Two different types of 2-thienyl bridge in dinuclear manganese and rhenium compounds

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Thermal and photochemical reactions of diphenyl-2-thienylphosphine (L) with $[Mn_2(CO)_{10}]$ gave simple substitution products $[Mn_2(CO)_{10-n}L_n]$ **1** ($n = 1$) and **2** ($n = 2$) with ligand L co-ordinated through the phosphorus atom. Under forcing conditions (refluxing xylene) oxidative addition with P–C cleavage occurred to give the μ-2-thienyl complex $[Mn_2(CO)_6(μ\text{-}PPh_2)(μ\text{-}η^1:η^5\text{-}C_4H_3S)]$ **3**. Loss of CO and P–C bond cleavage do not occur so easily in the case of $[Re_2(CO)_{10}]$. UV Treatment of the rhenium carbonyl with L gave $[Re_2(CO)_8(μ\text{-}P,S\text{-}Ph_2PC_4H_3S)]$ **4**, in which the ligand L is bridging through the two heteroatoms. Oxidative addition occurs internally at about 180° in decane with rupture of a P–C bond to produce an isomer of **4**, $[Re_2(CO)_8(μ\text{-}PPh_2)(μ\text{-}η^1:η^1\text{-}C,S\text{-}C_4H_3S)]$ **5**. Crystal structures revealed a novel form of bridging of L co-ordinated through *P* and *S* in **4** and two different modes of 2-thienyl bridge (μ-$η^2$:$η^5$ and μ-$η^1$:$η^1$-*C,S*) in **3** and **5** respectively. With the previously known μ-$η^1$:$η^2$-bridging form of thienyl, these new compounds **3** and **5** provide three distinct type of thienyl bridge. The type of bridge which is formed depends upon the electronic requirements of the metal atoms and the span between them.

Studies on the co-ordination of thiophene, spurred by a need to provide chemical background to the hydrodesulfurisation (HDS) process,[1] have led to the discovery of a range of co-ordination types for thiophene and its substituted derivatives at a single metal atom. Examples of these different modes are found in $[Re(η^1\text{-}S\text{-}C_4H_4S)(Cp^*)(CO)_2]$,[2] $[Cr(η^5\text{-}C_4H_4S)(CO)_3]$,[3] $[Rh(η^5\text{-}C_4H_4S)(PPh_3)_2]^+$,[4] $[Ir(η^4\text{-}2,5\text{-}Me_2C_4H_2S)(Cp^*)]$,[5] and $[Os(η^2\text{-}C_4H_4S)(NH_3)_5]^{2+}$.[6] In some cases equilibria between isomers with different modes of thiophene co-ordination are possible.[7] Thus $[Re(C_8H_6S)(Cp^*)(CO)_2]$, where C_8H_6S is benzothiophene, has isomers in solution involving $η^1$-*S* and $η^2$ co-ordination.[8]
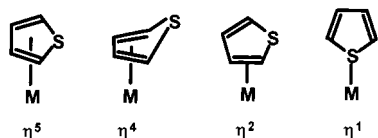
Thiophene can also undergo oxidative addition at an unsaturated metal centre M with ring-opening C–S bond cleavage to give a metallocycle or with C-H cleavage to give a hydrido(2-thienyl) complex (Scheme 1). Therefore 2-thienyl lig-
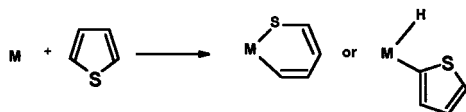
Scheme 1 Oxidative addition reactions of thiophene.

ands may be formed directly from thiophene by C–H cleavage.[9] In this study we have used oxidative addition of diphenyl-2-thienylphosphine ($Ph_2PC_4H_3S$) as a route to 2-thienyl ligands by P–C cleavage. It has been possible for us to synthesize and characterise two forms of thienyl bridge in dimanganese and dirhenium compounds. Recently we reported that the treatment of diphenyl-2-thienylphosphine with $[Ru_3(CO)_{12}]$ gave, in

addition to simple substitution compounds with the ligand co-ordinated through phosphorus as in other compounds of this ligand,[10] the products of C–H cleavage at the thiophene ring, namely $[Ru_3H(μ_3\text{-}Ph_2PC_4H_2S)(CO)_9]$ and $[Ru_3H(μ_3\text{-}Ph_2P\text{-}C_4H_2S)(CO)_8(Ph_2PC_4H_3S)]$.[11] The oxidative addition occurs *via* C–H rather than P–C cleavage. However, P–C cleavage can occur subsequently and the cluster $[Ru_3H(μ_3\text{-}Ph_2PC_4H_2S)\text{-}(CO)_9]$ reacts at higher temperatures with an excess of $[Ru_3(CO)_{12}]$ to give the thiophyne cluster $[Ru_4(μ_4\text{-}PPh)(μ_4\text{-}C_4H_2S)\text{-}(CO)_{11}]$. In reactions of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$, C–H bond cleavage predominates over other types of oxidative addition, whereas with $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ this is not usually the case. Therefore we have studied the reactions of diphenyl-2-thienylphosphine with these dinuclear compounds expecting P–C cleavage to occur to give 2-thienyl complexes and indeed have been able to characterise two dinuclear complexes containing $2\text{-}C_4H_3S$ bridges, but differences are observed between the chemistry of these two metals.

