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Incorporation of Thiophene Rings into Tri- and Tetraruthenium Clusters via Cyclometalation and C−P Bond Cleavage of the Ligand Diphenyl-2-thienylphosphine

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Diphenyl-2-thienylphosphine, $Ph_2PC_4H_3S$ (**1**), reacts with $[Ru_3(CO)_{12}]$ in refluxing toluene to give the compound $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_9]$ (**2**) (59%), cyclometalated at the thiophene ring, with smaller amounts of the cluster $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_8(Ph_2PC_4H_3S)]$ (**3**) (10%), which is a substituted derivative of **2** and may also be formed by substitution at **2** with ligand **1**. The single-crystal X-ray structure of cluster **2** shows that it contains the μ_3-ligand $Ph_2PC_4H_2S$ bound through phosphorus to one Ru atom, through a σ-Ru−C bond to another and by an η^2 interaction to the third. There is a dynamic interchange between the σ and η^2 interactions of the thienyl group leading to NMR coalescence and a time-averaged plane of symmetry. The corresponding process would be nondegenerate in the substituted compound **3** (X-ray structure reported) and is quenched. Thermal treatment of cluster **2** with $[Ru_3(CO)_{12}]$ gave two tetranuclear clusters, $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_2S)(CO)_{11}]$ (**5**) by elimination of benzene and the known cluster $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_6H_4)(CO)_{11}]$ (**6**) by elimination of thiophene. Although compounds **5** and **6** are stoichiometrically equivalent, their single-crystal X-ray structures show that they adopt different geometries. The structure of **6** was shown to be the same as that reported previously for the compound derived from PPh_3. Each has an approximate square of metal atoms capped on one side by μ_4-PPh and on the other by μ_4-thiophyne (C_4H_2S) or μ_4-benzyne (C_6H_4), respectively. The C_6H_4 ligand is coordinated as a 6-electron donor, tilted with respect to the Ru_4 plane, with the coordinated C−C bond parallel to an Ru−Ru edge, whereas C_4H_2S is coordinated as a 4-electron donor, perpendicularly and diagonally across the Ru_4 plane in a manner related to known alkyne clusters of the type $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}alkyne)(CO)_{11}]$.

Introduction

The organometallic chemistry of thiophene has been studied from the point of view the the hydrodesulfurization process required to remove thiophenic sulfur from oil.[1] Thiophene and its benzo derivatives are not particularly good ligands with transition metals, even with soft metals that normally bond strongly to sulfur. Most studies of their coordination chemistry have centered on the different observed types of coordination to a single metal atom through sulfur alone or by π-complexation through carbon and sulfur atoms (η^2, η^4, or η^5). Sometimes isomers with different types of thiophene attachment are found in equilibrium.[2−4] Oxidative addition reactions of thiophene are also important. These can lead to 2-thienyl hydrido complexes by C−H bond cleavage or to ring opening with C−S cleavage to give metallasulfacyclohexadiene systems.[1−3,5−9] It is the latter, in particular, that relates to the HDS process and the question of whether ring opening precedes or follows hydrogenation in the catalytic system has been addressed.[1] In a few cases thiophene has been incorporated into bidentate, polydentate, or macrocyclic ligands but this area has not been widely developed.[10−12]

We set out to extend the organometallic chemistry of thiophene by introducing the thiophene ring into clus-

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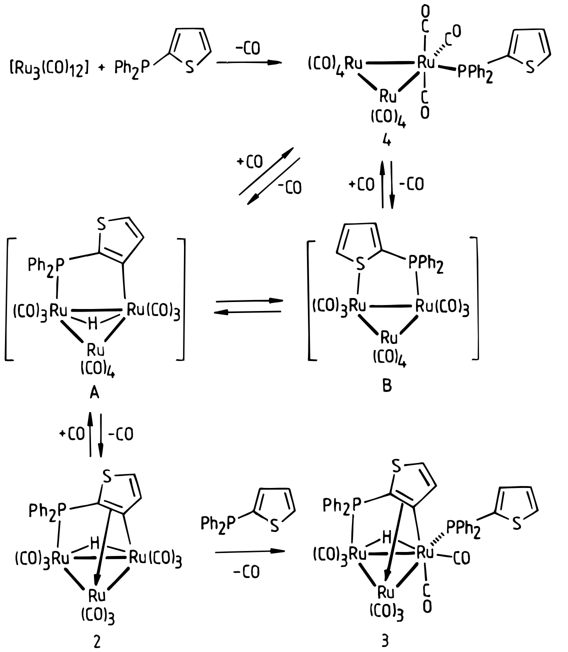
ters by the use of the known ligand diphenyl-2-thienylphosphine (**1**),[13-15] which might act as a bridge through the two heteroatoms or through phosphorus and the π-electrons of the heterocyclic component. Attempts to achieve this previously with **1** have not been reported. The only known complexes of **1** have the ligand as a simple tertiary phosphine coordinated through phosphorus such as in $[MCl_2(Ph_2PC_4H_3S)_2]$ (M = Pd, Pt)[16-19] and in $[Rh(cod)(Ph_2PC_4H_3S)_2]BF_4$,[20] both of which are a square-planar four-coordinate complexes. There is no evidence for coordination of thienyl groups in such compounds. However, we have recently synthesized a derivative of $[Re_2(CO)_{10}]$ and ligand **1**, $[Re_2(CO)_8(\mu\text{-}Ph_2PC_4H_3S)]$, and shown this to have a bridging ligand coordinated through both the sulfur and phosphorus atoms.[21] Recent work on tris(2-thienyl)phosphine with $[Ru_3(CO)_{12}]$ has led to trinuclear and mononuclear compounds in which the ligand behaves as a simple tertiary phosphine.[22] No sulfur coordination or cyclometalation was observed.

