent of the metal precursor then gives the binuclear species *cis*-[$\{Mo(CO)_4\}_2(\mu^2\text{-}L^2)$] and *fac*-[$\{MnCl(CO)_3\}_2(\mu^2\text{-}L^2)$, each of which contain two five-membered chelate rings from P,S coordination to each metal centre.

3. Experimental

Infrared spectra were recorded in CH_2Cl_2 solution using a Perkin–Elmer 1710 FTIR over the range 2200–1700 cm^{-1} or as CsI discs over the range 4000–200 cm^{-1}. Mass spectra were run by fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) matrix on a VG Analytical 70-250-SE Normal Geometry Double Focusing Mass Spectrometer or by electrospray or atmospheric pressure chemical ionisation (APCI) in MeCN solution using a VG Biotech platform. ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Bruker AM300 spectrometer. $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$- and ^{55}Mn-NMR spectra were recorded in CH_2Cl_2 containing ca. 10–15% $CDCl_3$ using a Bruker DPX400 spectrometer operating at 161.98, 100.63 or 99.09 MHz, respectively and are referenced to external 85% H_3PO_4, Me_4Si or aqueous $KMnO_4$ ($\delta = 0$). [Cr(acac)$_3$] was added to the NMR solutions prior to recording $^{13}C\{^1H\}$-NMR spectra and a pulse delay of 2 s. was introduced to accommodate the long relaxation times. Microanalyses were obtained from the University of Strathclyde microanalytical service.

The ligands L^1 and L^2 were prepared by literature methods [4,14,15].

3.1. Preparations

3.1.1. trans-[Cr(CO)$_4$(L^1)]

To a degassed solution of L^1 (0.100 g, 0.206 mmol) in $C_6H_5CH_3$ (30 cm^3) was added [Cr(CO)$_4$(nbd)] (0.057 g, 0.206 mmol). The resulting solution was stirred at 40 °C for 48 h. The solution was then concentrated in vacuo to ca. 5 cm^3 and hexane (ca. 30 cm^3) was added to afford a pale yellow solid which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 40%. $^{31}P\{^1H\}$-NMR: δ 56.5 (s, L^1). ^1H-NMR: δ 7.1–7.7 (m, Ph, 20H), 3.3–3.5 (m, CH_2O, 8H), 2.7–2.9 (m, CH_2P, 4H). $^{13}C\{^1H\}$-NMR: 222.7 (poorly resolved t, CO), 128.7–141.2 (Ph), 70.8 (CH_2O), 67.1 (CH_2O), 33.8 (CH_2P). ν(CO) (CH_2Cl_2, cm^{-1}): 1877s. Repeated attempts to obtain satisfactory microanalytical data for this compound showed low %C, however, the compound has been spectroscopically characterised.

3.1.2. cis-[Mo(CO)$_4$(L^1)]

[Mo(CO)$_4$(nbd)] (0.062 g, 0.206 mmol) was added to a degassed solution of L^1 (0.100 g, 0.206 mmol) in $CHCl_3$ (25 cm^3). The reaction mixture was stirred at room temperature (r.t.) for ca. 18 h until solution IR spectroscopy showed that all of the starting material had been consumed. The solution was then evaporated to dryness in vacuo and redissolved in CH_2Cl_2. Hexane was then added to precipitate the product which was collected by filtration, washed with hexane and dried in vacuo. Yield: 53%. Calc. for [$C_{34}H_{32}MoO_6P_2$]·1/2CH_2Cl_2: C, 56.2; H, 4.7. Found: C, 56.7; H, 4.8%. Electrospray mass spectrum (MeCN): Found $m/z = 641$, 613, 487; Calc. for [^{98}Mo(CO)$_2$(L^1)]$^+$ $m/z = 640$, [^{98}Mo(CO)(L^1)]$^+$ $m/z = 612$, [L^1]$^+$ $m/z = 486$. ^1H-NMR: δ 7.3–7.6 (m, Ph, 20H), 3.7 (m, CH_2O, 4H), 3.5 (s, CH_2O, 4H), 2.6 (m, CH_2P, 4H). $^{31}P\{^1H\}$-NMR: δ 17.8 (s, L^1). $^{13}C\{^1H\}$-NMR: 215.8 (t, CO *trans* CO), 210.1 (dd, CO *trans* P), 128.7–136.7 (Ph), 70.1 (CH_2O), 67.2 (CH_2O), 33.1 (CH_2P). ν(CO) (CH_2Cl_2, cm^{-1}): 2022s, 1924s, 1903s, 1885sh. ν(CO) (CsI disk, cm^{-1}): 2020s, 1918s, 1903s, 1885sh.