Results and discussion

The reaction of $[Mn_2(CO)_{10}]$ with an equimolar quantity of $Ph_2P(2\text{-}C_4H_3S)$ was carried out thermally in refluxing xylene. Little reaction occurred in refluxing solvents at lower temperatures. In addition to the simple substitution product $[Mn_2\text{-}(CO)_9\{Ph_2P(2\text{-}C_4H_3S)\}]$ **1** (40%), we obtained another product which we have characterized as $[Mn_2(CO)_6(μ\text{-}PPh_2)(μ\text{-}η^1:η^5\text{-}2\text{-}C_4H_3S)]$ **3** (20%). Compound **1** is a precursor of **3** and we have shown in a separate experiment that it converts into **3** in refluxing xylene. Compound **1** was straightforwardly identified as a simple monodentate tertiary phosphine derivative of $[Mn_2\text{-}(CO)_{10}]$ by comparison of its spectroscopic data with those of other compounds of the type $[Mn_2(CO)_9L]$.[12] Apart from the C–H cleavage chemistry we reported for $Ph_2P(2\text{-}C_4H_3S)$ with $[Ru_3(CO)_{12}]$,[11] the ligand was only known previously to behave as a simple monodentate through the P atom with no evidence for sulfur co-ordination or any type of ligand transformation.[10] Compound **1** clearly has the ligand co-ordinated through
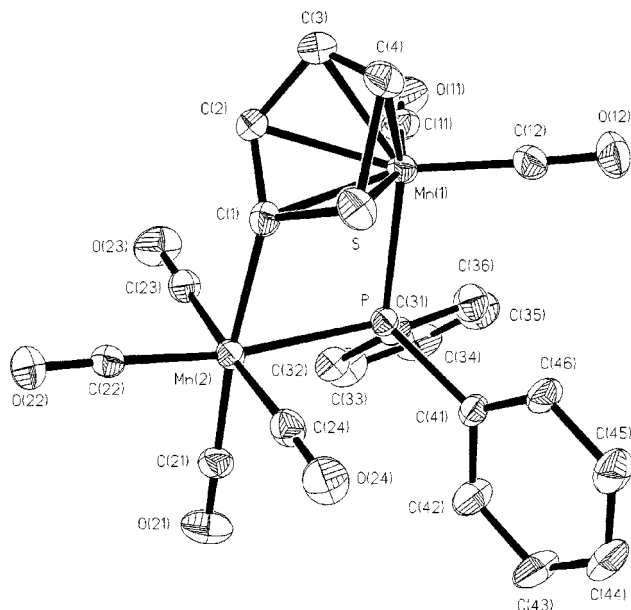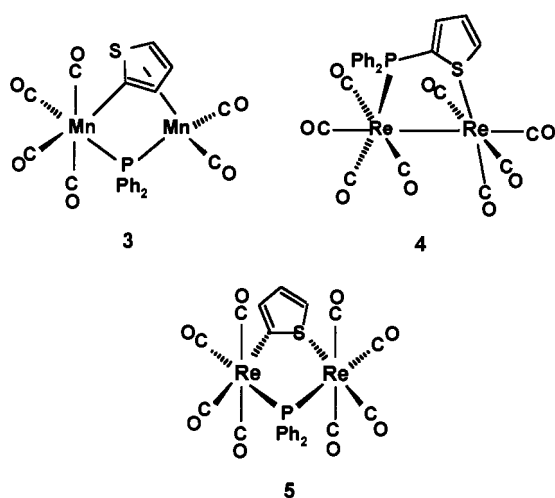
Fig. 1 Molecular structure of $[Mn_2(CO)_6(PPh_2)(C_4H_3S)]$ **3**.

3

4

5

Table 1 Selected bond lengths (Å) and angles (°) for compound **3**

Mn(1)–C(11)	1.777(3)	Mn(1)–C(12)	1.783(3)
Mn(1)–C(4)	2.130(3)	Mn(1)–C(3)	2.148(3)
Mn(1)–C(2)	2.174(3)	Mn(1)–C(1)	2.182(2)
Mn(1)–P	2.2929(8)	Mn(1)–S	2.3069(8)
Mn(2)–C(21)	1.819(3)	Mn(2)–C(22)	1.830(3)
Mn(2)–C(24)	1.842(3)	Mn(2)–C(23)	1.842(3)
Mn(2)–C(1)	2.079(2)	Mn(2)–P	2.3746(8)
S–C(4)	1.71(3)	S–C(1)	1.760(3)
C(1)–C(2)	1.409(4)	C(2)–C(3)	1.439(4)
C(3)–C(4)	1.380(5)		
C(1)–Mn(1)–P	75.65(7)	C(1)–Mn(2)–P	75.81(7)
Mn(1)–P–Mn(2)	97.32(3)	Mn(2)–C(1)–Mn(1)	110.66(11)
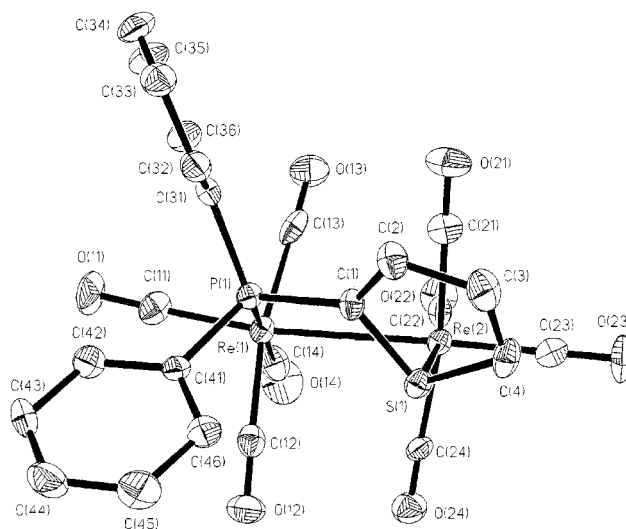
Fig. 2 Molecular structure of $[Re_2(CO)_8(PPh_2C_4H_3S)]$ **4**.

ation of the compound $[(OC)_3Mn(\mu-\eta^1:\eta^5-2-C_4H_3S)Cr(CO)_5]$ involves an interesting *trans*-metallation. The lithiated complex $[Cr(CO)_3(\eta^5-2-LiC_4H_3S)]$ reacts with $[MnCl(CO)_5]$ to give $[(OC)_3Cr(\mu-\eta^1:\eta^5-2-C_4H_3S)Mn(CO)_5]$ which isomerizes to the compound $[(OC)_3Mn(\mu-\eta^1:\eta^5-2-C_4H_3S)Cr(CO)_5]$ by CO transfer and an interchange of the η^1 and η^5 co-ordination between the two metal atoms.[13]

The ligand rupture might have been induced photochemically but treatment of $[Mn_2(CO)_{10}]$ with $Ph_2P(2-C_4H_3S)$ under UV irradiation gave only substitution derivatives: compound **1** and $[Mn_2(CO)_8\{Ph_2P(2-C_4H_3S)\}_2]$ **2**, which are closely comparable to the PPh_3 analogues.[12] No ligand cleaved products were obtained and none with bridging $Ph_2P(2-C_4H_3S)$ as for rhenium (see below).