In this paper we describe results on reactions of **1** with $[Ru_3(CO)_{12}]$ which do not lead to bridging-**1** systems related to $[Re_2(CO)_8(\mu\text{-}Ph_2PC_4H_3S)]$, as might be expected, but instead to the cyclometalated ligand μ_3-$Ph_2PC_4H_2S$, and reactions involving the interconversion of this with a cluster containing the unmetalated monodentate ligand **1**. In addition to C−H cleavage we have observed P−C cleavage to give an unprecedented μ_4-thiophyne ligand (C_4H_2S). Previously we have reported the thiophyne ligand in a μ_3-coordination mode and the parent thienyl ligand (C_4H_3S) in a μ_2-coordination mode in both osmium and ruthenium clusters.[23-27]

Results and Discussion

Reaction of $[Ru_3(CO)_{12}]$ with Diphenyl-2-thienylphosphine (1). The ligand diphenyl-2-thienylphosphine has been synthesized previously by the reaction of 2-thienylmagnesium iodide[15] or 2-thienyllithium[14] with Ph_2PCl or by reaction of 2-iodothiophene with Me_3SnPPh_2, a reaction which is catalyzed by $[PdCl_2(MeCN)_2]$.[13] We have used a modified method based on the 2-thienyllithium route (see Experimental Section). Reaction of **1** with an equimolar amount of $[Ru_3(CO)_{12}]$ in refluxing toluene for 30 min showed no evidence, either spectroscopic or after subsequent workup, for the formation of simple substitution derivatives such as $[Ru_3(CO)_{11}(\mathbf{1})]$, $[Ru_3(CO)_{10}(\mu\text{-}\mathbf{1})]$, $[Ru_3(CO)_{10}(\mathbf{1})_2]$, *etc.* Instead the major product was the cyclometalated thienylphosphine cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_9]$ (**2**) (59%) in addition to a small amount of a substituted derivative of compound **2**, $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_8(Ph_2PC_4H_3S)]$ (**3**) (10%), and some unreacted $[Ru_3(CO)_{12}]$. Unreacted $[Ru_3(CO)_{12}]$ is expected because two ligands **1** are incorporated into the cluster **3** leaving a deficiency of ligand **1** for complete conversion of the starting metal carbonyl. We have established that the cluster $[Ru_3(CO)_{11}(Ph_2PC_4H_3S)]$ (**4**), formed by treatment of **2** with CO in a sealed tube at 80 °C, is reactive toward decarbonylation to give cluster **2**. Therefore it is not surprising that **4** was not observed spectroscopically during the thermal reaction of **1** with $[Ru_3(CO)_{12}]$ in refluxing toluene.

Scheme 1



Scheme 1 shows the formation of clusters **2**−**4** from ligand **1**. We presume that cluster **4** is formed initially but readily loses CO to form either or both of the unobserved intermediates **A** and **B**. Loss of CO from $[Re_2(CO)_9(Ph_2PC_4H_3S)]$ leads to $[Re_2(CO)_8(\mu\text{-}Ph_2PC_4H_5S)]$, containing the μ-ligand bonded through P and S atoms as in the supposed intermediate **B**,[21] but intermediate **B** is less likely than **A** to be directly on the route from **4** to **2**. The ready formation of **2** from **4** means that intermediate **A** also readily loses CO to give **4**. Treatment of **2** with CO gives **4** and not **A** (or **B**) so **A** must both readily lose and pick up CO and therefore be inaccessible by the thermal methods that we have used. There is evidence that the 2-thienyl substituent on **1** cyclometalates more rapidly than the phenyl substituent and also that the P−thienyl bond is not so readily cleaved as P−Ph bonds. Thiophene is known to be more reactive toward electrophiles than benzene, and this may relate to its enhanced susceptibilty toward metalation.[28] Scheme 2 shows the corresponding behavior established for PR_2Ph ligands, including PPh_3, where ready formation of μ_3-C_6H_4 occurs following cyclometalation both with ruthenium and osmium.[29-33] With ruthenium but not osmium there are subsequent reactions leading to Ru_4− and Ru_5−C_6H_4 species.[32,33] The

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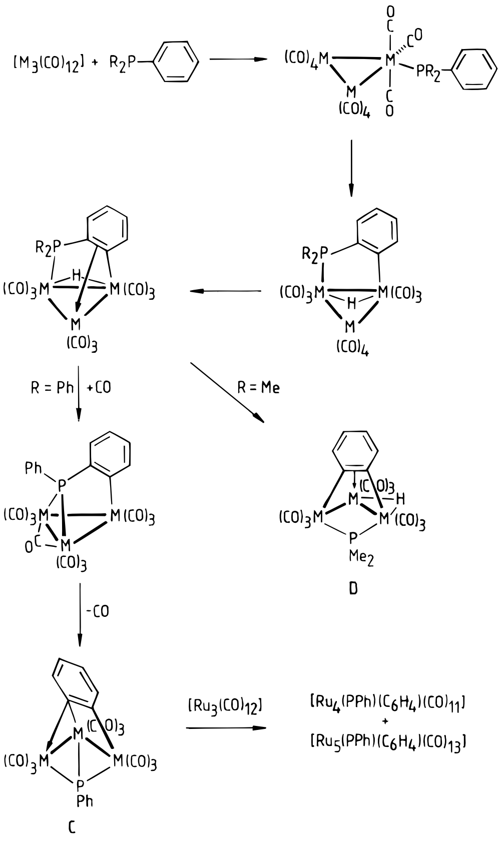
Scheme 2



chemistry in Scheme 2 is a composite of that known for ruthenium and osmium, the intermediates being more easily characterized for osmium than ruthenium. There seems to be a much reduced tendency for compound **2** either to loose benzene to give $[Ru_3(\mu_3\text{-}PPh)(\mu_3\text{-}C_4H_2S)(CO)_9]$ or to cleave the P−C bond to give $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu_3\text{-}C_4H_2S)(CO)_9]$. Both of these compounds are unobserved, but as analogues of compounds **C** and **D** in Scheme 2, they would be formed if the chemistry of **1** followed that of PPh_3.

Structures of Clusters 2 and 3. The structures of clusters **2** and **3** were determined by single-crystal X-ray diffraction, and Figures 1 and 2 show their structures, respectively. Selected bond lengths and angles are in Tables 1 and 2. Compound **2** contains the μ_3-ligand $Ph_2PC_4H_2S$ bonded through the P(1) atom to Ru(3), through a σ Ru(2)−C(2) bond and through an η^2-interaction between C(1), C(2), and Ru(1), thus forming an σ, η^2-vinyl type bridge between metal atoms Ru(1) and Ru(2). The structure corresponds closely to that of $[Os_3(\mu\text{-}H)(\mu_3\text{-}PMePhC_6H_4)(CO)_9]$.[31]