3.1.3. cis-[W(CO)$_4$(L^1)]

To a solution of L^1 (0.100 g, 0.206 mmol) in degassed $CHCl_3$ (25 cm^3) was added [W(CO)$_4$(TMPA)] (0.089 g, 0.206 mmol). The resulting mixture was refluxed for 5 h and then concentrated in vacuo to ca. 5 cm^3. Hexane (ca. 30 cm^3) was added to afford a brown solid, which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 73%. Calc. for [$C_{34}H_{32}O_6P_2W$]·2CH_2Cl_2: C, 45.4; H, 3.8. Found: C, 45.7; H, 5.1%. APCI mass spectrum (MeCN): Found: $m/z = 726$, 669; Calc. for [^{183}W(CO)$_2$(L^1)]$^+$ $m/z = 725$, [^{183}W((L^1)]$^+$ $m/z = 669$. ^1H-NMR: δ 7.3–7.7 (*m*, Ph, 20H), 3.6 (m, CH_2O, 4H), 3.5 (s, CH_2O, 4H), 2.6 (m, CH_2P, 4H). $^{31}P\{^1H\}$-NMR: δ 3.9 (s, L^1, $^1J_{WP} = 232$ Hz). $^{13}C\{^1H\}$-NMR: 205.7 (t, CO *trans* CO), 203.5 (dd, CO *trans* P), 127.7–139.4 (Ph), 71.1 (CH_2O), 67.5 (CH_2O), 32.8 (CH_2P). ν(CO) (CH_2Cl_2, cm^{-1}): 2017s, 1916s, 1883sbr. ν(CO) (CsI disk, cm^{-1}): 2013s, 1905sh, 1883brs.

3.1.4. Mer-trans-[MnCl(CO)$_3$(L^1)]

To a solution of L^1 (0.320 g, 0.65 mmol) in degassed $CHCl_3$ (50 cm^3) in a foil-wrapped flask was added [MnCl(CO)$_5$] (0.150 g, 0.65 mmol). The reaction mixture was refluxed under N_2 for 48 h until the solution IR spectrum showed that all of the [MnCl(CO)$_5$] had been consumed and that there were no further changes in the ν(CO) region. The solution was then concentrated in vacuo to ca. 5 cm^3, and this was then added to ice-cold C_6H_{14} to afford a bright yellow solid which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 0.27 g, 63%. Calc. for [$C_{33}H_{32}ClMnO_5P_2$]: C, 60.0; H, 4.9. Found: C, 60.3; H, 4.7%. Electrospray mass spectrum (MeCN): Found $m/z = 625$, 597, 569, 541, 487; Calc. for [Mn(CO)$_3$(L^1)]$^+$ $m/z = 625$, [Mn(CO)$_2$(L^1)]$^+$ $m/z = 597$, [Mn(CO)(L^1)]$^+$ $m/z = 569$, [Mn(L^1)]$^+$ $m/z = 541$, [L^1]$^+$ $m/z = 486$. ^1H-NMR: δ 7.2–7.9 (br m, Ph, 20H), 3.4 (br m, CH_2O, 4H), 3.3 (br s, CH_2O, 4H), 2.9 (br m, CH_2P, 4H). $^{31}P\{^1H\}$-NMR: δ 44 (s, L^1, *mer-cis* isomer). ^{55}Mn-NMR: δ −1300 (br, $w_{1/2}$ ca. 19,000 Hz). $^{13}C\{^1H\}$-NMR: 211.7 (br, CO), 127.5–137.4 (Ph), 70.2 (CH_2O), 66.4 (CH_2O), 27.9 (CH_2P). ν(CO) (CH_2Cl_2, cm^{-1}): 2045m, 1949s, 1909m.

3.1.5. Fac-[MnCl(CO)$_3$(L^1)]

Method as above, except that the reaction was stirred at r.t. under N_2 for 2 h. The solvent was removed in vacuo and the residue was redissolved in CH_2Cl_2 and added to ice-cold C_6H_{14} to give a bright yellow solid. Yield: 51%. Required for [$C_{33}H_{32}ClMnO_5P_2$]·1/3CH_2Cl_2: C, 58.1; H, 4.8. Found: C, 58.0; H, 4.7%. ^1H-NMR: 7.3–7.7 (br m, Ph, 20H), 3.5 (br m, CH_2O, 4H), 3.4 (br s, CH_2O, 4H), 2.5 (br m, CH_2P, 4H). $^{31}P\{^1H\}$-NMR: 29.9 (s, L^1, *fac* isomer, major), 44 (s, L^1, *mer-trans* isomer, minor). ν(CO) (CH_2Cl_2, cm^{-1}): 2027s, 1957s, 1910s.