UV Irradiation of a solution of $[Re_2(CO)_{10}]$ and $Ph_2P-(2-C_4H_3S)$ (1:1 mol ratio) in toluene resulted in a change from colourless to pale yellow over 5 h. Some starting materials were recovered but there was also a 32% yield of the yellow compound $[Re_2(CO)_8\{\mu-Ph_2P(2-C_4H_3S)\}]$ **4**. The IR $\nu(CO)$ spectrum is very similar to that of a complex we have obtained from $[Mn_2(CO)_{10}]$ with diphenyl-2-pyridylphosphine, namely $[Mn_2(CO)_8\{\mu-P,N-Ph_2P(2-C_5H_4N)\}]$ **6**, which was shown to contain the pyridylphosphine ligand bridging the two manganese atoms.[14] Spectroscopic data for **4** support the intact bridging nature of the thienylphosphine. The ^1H and ^{13}C-$\{^1H\}$ NMR spectra show ^{31}P coupling to the ^1H and ^{13}C nuclei of the thienyl group consistent with there being no fragmentation of the ligand and chemical shifts of the thienyl group are consistent with σ bonding through sulfur rather than π thienyl co-ordination. The crystal structure (Fig. 2) confirms these deductions. Selected bond lengths and angles are given in Table 2. The *P,S* co-ordinated bridge spans the Re–Re bond [3.0428(9) Å] with a torsional angle P(1)Re(1)Re(2)S(1) of 28.4°. The complex adopts therefore a conformation between staggered and

phosphorus since the NMR signals of the thienyl group are only very slightly shifted from those of the "free" ligand.

The product **3**, derived by decarbonylation of **1**, has a very different NMR spectrum. The three ^1H NMR signals for the thienyl group show only small residual coupling to phosphorus (just detected for the 5-H signal), indicating a separation of the PPh_2 and thienyl groups. Furthermore the ^1H NMR shifts of these signals (δ 6.15, 5.83 and 5.75) seem to indicate π complexation of the thienyl ring. The structure of **3** was determined by X-ray diffraction (Fig. 1) and selected bond lengths and angles are given in Table 1. The complex contains no Mn–Mn bond [Mn(1)···Mn(2) 3.505(1) Å], and the $Mn(CO)_4$ and $Mn(CO)_2$ units are bridged by 2-thienyl and diphenylphosphido groups. Each metal can be regarded as an 18-electron atom if the thienyl donates one electron to Mn(2) and six electrons to Mn(1), while the phosphido bridge donates one electron to Mn(1) and two electrons to Mn(2). This interpretation is supported by the different Mn–P distances [Mn(1)–P 2.2929(8) and Mn(2)–P 2.3746(8) Å]. The thienyl ligand is η^5 co-ordinated to Mn(1) with Mn(1)-C distances in the same small range, 2.130(3) to 2.182(3) Å. As expected these distances are longer than the σ Mn–C bond length [Mn(2)–C(1) 2.079(2) Å]. The five-membered ring is approximately planar except that the sulfur atom is 0.117 Å out of the plane of the four carbon atoms. The atom Mn(2) lies out of the thienyl plane by 0.653 Å. There are other examples of this type of thienyl bridge. The form-
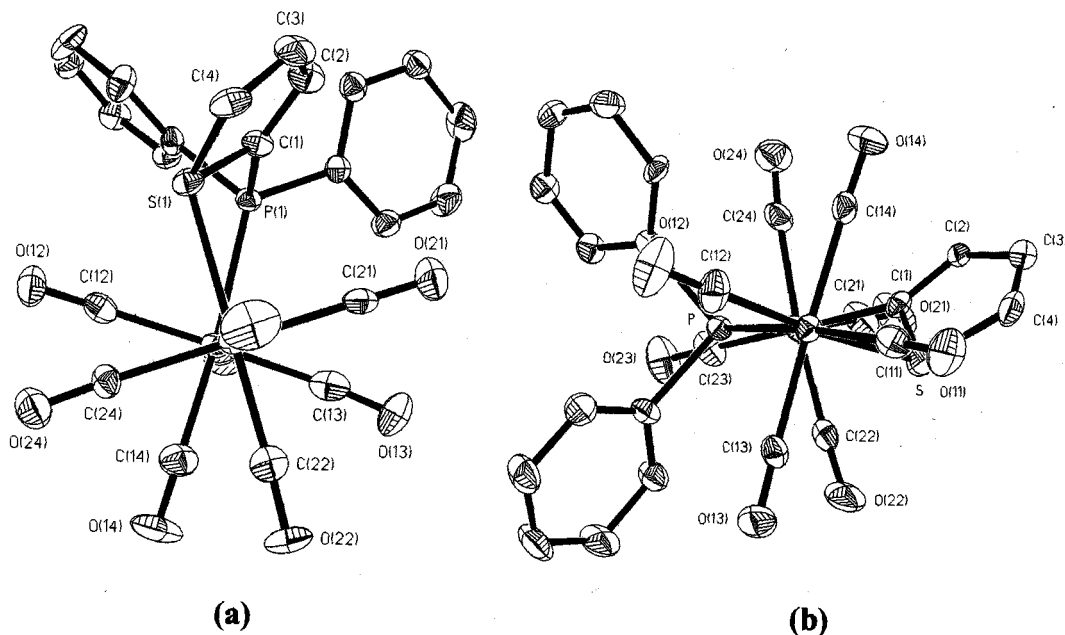
Fig. 3 Views down the Re–Re axes in compounds **4** (a) and **5** (b) showing a conformation between eclipsed and staggered in each.

Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

Re(1)–C(11)	1.903(12)	Re(1)–C(12)	1.958(12)
Re(1)–C(13)	1.969(14)	Re(1)–C(14)	1.949(13)
Re(1)–P(1)	2.435(2)	Re(1)–Re(2)	3.0428(9)
Re(2)–C(21)	1.991(12)	Re(2)–C(22)	1.894(12)
Re(2)–C(23)	1.905(12)	Re(2)–C(24)	1.979(11)
Re(2)–S(1)	2.473(3)	S(1)–C(1)	1.744(10)
S(1)–C(4)	1.746(11)	C(1)–C(2)	1.33(2)
C(2)–C(3)	1.43(2)	C(3)–C(4)	1.36(2)
P(1)–Re(1)–Re(2)	89.72(6)	S(1)–Re(2)–Re(1)	83.67(7)
C(1)–S(1)–Re(2)	106.5(3)	C(4)–S(1)–Re(2)	113.2(4)
C(31)–P(1)–C(1)	103.6(5)	C(31)–P(1)–C(41)	100.5(4)
C(1)–P(1)–C(41)	103.2(5)	C(31)–P(1)–Re(1)	120.6(4)
C(1)–P(1)–Re(1)	112.4(3)	C(41)–P(1)–Re(1)	114.4(3)

eclipsed, Fig. 3(a). This twist is compatible with a pyramidal S atom; indeed the geometry of the thienylphosphine bridge probably controls this torsional angle. The pyramidal S atom implies a stereochemically active lone pair at the sulfur atom, which is consistent with known geometries of *S*-bonded thiophene.[1,2] NMR Spectra of solutions of **4** show the equivalence of the Ph groups even at −85 °C and therefore there must be rapid enantiomerization by inversion at sulfur with coupled rotation about the Re–Re axis even at this low temperature. The structure allows a comparison between the *trans* influences of the tertiary phosphine and thiophene components of the ligand. The distance Re(1)–C(14) [1.949(13) Å] (*trans* to phosphorus) is longer than Re(2)–C(22) [1.894(12) Å] (*trans* to sulfur), consistent with a higher *trans* influence of the phosphine, although, as might be expected, the longest Mn–CO distances are those associated with the mutually *trans*-CO ligands. The Re(1)–P(1) distance [2.435(2) Å] is slightly shorter than Re(2)–S(1) [2.473(3) Å] and indicates a stronger phosphorus than sulfur co-ordination.

Diphenyl-2-thienylphosphine does not react thermally with [Re₂(CO)₁₀] to give compound **4**. Rather harsh conditions are required to get any reaction at all but in refluxing decane (180 °C) reaction occurs to give only one isolable product, compound **5**, which is an isomer of **4**. This was characterized as [Re₂(CO)₈(μ-PPh₂)(μ- η¹:η¹-*C,S*-2-C₄H₃S)], mainly by X-ray diffraction (Fig. 4). Selected bond lengths and angles are given in Table 3. The structure is made up of two Re(CO)₄ units bridged by two 3-electron donating bridges, the 2-thienyl and diphenylphosphide ligands. The isomerisation of **4** to **5** leads to
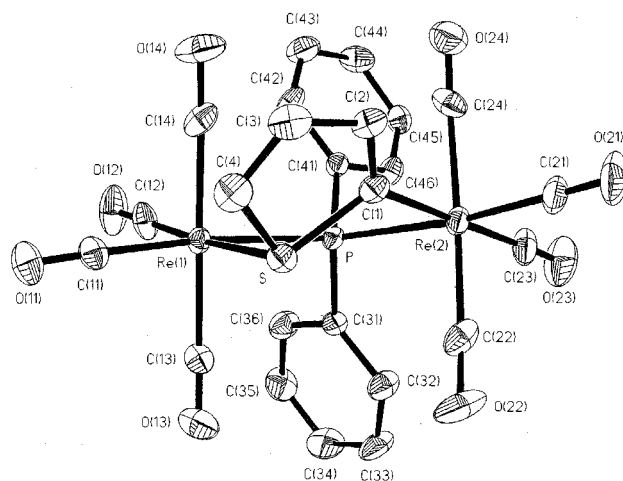

Fig. 4 Molecular structure of [Re₂(CO)₈(PPh₂)(C₄H₃S)] **5**.

Table 3 Selected bond lengths (Å) and angles (°) for compound **5**

Re(1)–C(11)	1.944(12)	Re(1)–C(12)	1.90(2)
Re(1)–C(13)	1.984(12)	Re(1)–C(14)	1.987(13)
Re(1)–S	2.481(3)	Re(1)–P	2.541(3)
Re(2)–C(21)	1.961(13)	Re(2)–C(22)	1.97(2)
Re(2)–C(23)	1.972(13)	Re(2)–C(24)	2.021(13)
Re(2)–C(1)	2.160(11)	Re(2)–P	2.522(3)
S–C(4)	1.739(13)	S–C(1)	1.781(11)
C(1)–C(2)	1.34(2)	C(2)–C(3)	1.44(2)
C(3)–C(4)	1.33(2)		
S–Re(1)–P	85.52(9)	C(1)–Re(2)–P	86.5(3)
C(4)–S–C(1)	94.5(6)	C(4)–S–Re(1)	109.5(5)
C(1)–S–Re(1)	106.2(4)	S–C(1)–Re(2)	118.6(6)
Re(2)–P–Re(1)	113.43(10)		

the cleavage of a P–C as well as a Re–Re bond; the Re · · · Re distance of 4.231(1) Å is much longer than a bonding distance.