The Ph groups are nonequivalent, and all nine CO ligands are in distinguishable sites. Low-temperature ^1H and $^{13}C\{^1H\}$ NMR data are consistent with the molecular stucture found in the crystal persisting in solution. Figure 3 shows that two sets of *ortho* proton signals (δ 7.13 and 7.83) in the ^1H NMR spectrum for these nonequivalent Ph groups coalesce at around 35 °C to give a single signal at δ 7.45 at 90 °C. The $^{13}C\{^1H\}$ NMR spectrum (Figure 4) shows that this is not the result of restricted rotation about the P−Ph bonds since there is also coalescence of the *ipso* phenyl ^{13}C resonances. The *ipso* signals are doublets at δ 134.9 (J_{PC} = 35 Hz) and 134.3 (J_{PC} = 61 Hz) at −70 °C which give a single doublet at δ 135.8 (J_{PC} = 47 Hz) at 90 °C. There is a temperature drift of δ, but the averaged J_{PC} value is as expected. There are corresponding coalescences of the *ortho* and *meta* signals. Our proposed mechanism in Scheme 3 involves a hydride shift as well as an oscillation of the σ, η^2-vinyl group between two metal centers to give a time-averaged symmetry plane. If no other dynamic process were occurring, there would be a pairwise exchange of carbonyls **b** to **i** leaving carbonyl **a** unaffected. Indeed Figure 5 shows that all but one of the nine CO signals in the $^{13}C\{^1H\}$ NMR spectrum (there is accidental coincidence of two at low temperatures) broaden above −20 °C and at room temperature only the doublet for carbonyl **a** remains sharp (δ 200.1, J_{PC} = 97.5 Hz). The large coupling to

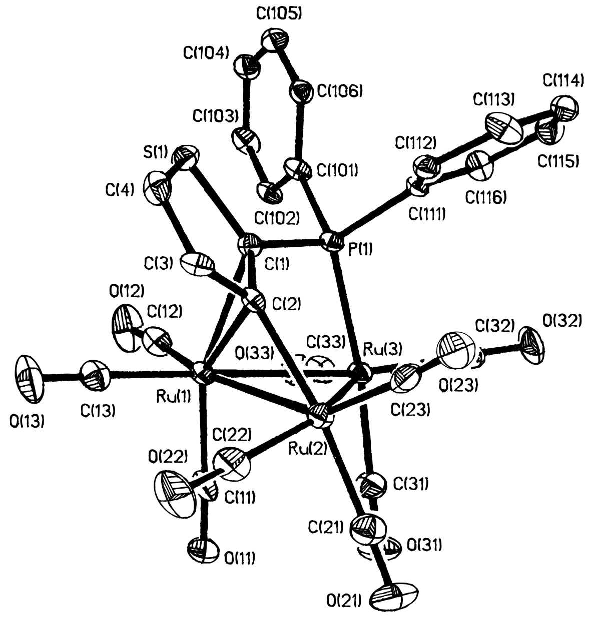


Figure 1. ORTEP view of the cluster $[Ru_3H(PPh_2C_4H_2S)(CO)_9]$ (**2**) showing 30% ellipsoids.

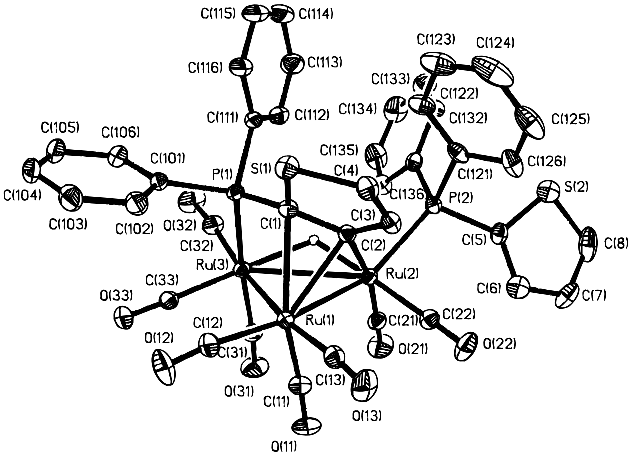


Figure 2. ORTEP view of the cluster $[Ru_3H(PPh_2C_4H_2S)(CO)_8(Ph_2PC_4H_3S)]$ (**3**) showing 30% ellipsoids.

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Table 1. Bond Lengths (Å) and Angles (deg) for 2

molecule A		molecule B	
Ru(1)−Ru(2)	2.740(1)	Ru(4)−Ru(5)	2.723(1)
Ru(1)−Ru(3)	2.832(2)	Ru(5)−Ru(6)	2.837(2)
Ru(2)−Ru(3)	3.025(1)	Ru(4)−Ru(6)	3.036(1)
Ru(1)−C(1)	2.36(1)	Ru(5)−C(5)	2.38(1)
Ru(1)−C(2)	2.342(9)	Ru(5)−C(6)	2.34(1)
Ru(2)−C(2)	2.10(1)	Ru(4)−C(6)	2.106(9)
Ru(3)−P(1)	2.350(3)	Ru(6)−P(2)	2.361(3)
P(1)−C(1)	1.79(1)	P(2)−C(5)	1.80(1)
S(1)−C(1)	1.75(1)	S(2)−C(5)	1.759(9)
S(1)−C(4)	1.71(1)	S(2)−C(8)	1.69(1)
C(1)−C(2)	1.42(1)	C(5)−C(6)	1.40(1)
C(2)−C(3)	1.45(2)	C(6)−C(7)	1.45(2)
C(3)−C(4)	1.35(2)	C(7)−C(8)	1.34(2)
Ru(2)−Ru(1)−C(1)	76.0(2)	Ru(4)−Ru(5)−C(5)	75.7(2)
Ru(3)−Ru(1)−C(1)	78.2(3)	Ru(6)−Ru(5)−C(5)	78.1(3)
Ru(2)−Ru(1)−C(2)	48.0(2)	Ru(4)−Ru(5)−C(6)	48.5(2)
Ru(3)−Ru(1)−C(2)	86.2(3)	Ru(6)−Ru(5)−C(6)	86.5(3)
Ru(1)−Ru(2)−C(2)	56.0(3)	Ru(6)−Ru(4)−C(6)	85.7(3)
Ru(3)−Ru(2)−C(2)	85.8(3)	Ru(5)−Ru(4)−C(6)	56.1(3)
Ru(1)−Ru(3)−P(1)	73.4(1)	Ru(5)−Ru(6)−P(2)	73.6(1)
Ru(2)−Ru(3)−P(1)	85.2(1)	Ru(4)−Ru(6)−P(2)	85.2(1)
C(1)−S(1)−C(4)	91.1(5)	C(5)−S(2)−C(8)	89.6(5)
Ru(1)−C(1)−C(2)	71.6(6)	Ru(5)−C(5)−C(6)	71.2(6)
P(1)−C(1)−C(2)	120.8(8)	P(2)−C(5)−C(6)	122.2(7)
S(1)−C(1)−C(2)	112.3(8)	S(2)−C(5)−C(6)	112.6(8)
Ru(1)−C(2)−Ru(2)	76.0(3)	Ru(4)−C(6)−Ru(5)	75.4(3)
Ru(2)−C(2)−C(1)	126.1(8)	Ru(4)−C(6)−C(5)	126.1(8)
Ru(2)−C(2)−C(3)	125.3(7)	Ru(5)−C(6)−C(7)	124.8(9)