3.1.6. $[\mathrm{ReBr(CO)_3(L^1)}]$

To a degassed solution of L^1(0.100 g, 0.206 mmol) in $CHCl_3$ (30 cm^3) was added $[\mathrm{ReBr(CO)_5}]$ (0.08 g, 0.206 mmol). The resulting solution was refluxed for 24 h and then concentrated to ca. 5 cm^3 in vacuo. Ice-cold C_6H_{14} (50 cm^3) was then added to afford a cream/fawn solid which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 23%. Calc. for $[\mathrm{C_{33}H_{32}BrO_5P_2Re}]\cdot 2/3\mathrm{CHCl_3}$: C, 44.1; H, 3.6. Found: C, 44.0; H, 4.0%. FAB mass spectrum: Found $m/z = 729$, 727; Calc. for $[^{187}\mathrm{Re(CO)_2(L^1)}]^+$ $m/z = 729$, $[^{185}\mathrm{Re(CO)_2(L^1)}]^+$ $m/z = 727$. ^{1}H-NMR: δ 7.3–7.7 (br *m*, Ph, 20H), 3.5 (*m*, CH_2O, 4H), 3.4 (*m*, CH_2O, 4H), 2.5 (*m*, CH_2P, 4H). $^{31}P\{^1H\}$-NMR: δ -12.8 (s, L^1), -13.4 (s, L^1). IR spectrum (CsI disc): 2108m, 2036s, 1950s, 1910brs cm^{-1}.

3.1.7. $[\{\mathrm{MnCl(CO)_3}\}_2(\mu^2\text{-}\mathrm{L^2})]$

To a degassed solution of L^2 (0.200 g, 0.39 mmol) in CH_2Cl_2 (30 cm^3) in a foil-wrapped flask, was added $\mathrm{MnCl(CO)_5}$ (0.180 g, 0.77 mmol). The resulting solution was stirred for 4 h. The yellow solution was concentrated in vacuo to ca. 5 cm^3 and C_6H_{14} (50 cm^3) was then added, giving a yellow solid which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 61%. Calc. for $[\mathrm{C_{36}H_{32}Cl_2Mn_2O_6P_2S_2}]\cdot 1/2\mathrm{CH_2Cl_2}$: C, 48.2; H, 3.7. Found: C, 48.2; H, 4.0%. ^{1}H-NMR: δ 7.0–7.8 (br m, Ph, 20H), 2.5–3.4 (br m, CH_2, 12H). $^{31}P\{^1H\}$-NMR: δ 70.6 (s, L^2). $^{13}C\{^1H\}$-NMR: 221–218 (br, CO), 129.9–138.4 (Ph), 34.7, 31.9, 27.3 (CH_2). IR spectrum (CH_2Cl_2): 2033, 1950, 1921 cm^{-1}.

3.1.8. $[\mathrm{MnCl(CO)_3(L^2)}]$

As above but using a 1:1 ratio of $\mathrm{MnCl(CO)_5}$:L^2. Yellow solid. Yield: 59%. Calc. for $[\mathrm{C_{33}H_{32}ClMnO_3P_2S_2}]\cdot 1/2\mathrm{CH_2Cl_2}$: C, 54.7; H, 4.5. Found: C, 55.2; H, 4.7%. Electrospray mass spectrum (MeCN): Found $m/z = 693$, 657, 629; Calc. for $[\mathrm{Mn^{35}Cl(CO)_3(L^2)}]^+$ $m/z = 692$, $[\mathrm{Mn(CO)_3(L^2)}]^+$ $m/z = 657$, $[\mathrm{Mn(CO)_2(L^2)}]^+$ $m/z = 629$. ^{1}H-NMR: δ 7.1–7.8 (br m, Ph, 20H), 2.5–3.4 (br m, CH_2, 12H). $^{31}P\{^1H\}$-NMR: δ 70.9 (s, coordinated PPh_2 on L^2), -16.6 (s, uncoordinated PPh_2 on L^2). $^{13}C\{^1H\}$-NMR: 222, 218, 216 (br, CO), 129.2–138.4 (Ph), 38.5–23.0 (CH_2). ^{55}Mn-NMR: -700 ($w_{1/2}$ ca. 15,000 Hz). IR spectrum (CsI disc): 2032, 1957, 1919 cm^{-1}.