The thienyl bridge is bonded through a σ-Re(2)–C(1) bond [2.160(11) Å] and a σ-Re(1)–S bond [2.481(3) Å], a little longer than that in compound **4**. The pyramidal nature of the sulfur atom makes the phenyl groups non-equivalent by destroying a plane of symmetry through the 5-membered Re₂SC(1)P ring. The ¹³C{¹H} NMR spectrum at room temperature confirms the non-equivalence of the Ph groups (two sets of *ipso*, *ortho*,
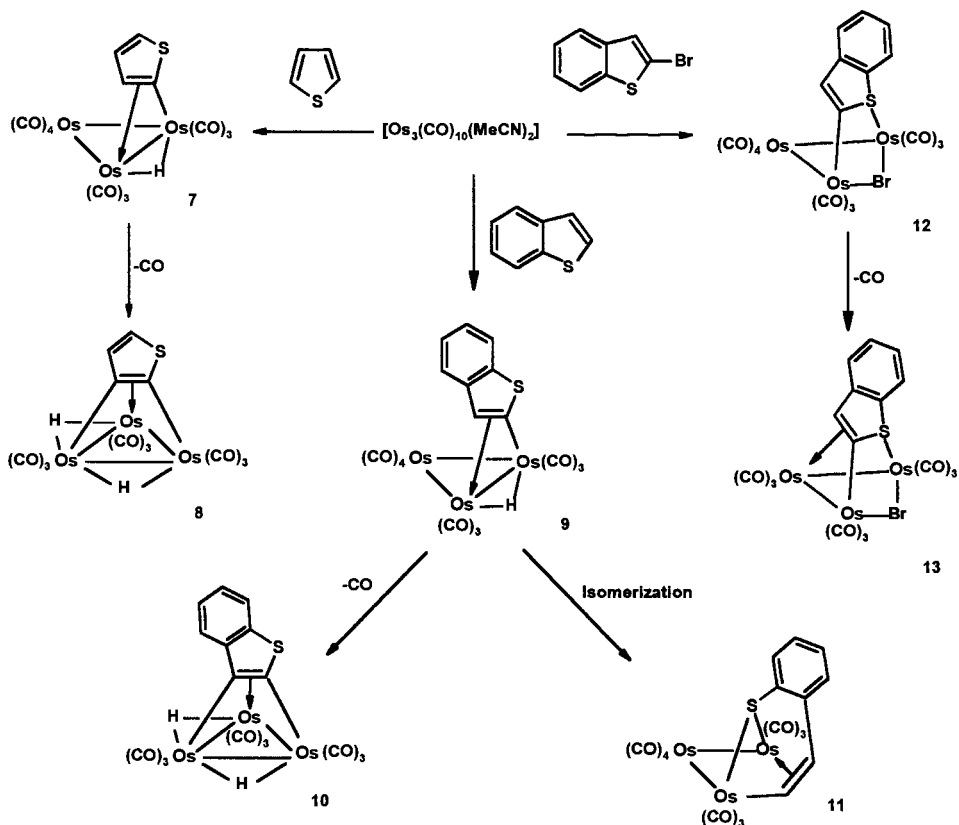
Scheme 2 Transformations of thiophene, benzothiophene and 2-bromobenzothiophene.

meta and *para* Ph signals are observed). The CO signals were very broad at room temperature but sharpened at −50 °C to give a series of doublets: all eight CO signals were resolved apart from one accidental overlap. The molecule is non-fluxional at −50 °C. The broadening of CO signals between −50 °C and room temperature surprisingly does not appear to involve dynamic exchange of Ph groups and therefore inversion at sulfur is not so facile as for compound **4**. This is the first example of this mode of bonding for thienyl, although the benzothienyl compound $[Os_3(\mu\text{-Br})(\mu\text{-}C_8H_5S)(CO)_{10}]$ involves similar co-ordination.[15] Scheme 2 shows the reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with thiophene, benzothiophene and 2-bromobenzothiophene to give products **7** to **13**. Initially the C–H or C–Br bond at the 2 position is cleaved in each case. With benzothiophene a subsequent isomerization of **9** occurs to give a ring-opened product **11**. Decarbonylations of **7** and **9** lead to further H-atom transfer to give μ_3-thiophyne **8** and benzothiophyne **10** systems, whereas a μ_3-S-bonded benzo-thienyl ligand is formed in **13** on decarbonylation of **12**. Recently we reported the reactions of 2-(methylthio)thiophene with $[Os_3(CO)_{10}(MeCN)_2]$.[16] Various products were obtained including the oxidative addition compound **14**, which was assigned the structure shown in Scheme 3 on the basis of
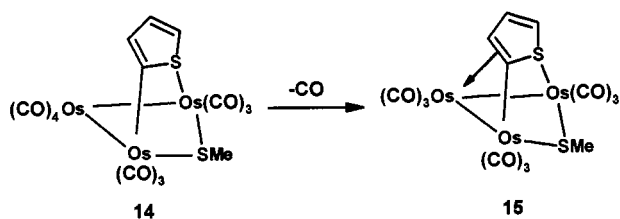
Scheme 3 Conversion of μ-C,S-thienyl into μ_3-thienyl ligands.

comparison with cluster **12** of Adams and Qu.[15] Decarbonyl-ation of **14** gives **15** containing μ_3-thienyl corresponding to compound **13**.

As a result of these studies of ours and those of Adams and
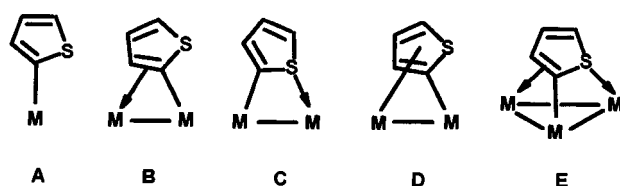

Qu[15] a range of thienyl co-ordination modes has been charac-terised. Terminal thienyl **A** is known in a number of systems.[13,17]