Table 2. Bond Lengths (Å) and Angles (deg) for Cluster 3

Ru(1)−Ru(2)	2.734(1)	P(1)−C(101)	1.820(4)
Ru(1)−Ru(3)	2.843(1)	P(1)−C(111)	1.825(4)
Ru(2)−Ru(3)	3.036(1)	P(2)−C(5)	1.817(4)
Ru(1)−C(1)	2.438(4)	S(1)−C(1)	1.762(4)
Ru(1)−C(2)	2.314(4)	S(1)−C(4)	1.722(5)
Ru(2)−P(2)	2.336(1)	C(1)−C(2)	1.425(5)
Ru(2)−C(2)	2.114(4)	C(2)−C(3)	1.462(6)
Ru(3)−P(1)	2.326(1)	C(3)−C(4)	1.331(6)
P(1)−C(1)	1.783(4)		
Ru(3)−Ru(1)−C(1)	77.1(1)	C(1)−S(1)−C(4)	90.4(2)
Ru(2)−Ru(1)−C(2)	48.6(1)	Ru(1)−C(1)−P(1)	95.2(2)
Ru(3)−Ru(1)−C(2)	85.9(1)	P(1)−C(1)−S(1)	121.4(2)
Ru(1)−Ru(2)−P(2)	149.9(1)	P(1)−C(1)−C(2)	120.8(3)
Ru(3)−Ru(2)−P(2)	122.3(1)	S(1)−C(1)−C(2)	112.7(3)
Ru(3)−Ru(2)−C(2)	84.7(1)	Ru(2)−C(2)−C(1)	127.6(3)
Ru(1)−Ru(3)−P(1)	74.3(1)	Ru(1)−C(2)−C(3)	119.6(2)
Ru(2)−Ru(3)−P(1)	85.5(1)	C(1)−C(2)−C(3)	107.8(3)
Ru(3)−P(1)−C(1)	106.4(1)	C(2)−C(3)−C(4)	115.3(4)
Ru(3)−P(1)−C(101)	113.7(2)	S(1)−C(4)−C(3)	113.7(3)

phosphorus confirms the assignment. At higher temperatures other CO exchanges cause this signal to coalesce. A related process was discussed for the isomerization of diastereomers of the cluster [$Os_3H(PhSC_9H_{14})(CO)_9$] (Scheme 4), although the mechanism in that case could not be clearly established because of other possibilities such as inversion at sulfur could not be ruled out.[34]

Cluster **3** was shown to be derived from **2** by substitution of one CO ligand by **1**. The geometry of the μ_3-ligand in **3** is closely similar to that in **2**. Oscillation of the thienyl group between Ru(1) and Ru(2) would generate another isomer, but only one was observed. The oscillation process is quenched in this case either because the steric bulk of the introduced tertiary phosphines favors one orientation over the other or because the tertiary phosphine stabilizes the σ-Ru−C bond rather than the η^2-bond at the Ru atom to which it is bonded. This stabilization is not apparent from differences in the corresponding Ru−C bond lengths in **2** and **3**.

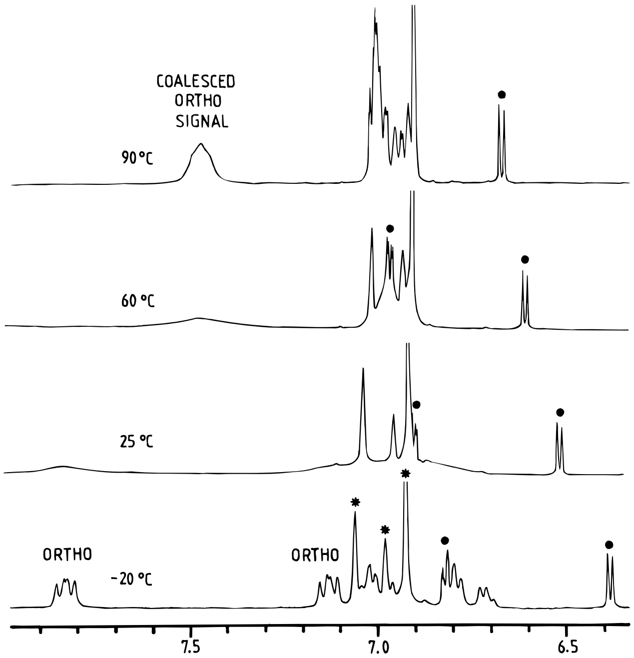


Figure 3. Variable-temperature ^1H NMR spectrum for the cluster **2** in toluene-d_8 solution (* = solvent; ● = thienyl).

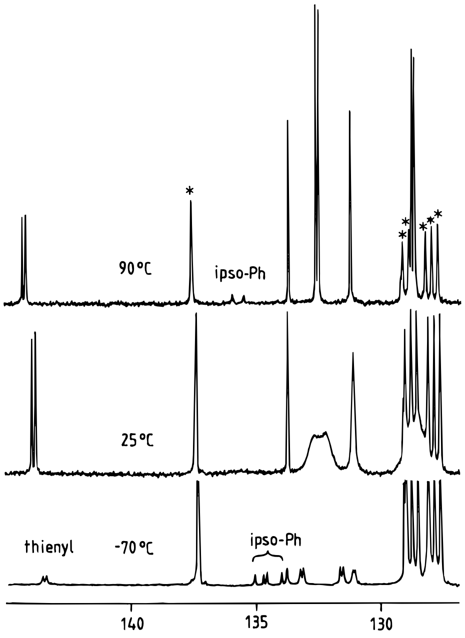
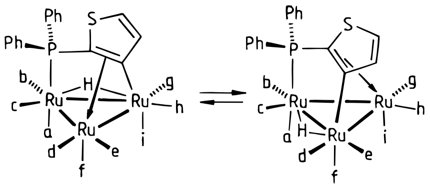


Figure 4. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum for the cluster **2** in toluene-d_8 solution in the phenyl region (* = solvent).