3.1.9. $[\{\mathrm{Mo(CO)_4}\}_2(\mathrm{L^2})]$

To a degassed solution of L^2 (0.100 g, 0.19 mmol) in CH_2Cl_2 (30 cm^3) was added $[\mathrm{Mo(CO)_4(nbd)}]$ (0.120 g, 0.40 mmol). The resulting solution was stirred for 12 h. The solution was then concentrated in vacuo to ca. 5 cm^3 and C_6H_{14} (30 cm^3) was added to afford a fawn coloured solid which was filtered, washed with C_6H_{14} and dried in vacuo. Yield: 52%. Calc. for $[\mathrm{C_{38}H_{32}Mo_2O_8P_2S_2}]$: C, 48.8; H, 3.5. Found: C, 49.6; H, 3.6%. ^{1}H-NMR: δ 7.3–7.7 (br m, Ph, 20H), 3.1 (s, SCH_2CH_2S, 4H), 2.9 (m, CH_2, 4H), 2.5 (m, CH_2, 4H). $^{31}P\{^1H\}$-NMR: δ 53.0 (s, L^2). $^{13}C\{^1H\}$-NMR: 217.3 (d, 7 Hz, $CO_{\mathrm{trans\ S}}$), 215.1 (d, 28 Hz, $CO_{\mathrm{trans\ P}}$), 206.9 (d, 9 Hz, $CO_{\mathrm{trans\ CO}}$), 134.8–128.0 (Ph), 39.2 (s, SCH_2CH_2S), 34.7 (d, 15 Hz, SCH_2CH_2P), 26.2 (d, 23 Hz, PCH_2). IR spectrum (CsI disc): 2033, 1950, 1921 cm^{-1}.

3.1.10. $[\mathrm{Mo(CO)_4(L^2)}]$

Method as above but using a 1:1 $[\mathrm{Mo(CO)_4(nbd)}]$–L^2 ratio. Fawn coloured solid. Yield: 57%. Calc. for $[\mathrm{C_{34}H_{32}MoO_4P_2S_2}]1/4\mathrm{CH_2Cl_2}$: C, 55.0; H, 4.4. Found: C, 54.9; H, 4.6%. ^{1}H-NMR: δ 7.3–7.7 (br m, Ph, 20H), 2.1–2.7 (br m, CH_2, 12H). $^{31}P\{^1H\}$-NMR: δ 26.2 (s, coordinated PPh_2 in P_2-chelating L^2), +52.9 (s, coordinated PPh_2 in P,S-chelating L^2), -16.6 (s, uncoordinated PPh_2 on P,S-chelating L^2). $^{13}C\{^1H\}$-NMR: 217.5 (d, 7 Hz, $CO_{\mathrm{trans\ S}}$, P,S-chelate), 215.0 (d, 28 Hz, $CO_{\mathrm{trans\ P}}$ in P,S chelate), 214.8 (poorly resolved dd, $CO_{\mathrm{trans\ P}}$ in P_2 chelate), 209.0 (poorly resolved t, $CO_{\mathrm{trans\ CO}}$ in P_2-chelate), 207.2 (d, 9 Hz, $CO_{\mathrm{trans\ CO}}$ in P,S chelate), 136.2–128.9 (Ph), 41.9–26.7 (CH_2). IR spectrum (CH_2Cl_2): 2022s, 1918 sh, 1908s, 1881s cm^{-1}.

4. X-Ray crystallography

Details of the crystallographic parameters are given in Table 2. Crystals of $[\mathrm{Mo(CO)_4(L^1)}]$ were grown by vapour diffusion of diethyl ether onto a solution of the complex in CH_2Cl_2 at ca. -15 °C. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems open-flow cryostat operating at 150 K, using graphite-monochromated Mo–K_α X-radiation ($\lambda = 0.71073$ Å). Structure solution and refine-

Table 2
Crystallographic parameters

Complex	*cis*-$[\mathrm{Mo(CO)_4(L^1)}]$
Empirical formula	$C_{34}H_{32}MoO_6P_2$
Formula weight	694.51
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	15.776(4)
b (Å)	12.543(3)
c (Å)	16.296(3)
β (°)	102.28(2)
U (Å^3)	3150(1)
Z	4
μ(Mo–K_α) (cm^{-1})	5.47
Unique observed reflections	5833
Observed reflections with $[I_o > 2\sigma(I_o)]$	3885
R	0.038
R_w	0.047

$R = \Sigma\ (|F_{obs}|_i - |F_{calc}|_i)/\Sigma\ |F_{obs}|_i$;
$R_w = ([\Sigma\ w_i(|F_{obs}|_i - |F_{calc}|_i)2/\Sigma\ w_i|F_{obs}|_i^2)^{1/2}$.

ment were routine [16,17]. Selected bond lengths and angles are given in Table 1.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 179097 for compound *cis*-[Mo(CO)$_4$(L^1)]. 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).

Acknowledgements

We thank the EPSRC for support.

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