There are three distinct types of doubly bridging thienyl, **B** to **D**. All known examples of μ-η^2-thienyl[18] involve M–M bonded systems where the metal–metal distance is below 3 Å. Where there is no metal–metal bond or when the distance is above 3 Å for whatever reason, it becomes increasingly difficult for the thienyl to bridge in this way and instead the S-bonded mode **C** occurs. For example, in $[Os_3(\mu\text{-H})(\mu\text{-MeC}_4H_2S)(CO)_{10}]$ mode **B** is associated with a bridged Os–Os distance of 2.816(2) Å[18] whereas in $[Os_3(\mu\text{-Br})(\mu\text{-}C_8H_5S)(CO)_{10}]$ mode **C** is found with a bridged Os–Os distance of 3.742(1) Å.[15] In compound **5** the Re···Re distance is 4.231(1) Å and mode **C** is adopted as expected. One would predict that at some intermediate M–M distance modes **B** and **C** would be finely balanced and isomeric forms might exist. We have proposed that the rapid interconver-sion of the *exo* and *endo* isomers of $[Os_3(\mu\text{-H})(\mu\text{-}C_4H_3S)(CO)_{10}]$ (mode **B**) involves an intermediate with C,S co-ordination (form **C**).[18] The corresponding furyl complex is non-dynamic, consistent with the relative inaccessibility of the oxygen analogue of mode **C** with soft metal atoms. In contrast, the lack of dynamic behaviour associated with the μ-thienyl ligand in **5** indicates that mode **B** is inaccessibly high in energy with respect to **C** in that case. Mode **D** is favoured when a 7-electron donor bridge is required as in compound **3**.

Conclusion

Products formed by the treatment of $[M_2(CO)_{10}]$ (M = Mn or Re) with diphenyl-2-thienylphosphine contain *P*-bonded
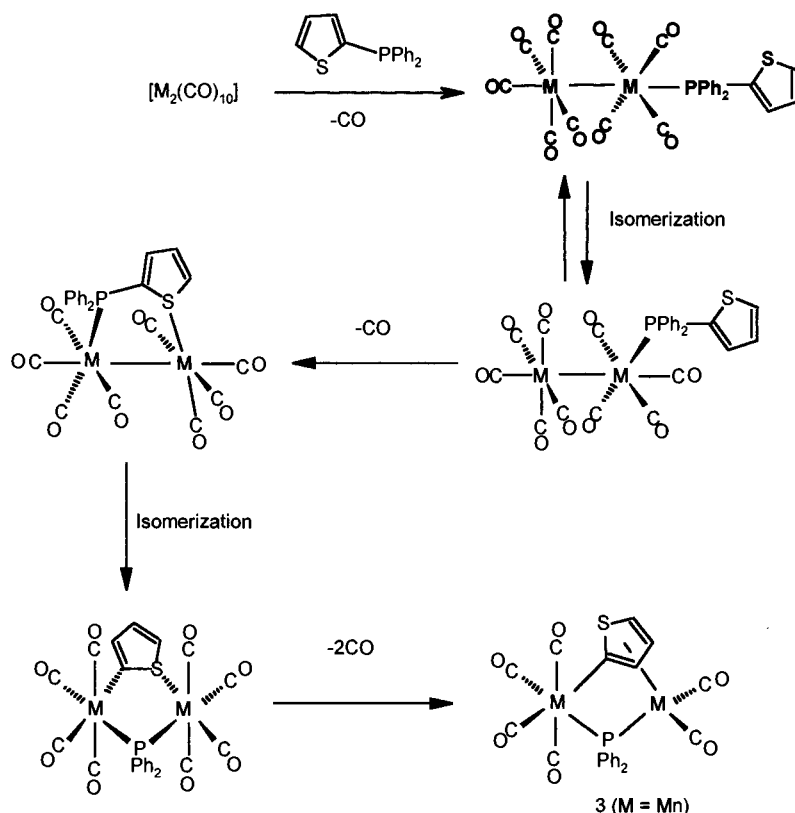
Scheme 4 Probable route for the formation of complex **3** *via* intermediates analogous to those characterised for M = Re.

Ph₂PC₄H₃S, μ-*S*,*C*-thienyl and μ-η¹:η⁵ thienyl ligands. It has not been possible to establish a complete scheme for the formation of these systems for both manganese and rhenium. However, it is reasonable to propose a route for formation of $[Mn_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^5\text{-}C_4H_3S)]$ **3** based on the assumption that manganese intermediates closely related to isolated rhenium compounds are involved. On this basis we propose the route given in Scheme 4. The greater strength of Re–CO and Re–Re bonds relative to the corresponding manganese values allows the isolation of complexes **4** and **5** but prevents the formation of the rhenium analogue of **3**.

Experimental

Diphenyl-2-thienylphosphine was prepared as reported by treating chlorodiphenylphosphine (from Avocado) with 2-lithiothiophene.[19] All UV irradiations (medium-pressure mercury lamp) were carried out in Pyrex vessels with water-cooled apparatus. The carbonyls $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ were used as supplied by Strem Chemicals.

Thermal treatment of [Mn₂(CO)₁₀] with diphenyl-2-thienylphosphine

A solution of $[Mn_2(CO)_{10}]$ (0.168 g, 0.430 mmol) and Ph₂-P(2-C₄H₃S) (0.124 g, 1.0 mol per mol metal carbonyl) in xylene (20 cm³) was heated under reflux under nitrogen for 10 h. The IR spectrum of the solution, recorded periodically, showed essentially complete conversion of the parent carbonyl after 10 h. The solvent was removed under reduced pressure to give an orange-brown solid which was separated by TLC [SiO₂; eluent, hexane–dichloromethane (5:2 v/v)] to give three bands. The first yellow band yielded a trace of starting carbonyl compound. The second yellow band gave $[Mn_2(CO)_9\{Ph_2P(2\text{-}C_4H_3S)\}]$ **1** as a yellow solid (0.109 g, 40%) (Found: C, 48.1; H, 2.95; S, 4.9. C₂₅H₁₃Mn₂O₉PS requires C, 47.65; H, 2.1; S, 5.1%). $\tilde{v}(CO)/cm^{-1}$ (cyclohexane): 2093m, 2013m, 1995vs, 1974m, 1963vw and 1941s. ³¹P-{¹H} NMR (CDCl₃): δ 65.5 (s). The