Scheme 3



Thermal Treatment of cluster 2. Cluster **2** is the main species formed from **1** and [$Ru_3(CO)_{12}$] after 30 min in refluxing toluene, but after 19 h only a low yield of **2** is obtained. In addition two related tetranuclear

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[34] Adams, R. D.; Qu, X.; Wu, W. *Organometallics* **1993**, *12*, 4117.

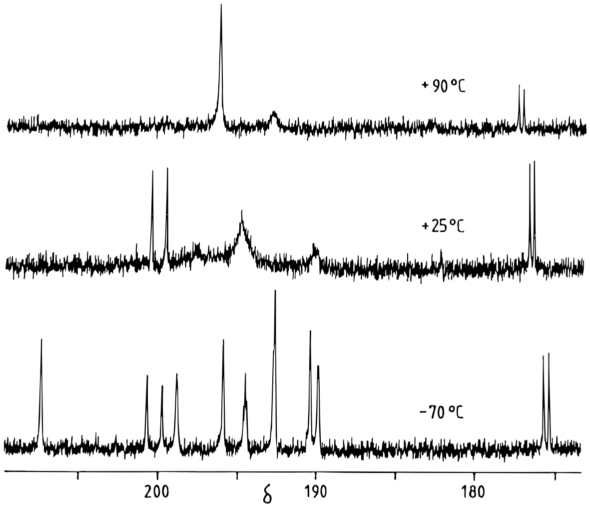
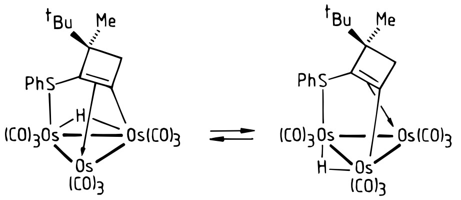
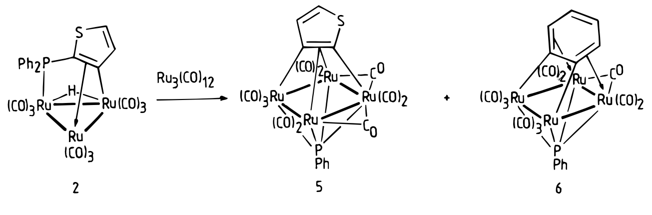


Figure 5. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum for the cluster **2** in toluene-d_8 solution in the carbonyl ligand region (* = solvent, ● = thienyl).

Scheme 4



Scheme 5



clusters could be isolated: $[Ru_4(PPh)(C_4H_2S)(CO)_{11}]$ (**5**) and $[Ru_4(PPh)(C_6H_4)(CO)_{11}]$ (**6**) (Scheme 5). Thermal treatment of **2** in refluxing toluene gave the same products in similar yields which were not markedly enhanced by addition of more $[Ru_3(CO)_{12}]$. Cluster **6** was shown spectroscopically to be identical to a product from the reaction of PPh_3 with $[Ru_3(CO)_{12}]$. The X-ray structure of **6** is known,[32] but we redetermined this and found closely corresponding structural data. The recently reported structure of $[Ru_4(PFc)(C_6H_4)(CO)_{11}]$ (Fc = ferrocenyl) is very similar.[35] The main structural interest in **6** is the mode of attachment of the C_6H_4 ligand which is σ-bonded to two Ru atoms and η^2-coordinated to each of the other two Ru atoms. With the C_6H_4 as a 6-electron donor the structure is electron-precise with four Ru−Ru bonds which have an average length of 2.876 Å. The IR ν(CO) data for **5** and **6** are fairly similar and both show bridging CO [ν(CO) 1852 cm^{-1} for **5** and 1826 cm^{-1} for **6**], but there were sufficient differences in the spectra to show that **5** and **6** are not isostructural. An X-ray structure of **5** was determined to confirm this.

Table 3 contains selected bond lengths and angles, and an ORTEP picture of **5** is shown in Figure 6. The basic shapes of clusters **5** and **6** are the same with a μ_4-PPh ligand on one face of a square of Ru atoms and a μ_4-C_6H_4 or a μ_4-C_4H_2S ligand bonded on the opposite face of the metal atoms. However, the thiophyne ligand is vertical and oriented differently. Whereas the coordinated C−C bond of C_6H_4 is parallel to a Ru−Ru edge and the C_6 plane tilted to allow two η^2-contacts (dihedral angles between the C_6 and Ru_4 planes = 49.7 and 54.7° for the two independent molecules in the crystal), the C_4H_2S ligand is vertical (dihedral angle between C_4S and Ru_4 planes = 90.9°) and the coordinated C−C bond is diagonally disposed across the Ru_4 square. Cluster **5** contains two bridging CO ligands along the edges Ru(2)−Ru(4) and Ru(3)−Ru(4) while **6** only has one μ-CO. The structure of **5** is structurally related to the alkyne clusters of the type $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}alkyne)(CO)_{11}]$.[36,37] There are two possible orientations of the thiophyne ligand in **5**, that shown in Figure 6 and another with the ligand rotated by 180° so that the S and C(3) atoms are exchanged. The refinement of a disordered model

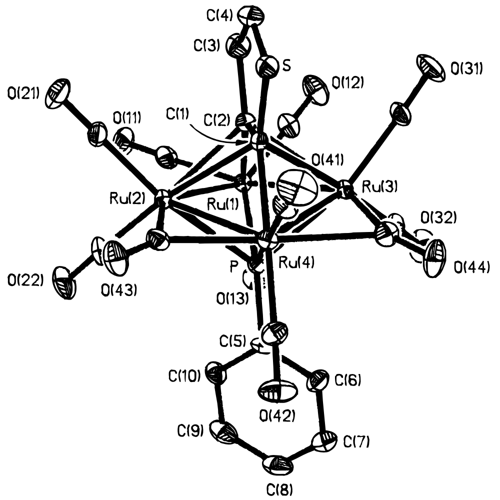


Figure 6. ORTEP view of the cluster $[Ru_4(PPh)(C_4H_2S)(CO)_{11}]$ (**5**) showing 30% ellipsoids.