¹H and ¹³C NMR spectra are broad. An orange-yellow band gave $[Mn_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^5\text{-}2\text{-}C_4H_3S)]$ **3** as orange-yellow crystals (0.047 g, 20%) (Found: C, 48.2; H, 2.6; P, 5.6; S, 5.4. C₂₂H₁₃Mn₂O₆PS requires C, 48.4; H, 2.4; P, 5.7; S, 5.9%). $\tilde{v}(CO)/cm^{-1}$ (cyclohexane): 2067s, 1991m, 1978s, 1970s, 1959s and 1922s. ¹H NMR (CDCl₃, 293 K, 400 MHz): phenyl, δ 7.75 (m, *ortho*), 7.58 (m, *ortho*), 7.22–7.37 (m, *meta*, *para*); thienyl, 6.15 (dd, H⁵, J_{HH} = 3.1, J_{PH} = 2.4), 5.83 (d, H³, J_{HH} = 3.1) and 5.75 (dd, H⁴, J_{HH} = 3.1 Hz). ³¹P-{¹H} NMR (CDCl₃): δ −25.7 (s). ¹³C-{¹H} NMR: phenyl, δ 134.2 (d, *J* = 9.2, *ortho*), 133.1 (d, *J* = 9.5, *ortho*), 128.6 (d, *J* = 2.2, *para*), 128.1 (d, *J* = 9.1, *meta*), 127.8 (d, *J* = 3.1, *para*), 127.7, (*J* = 8.6 Hz, *meta*) (*ipso* signals unobserved); thienyl, 105.3 (d, *J* = 2.1 Hz), 98.1 (s) and 97.1 (s) (CO signals unobserved). The parent molecular ion was observed in the EI MS.

Photochemical treatment of [Mn₂(CO)₁₀] with diphenyl-2-thienylphosphine

A stirred solution of $[Mn_2(CO)_{10}]$ (0.188 g, 0.476 mmol) and Ph₂P(2-C₄H₃S) (0.141 g, 1.0 mol per mol metal carbonyl) in toluene (100 cm³) was UV photolysed under nitrogen for 10 h. The IR spectrum showed almost complete reaction after that time. Solvent was removed under reduced pressure to yield an orange-brown solid. TLC separation [SiO₂; eluent, hexane–dichloromethane (5:2 v/v)] gave three bands yielding traces of $[Mn_2(CO)_{10}]$, $[Mn_2(CO)_9\{Ph_2P(2\text{-}C_4H_3S)\}]$ **1** as an orange solid (0.143 g, 47%) and $[Mn_2(CO)_8\{Ph_2P(2\text{-}C_4H_3S)\}_2]$ **2** as an orange solid (0.082 g, 19%) (Found: C, 52.4; H, 3.3; P, 6.3; S, 6.7. C₄₀H₂₆Mn₂O₈P₂S₂ requires C, 55.2; H, 3.0; P, 7.1; S, 7.4%). $\tilde{v}(CO)/cm^{-1}$ (cyclohexane): 1995vs and 1963vs. The parent molecular ion was observed in EI MS.

Thermolysis of [Mn₂(CO)₉{Ph₂P(2-C₄H₃S)}] 1

A stirred solution of compound **1** (0.031 g, 0.05 mmol) in xylene (8 cm³) was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure from the solution to give an orange solid. TLC separation [SiO₂; eluent, hexane–

Table 4 Crystal data and structure solution refinement parameters for the compounds **3**, **4** and **5**[a]

	3	**4**	**5**
Formula	$C_{22}H_{13}Mn_2O_6PS$	$C_{24}H_{13}O_8PRe_2S$	$C_{24}H_{13}O_8PRe_2S$
M	546.23	864.77	864.77
Colour	Orange-yellow	Yellow	Yellow
Crystal size/mm	$0.50 \times 0.38 \times 0.25$	$0.35 \times 0.28 \times 0.22$	$0.45 \times 0.32 \times 0.25$
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pcab$	$P2_1/a$
a/Å	16.217(3)	14.781(5)	9.367(2)
b/Å	9.1007(12)	16.863(5)	30.236(13)
c/Å	16.280(3)	20.407(7)	9.481(3)
β/°	112.084(13)	90	105.37(2)
U/Å^3, Z	2226.4(6), 4	5087(3), 8	2589(2), 4
D_c/g cm^{-3}	1.630	2.259	2.218
μ(Mo-Kα)/mm^{-1}	1.336	9.702	9.530
$F(000)$	1096	3216	1608
2θ range/°	5 to 55	5 to 50	5 to 50
Total data	4168	4392	4763
Unique data	3997	4392	4483
$wR2$ (all data)	0.0850	0.1146	0.1356
$\quad[I > 2\sigma(I)]$	0.0766	0.0995	0.1260
R (all data)	0.0397	0.0568	0.0596
$\quad[I > 2\sigma(I)]$	0.0311	0.0407	0.0493
Goodness of fit on F^2	1.039	1.034	1.033
Data/parameters	3990/289	4384/326	4480/425
Maximum peak, hole in final Fourier-difference map/e Å^{-3}	0.246, −0.265	1.68, −1.94	1.90, −2.08

[a] Data common to compounds: graphite-monochromated Mo-K$_\alpha$ radiation, $\lambda = 0.710\ 73$ Å; Nicolet R3m/v; data collection temperature = 293(2) K; three check reflections; no decay; correction for Lorentz-polarisation effects and for absorption by azimuthal scan method; maximum and minimum transmission factors, 1.000 and 0.657 for **1**, 1.000 and 0.690 for **4**, 1.000 and 0.455 for **5**; direct methods structure solution; full matrix least-square refinement on F^2.

dichloromethane (5:2 v/v)] gave unchanged compound **1** (0.020 g, 22%) and **3** (0.061 g, 59%) as the only products.