Table 3. Bond Lengths (Å) and Angles (deg) for 5

Ru(1)−Ru(2)	2.878(1)	Ru(4)−C(1)	2.163(5)
Ru(1)−Ru(3)	2.845(1)	Ru(3)−P	2.417(1)
Ru(1)−P	2.370(1)	Ru(3)−C(1)	2.323(5)
Ru(1)−C(2)	2.113(6)	Ru(3)−C(2)	2.497(5)
Ru(2)−Ru(4)	2.758(1)	S−C(1)	1.741(5)
Ru(2)−P	2.448(1)	S−C(4)	1.641(7)
Ru(2)−C(1)	2.384(5)	C(1)−C(2)	1.431(7)
Ru(2)−C(2)	2.416(5)	C(2)−C(3)	1.571(7)
Ru(4)−Ru(3)	2.781(1)	C(3)−C(4)	1.378(9)
Ru(4)−P	2.409(1)		
Ru(2)−Ru(1)−Ru(3)	82.2(1)	Ru(3)−Ru(4)−P	54.9(1)
Ru(2)−Ru(1)−P	54.6(1)	Ru(2)−Ru(4)−C(1)	56.4(1)
Ru(3)−Ru(1)−P	54.3(1)	Ru(3)−Ru(4)−C(1)	54.3(1)
Ru(2)−Ru(1)−C(2)	55.4(1)	P−Ru(4)−C(1)	78.7(1)
Ru(3)−Ru(1)−C(2)	58.3(1)	Ru(1)−Ru(3)−Ru(4)	94.6(1)
Ru(1)−Ru(2)−Ru(4)	94.3(1)	Ru(1)−Ru(3)−P	52.8(1)
Ru(1)−Ru(2)−P	52.1(1)	Ru(4)−Ru(3)−P	54.7(1)
Ru(4)−Ru(2)−P	54.7(1)	Ru(1)−Ru(3)−C(1)	74.7(1)
Ru(1)−Ru(2)−C(1)	73.3(1)	Ru(4)−Ru(3)−C(1)	49.2(1)
Ru(4)−Ru(2)−C(1)	49.1(1)	P−Ru(3)−C(1)	75.6(1)
P−Ru(2)−C(1)	74.0(1)	Ru(1)−Ru(3)−C(2)	46.0(1)
Ru(1)−Ru(2)−C(2)	46.0(1)	Ru(4)−Ru(3)−C(2)	77.3(1)
Ru(4)−Ru(2)−C(2)	79.1(1)	P−Ru(3)−C(2)	74.5(1)
Ru(2)−Ru(4)−Ru(3)	85.5(1)	C(1)−Ru(3)−C(2)	34.3(2)
Ru(2)−Ru(4)−P	56.1(1)		

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(35) Zheng, T. C.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1994**, *13*, 3594.

(36) Lunnis, J. L.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E, *Organometallics* **1985**, *4*, 2066.

(37) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 3160; **1993**, *12*, 1365.

Table 4. Crystallographic Data for Compounds $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_9]$ (2), $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_8(Ph_2PC_4H_3S)]$ (3), and $[Ru_4(PPh)(C_4H_2S)(CO)_{11}]$ (5)[a]

	2	3	5
formula	$C_{25}H_{13}O_9PRu_3S$	$C_{40}H_{26}O_8P_2Ru_3S_2$	$C_{21}H_7O_{11}PRu_4S$
M	823.62	1063.93	902.59
description	yellow plate	yellow prism	red prism
cryst size, mm^3	0.50 × 0.43 × 0.01	0.58 × 0.35 × 0.11	0.20 × 0.20 × 0.45
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	8.982(2)	10.057(1)	9.449(1)
b, Å	17.928(5)	20.014(4)	17.926(4)
c, Å	18.199(5)	17.858(3)	15.304(4)
α, deg	109.69(2)	90	90
β, deg	97.44(2)	99.79(1)	90.84(2)
γ, deg	89.60(2)	90	90
V, A^3	2734(1)	3976(1)	2592(1)
Z	4	4	4
D_{calc}, g cm^{-3}	2.00	1.78	2.31
μ(Mo Kα), cm^{-1}	17.9	13.3	24.4
$F(000)$	936	1400	1788
no. of unique data	7032	6950	4557
no. of data used, $I > 1.5\sigma(I)$	5556	6122	4053
no. of params	703	493	334
R^b	0.0501	0.0338	0.0324
$R_w{}^c$	0.0500	0.0349	0.0395
g	0.000 544	0.000 274	0.002 59
max shift/esd	0.02	0.02	0.001
largest residual, e A^{-3}	0.89	0.51	0.97

[a] Data common to compounds: Mo radiation (λ = 0.710 73 Å); Nicolet R3m/v diffractometer, intensity data collected at 20 °C with scan mode $\omega - 2\theta$ in the range $5 \leq 2\theta \leq 50°$, three check reflections, no decay, correction for Lorentz and polarization effects and for absorption by azimuthal scan method; direct methods structure solution. [b] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o) + g(F_o{}^2)]^{-1}$.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of 2

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
Ru(1)	4072(1)	5795(1)	6830(1)	30(1)	Ru(4)	1290(1)	1589(1)	8196(1)	32(1)
Ru(2)	5479(1)	6585(1)	8320(1)	34(1)	Ru(5)	1837(1)	725(1)	6716(1)	29(1)
Ru(3)	3378(1)	5163(1)	7983(1)	33(1)	Ru(6)	3156(1)	124(1)	7895(1)	30(1)
P(1)	5335(3)	4419(2)	7388(2)	29(1)	P(2)	844(3)	−588(2)	7354(2)	28(1)
S(1)	7340(3)	4653(2)	6223(2)	41(1)	S(2)	−1807(3)	−357(2)	6205(2)	41(1)
C(1)	6199(11)	5044(6)	6962(6)	31(4)	C(5)	−242(11)	42(6)	6919(6)	31(4)
C(2)	6578(11)	5856(6)	7405(6)	31(4)	C(6)	−341(11)	854(6)	7318(6)	34(4)
C(3)	7815(12)	6108(6)	7095(7)	40(4)	C(7)	−1758(12)	1127(7)	7035(7)	43(5)
C(4)	8309(12)	5545(7)	6487(7)	45(5)	C(8)	−2570(13)	545(8)	6460(7)	52(6)
C(101)	5114(11)	3460(6)	6602(6)	34(4)	C(121)	634(11)	−1568(6)	6600(6)	32(4)
C(102)	3718(12)	3162(6)	6146(6)	39(4)	C(122)	−717(12)	−2024(6)	6472(6)	38(4)
C(103)	3615(14)	2440(6)	5545(7)	46(5)	C(123)	−887(13)	−2759(6)	5894(6)	41(5)
C(104)	4874(14)	2001(6)	5375(7)	47(5)	C(124)	194(14)	−3046(7)	5429(7)	52(5)
C(105)	6238(13)	2282(6)	5829(6)	42(5)	C(125)	1505(14)	−2616(6)	5538(7)	48(5)
C(106)	6351(12)	3003(6)	6443(6)	36(4)	C(126)	1750(12)	−1879(6)	6116(6)	39(4)
C(111)	6781(11)	4223(6)	8098(6)	29(4)	C(131)	−181(10)	−710(6)	8108(6)	29(4)
C(112)	8142(12)	4645(6)	8365(6)	38(4)	C(132)	245(13)	−1308(7)	8416(7)	45(5)
C(113)	9156(13)	4512(7)	8967(7)	51(5)	C(133)	−384(15)	−1374(8)	9052(7)	57(6)
C(114)	8796(14)	3930(7)	9256(7)	50(5)	C(134)	−1459(15)	−868(9)	9359(8)	63(6)
C(115)	7436(15)	3504(7)	8985(7)	54(5)	C(135)	−1936(15)	−301(8)	9056(7)	59(6)
C(116)	6429(13)	3646(6)	8416(7)	44(5)	C(136)	−1282(13)	−228(7)	8423(7)	44(5)
C(11)	2551(14)	6514(7)	7165(7)	46(5)	C(41)	3004(16)	2244(7)	8849(7)	54(5)
O(11)	1597(11)	6922(6)	7318(5)	70(4)	O(41)	4001(10)	2647(5)	9215(6)	66(4)
C(12)	2912(13)	5032(7)	5958(8)	48(5)	C(42)	688(15)	2429(8)	7824(8)	58(6)
O(12)	2170(13)	4621(6)	5422(6)	87(5)	O(42)	323(14)	2923(5)	7599(6)	84(5)
C(13)	4767(13)	6318(7)	6170(7)	48(5)	C(43)	13(13)	1814(6)	8998(7)	41(5)
O(13)	5143(11)	6636(7)	5782(6)	86(6)	O(43)	−852(10)	1938(5)	9433(5)	62(4)
C(21)	4204(15)	7259(8)	9035(8)	58(6)	C(51)	3516(13)	1434(7)	7028(6)	39(5)
O(21)	3474(12)	7680(6)	9445(6)	86(5)	O(51)	4563(9)	1849(5)	7176(5)	57(4)
C(22)	5949(14)	7458(7)	8003(7)	52(5)	C(52)	2579(14)	−64(7)	5877(7)	46(5)
O(22)	6200(13)	7964(6)	7802(6)	84(5)	O(52)	3128(12)	−480(5)	5371(5)	76(5)
C(23)	7173(15)	6695(7)	9112(7)	48(5)	C(53)	779(12)	1206(7)	6039(6)	38(4)
O(23)	8256(11)	6749(6)	9544(5)	75(4)	O(53)	159(10)	1520(6)	5637(6)	73(5)
C(31)	1923(15)	5924(8)	8426(8)	56(6)	C(61)	4895(14)	863(7)	8291(7)	47(5)
O(31)	1025(11)	6333(6)	8686(6)	78(5)	O(61)	5943(10)	1250(5)	8518(6)	70(4)
C(32)	3407(13)	4704(7)	8814(8)	52(5)	C(62)	3552(12)	−316(7)	8740(7)	41(5)
O(32)	3394(12)	4437(7)	9291(6)	89(6)	O(62)	3875(12)	−573(6)	9224(6)	79(5)
C(33)	1752(13)	4542(7)	7285(8)	48(5)	C(63)	4397(13)	−559(7)	7197(7)	42(5)
O(33)	733(10)	4197(6)	6890(6)	71(4)	O(63)	5192(9)	−949(5)	6820(5)	63(4)

containing these two orientations gave a population of 0.79(1) of the rotamer shown and 0.21(1) of the other. Spectroscopic studies of **5** in solution showed only one isomer.

Clusters **5** and **6** have 62 and 64 valence electron counts, respectively, and **5** could be considered to be formally unsaturated. The different average Ru−Ru bond lengths support this view [2.816 Å for **5** and 2.876

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å $\times 10^3$) for 3

	x	*y*	*z*	U_{eq}
Ru(1)	2359(1)	1140(1)	7940(1)	30(1)
Ru(2)	684(1)	1783(1)	6887(1)	29(1)
Ru(3)	1245(1)	370(1)	6693(1)	31(1)
P(1)	65(1)	195(1)	7646(1)	31(1)
P(2)	−1309(1)	2216(1)	6504(1)	31(1)
S(1)	−71(1)	850(1)	9183(1)	46(1)
S(2)	−2629(3)	3412(2)	5772(2)	63(1)
S(2A)	−25(4)	3349(3)	5869(3)	58(1)
C(1)	332(4)	869(2)	8268(2)	32(1)
C(2)	356(3)	1505(2)	7974(2)	30(1)
C(3)	142(4)	1950(2)	8572(2)	37(1)
C(4)	−102(4)	1677(2)	9204(2)	45(2)
C(5)	−1306(4)	3006(2)	6069(2)	41(1)
C(6)	−329(11)	3382(5)	5978(6)	63(1)
C(6A)	−2433(20)	3403(10)	5605(11)	58(1)
C(7)	−631(6)	3953(2)	5518(3)	66(2)
C(8)	−1899(7)	4023(3)	5434(3)	80(3)
C(101)	495(4)	−532(2)	8196(2)	37(1)
C(102)	1290(5)	−548(2)	8893(3)	51(2)
C(103)	1662(5)	−1133(3)	9230(3)	61(2)
C(104)	1246(6)	−1696(3)	8878(4)	68(2)
C(105)	477(6)	−1696(2)	8183(4)	67(2)
C(106)	99(5)	−1115(2)	7842(3)	54(2)
C(111)	−1622(4)	106(2)	7363(2)	37(1)
C(112)	−2210(4)	255(2)	6630(3)	46(2)
C(113)	−3488(5)	202(3)	6417(3)	62(2)
C(114)	−4198(5)	−12(3)	6931(3)	69(2)
C(115)	−3638(5)	−170(3)	7655(4)	70(2)
C(116)	−2352(4)	−111(2)	7881(3)	52(2)
C(121)	−2165(4)	2345(2)	7294(2)	41(1)
C(122)	−2777(4)	1839(3)	7577(3)	52(2)
C(123)	−3317(5)	1925(4)	8207(3)	76(2)
C(124)	−3242(6)	2502(5)	8576(3)	98(3)
C(125)	−2625(6)	3003(4)	8317(3)	80(3)
C(126)	−2074(5)	2941(3)	7675(3)	57(2)
C(131)	−2446(4)	1820(2)	5777(2)	37(1)
C(132)	−3765(4)	1875(2)	5737(3)	42(1)
C(133)	−4556(5)	1640(3)	5138(3)	66(2)
C(134)	−4111(6)	1343(3)	4566(3)	77(2)
C(135)	−2888(6)	1278(3)	4584(3)	72(2)
C(136)	−2009(5)	1495(2)	5173(2)	47(2)
C(11)	3375(4)	1426(2)	7256(3)	45(2)
O(11)	4078(3)	1590(2)	6885(2)	63(1)
C(12)	3414(5)	527(2)	8509(3)	47(2)
O(12)	4147(4)	201(2)	8850(2)	80(2)
C(13)	2967(4)	1797(2)	8663(3)	45(2)
O(13)	3406(4)	2187(2)	9061(2)	71(1)
C(21)	1256(4)	1950(2)	5959(3)	42(1)
O(21)	1621(4)	2042(2)	5402(2)	70(2)
C(22)	1327(4)	2557(2)	7321(2)	40(1)
O(22)	1744(4)	3016(2)	7611(2)	69(1)
C(31)	2305(4)	607(2)	5961(3)	45(2)
O(31)	2928(4)	696(2)	5518(2)	72(2)
C(32)	263(5)	−201(2)	5992(3)	48(2)
O(32)	−259(4)	−593(2)	5614(2)	76(2)
C(33)	2441(4)	−242(2)	7141(3)	40(1)
O(33)	3134(3)	−620(2)	7394(2)	60(1)