Photochemical treatment of [Re$_2$(CO)$_{10}$] with diphenyl-2-thienylphosphine

A stirred solution of [Re$_2$(CO)$_{10}$] (0.108 g, 0.166 mmol) and Ph$_2$P(2-C$_4$H$_3$S) (0.053 g, 1.0 mol per mol metal carbonyl) in toluene (100 cm^3) was UV photolysed under nitrogen for 5 h. Solvent was removed under reduced pressure to give a pale yellow solid. TLC separation [SiO$_2$; eluent, hexane–dichloromethane (5:3 v/v)] gave two bands yielding unreacted [Re$_2$(CO)$_{10}$] and the compound [Re$_2$(CO)$_8${μ-Ph$_2$P(2-C$_4$H$_3$S)}] **4** as yellow crystals (0.046 g, 32%) from a cooled dichloromethane–heptane solution (Found: C, 33.4; H, 1.7; P, 3.0; S, 3.8. C$_{24}$H$_{13}$O$_8$PRe$_2$S requires C, 33.3; H, 1.5; P, 3.6; S, 3.7%). $\tilde{v}$(CO)/cm^{-1} (cyclohexane): 2108w, 2081m, 2029s, 2012s, 1990(sh), 1983s, 1966w, 1951m and 1930s. ^{1}H NMR (CDCl$_3$, 293 K, 400 MHz): phenyl, δ 7.43–7.48 (m, 10 H); thienyl, 7.71 (dt), 7.33 (ddd) and 6.67 (dt). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ −10.6 (s). ^{13}C-{^{1}H} NMR: phenyl, δ 132.1 (d, $J = 12.2$, *ortho*), 131.1 (d, $J = 2.1$, *para*) and 128.9 (d, $J = 10.9$, *meta*); thienyl, 146.8 (d, $J = 3.4$), 135.7 (d, $J = 5.3$) and 133.1 (d, $J = 7.8$ Hz) (*ipso* and CO signals unobserved). The parent molecular ion was observed in EI and FAB MS.

Thermal treatment of [Re$_2$(CO)$_{10}$] with diphenyl-2-thienylphosphine

A solution of [Re$_2$(CO)$_{10}$] (0.088 g, 0.13 mmol) and Ph$_2$P(2-C$_4$H$_3$S) (0.324 mmol) in decane (10 cm^3) was heated under reflux under nitrogen for 2 h. Removal of solvent under reduced pressure gave a yellow oily solid. TLC separation [SiO$_2$; eluent, hexane–dichloromethane (5:2 v/v)] gave only compound [Re$_2$(CO)$_8${μ-PPh$_2$)(μ-C,S-2-C$_4$H$_3$S)}] **5**, as yellow crystals (0.097 g, 35%) from a cooled dichloromethane–heptane solution. $\tilde{v}$(CO)(cm^{-1}) (cyclohexane): 2106w, 2084m, 2012s, 1999vs, 1978m, 1967s, 1956s and 1945m. ^{1}H NMR (CDCl$_3$, 293 K, 400 MHz): phenyl, δ 7.58 (dd, $J = 7.7$, 10.8, *ortho*), 7.47–7.42 (m,

two *ortho* and two *para*), 7.34 (dt, $J = 1.7$, 7.9, *meta*) and 7.24 (dt, $J = 1.3$, 7.5, *meta*); thienyl, 7.72 (d, $J = 5.0$), 7.07 (m) and 7.05 (m). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ −21.5 (s). ^{13}C-{^{1}H} NMR: phenyl, δ 142.4 (d, $J = 27.5$, *ipso*), 137.8 (d, $J = 54.3$, *ipso*), 133.5 (d, $J = 10.3$, *meta*), 131.2 (d, $J = 12.0$, *ortho*), 130.5 (d, $J = 2.3$, *para*), 128.5 (d, $J = 2.6$, *para*), 128.5 (d, $J = 10.7$, *ortho*) and 128.1 (d, $J = 9.1$, *meta*); thienyl, 197.9 (d, $J = 5.5$), 167.5 (s), 135.2 (s) and 130.4 (s); CO (at −50 °C), 193.2 (m, two overlapping), 190.8 (d, $J = 7.8$), 188.6 (d, $J = 38.6$, *trans* to PPh$_2$), 188.4 (d, $J = 7.2$), 187.7 (d, $J = 6.4$), 186.3 (d, $J = 6.4$) and 185.3 (d, $J = 32.9$ Hz, *trans* PPh$_2$). The parent molecular ion was observed at low intensity in the EI MS. The sample could not be obtained in a form suitable for elemental analysis but was characterised by spectroscopic data and its crystal structure.

Thermolysis of [Re$_2$(CO)$_8${μ-Ph$_2$P(2-C$_4$H$_3$S)}] 4

A solution of compound **4** (0.078 g) in toluene (15 cm^3) was refluxed for 4 h. The solvent was removed under reduced pressure to give a yellow solid. TLC separation [SiO$_2$; eluent, hexane–dichloromethane (5:2 v/v)] gave some unchanged starting material (0.070 g, 90%) and [Re$_2$(CO)$_8${μ-PPh$_2$(μ-C,S-2-C$_4$H$_3$S)}] **5**, as yellow crystals (0.005 g, 7%).

Crystallographic studies of compounds 3, 4 and 5

Yellow-orange crystals of compound **3** and yellow crystals of **4** and **5** were obtained by cooling dichloromethane–heptane solutions. X-Ray data for each were collected at room temperature using a Nicolet R3v/m diffractometer with crystals mounted in air. Details of the crystal structure determinations are given in Table 4. Unit cells were determined from the setting angles of 35 orientation reflections ($16 \leq 2\theta \leq 30°$) for **3**, of 33 orientation reflections ($12 \leq 2\theta \leq 27°$) for **4** and of 25 orientation reflections ($14 \leq 2\theta \leq 27°$) for **5**. Structures were solved by direct methods using SHELXTL PLUS[20] and refined using SHELXL 93.[21] All the non-H atoms were refined anisotropically. The H atoms in each crystal were included in idealised positions, riding upon their respective carbon atoms, with C–H

distance fixed at 0.96 Å and isotropic thermal parameters at 0.08 Å³.

Acknowledgements

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