Å for **6**]. However, in spite of its lower electron count, cluster **5** does not react with CO under mild conditions.

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times 10^3$) for 5

	x	*y*	*z*	U_{eq}
Ru(1)	611(1)	7021(1)	9038(1)	28(1)
Ru(2)	3055(1)	6066(1)	8957(1)	28(1)
Ru(4)	3555(1)	6364(1)	7221(1)	30(1)
Ru(3)	1678(1)	7545(1)	7422(1)	28(1)
P	1227(1)	6266(1)	7831(1)	27(1)
S	5199(2)	7732(1)	8325(1)	40(1)
C(1)	3663(5)	7200(3)	8240(3)	30(1)
C(2)	2717(6)	7401(3)	8923(3)	35(2)
C(3)	3403(5)	8000(2)	9548(3)	54(1)
C(4)	4704(8)	8175(4)	9207(5)	59(2)
C(5)	−26(6)	5639(3)	7316(4)	35(2)
C(6)	−321(7)	5726(4)	6420(4)	51(2)
C(7)	−1318(9)	5276(4)	6021(5)	65(3)
C(8)	−1980(8)	4734(4)	6477(6)	67(3)
C(9)	−1665(7)	4619(4)	7364(5)	61(3)
C(10)	−697(6)	5070(3)	7777(4)	46(2)
C(11)	758(7)	6704(4)	10222(4)	48(2)
O(11)	778(6)	6539(3)	10940(3)	69(2)
C(12)	47(7)	8011(4)	9294(4)	48(2)
O(12)	−244(6)	8621(3)	9445(4)	76(2)
C(13)	−1325(6)	6660(3)	8905(4)	41(2)
O(13)	−2432(5)	6442(3)	8820(4)	65(2)
C(21)	4393(7)	6105(3)	9881(4)	45(2)
O(21)	5230(6)	6129(3)	10425(3)	69(2)
C(22)	2322(6)	5201(3)	9426(4)	44(2)
O(22)	1804(6)	4674(3)	9706(4)	74(2)
C(31)	2207(7)	8580(3)	7385(5)	46(2)
O(31)	2549(7)	9175(3)	7386(4)	82(2)
C(32)	−151(7)	7752(4)	7011(4)	47(2)
O(32)	−1287(5)	7889(3)	6802(4)	82(2)
C(41)	5385(6)	6585(3)	6765(4)	42(2)
O(41)	6450(5)	6694(3)	6468(4)	74(2)
C(42)	3303(7)	5617(4)	6357(4)	47(2)
O(42)	3146(7)	5158(3)	5851(3)	80(2)
C(43)	4437(6)	5573(3)	8119(4)	39(2)
O(43)	5247(5)	5088(3)	8104(3)	59(2)
C(44)	2515(7)	7300(4)	6301(4)	44(2)
O(44)	2615(6)	7375(3)	5550(3)	68(2)

Experimental Section

[$Ru_3(CO)_{12}$] was purchased from Aldrich plc. TLC separations were carried out on laboratory prepared 1 mm layers of silica [HF_{254} (type 60), Merck]. IR spectra were recoded on a Perkin-Elmer 983 spectrometer; ^1H, ^{13}C, and ^{31}P NMR were recorded for $CDCl_3$ solutions (unless stated otherwise) using a Varian VXR400 spectrometer. Analyses were determined in the analytical laboratory at UCL, and mass spectra were recorded on a VG ZAB-8E mass spectrometer.

Synthesis of Diphenyl-2-thienylphosphine (1). Using a method modified from that reported,[14] BuLi (0.0592 mol) in diethyl ether (37 mL) was added to a solution of thiophene (4.75 mL, 0.0593 mol) in dry diethyl ether (150 mL) under N_2 at −10 °C. The red mixture was stirred at 5 °C for 20 min and cooled to −70 °C, and a solution of Ph_2PCl (7 mL, 0.0382 mol) in dry diethyl ether (20 mL) was added dropwise. The colorless reaction mixture turned light brown on warming to 20 °C and was hydrolyzed after 30 min with saturated aqueous ammonium chloride (50 mL). The diethyl ether layer was separated, dried (Mg_2SO_4), and evaporated to give a light brown solid, which was recrystallized from ethanol to give off-white crystals (5.63 g, 0.0210 mol, 55%), mp 43−46 °C (lit. 36−38 °C[15] and 44−46 °C[13]). Anal. Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88; P, 11.54; S, 11.95. Found: C, 71.25; H, 4.84; P, 11.96; S, 11.67. The parent molecular ion was observed in the mass spectrum (EI). ^1H NMR: δ 7.58 (dd, J = 4.9, 0.9, 1H), 7.4−7.3 (m, 11H), 7.13 (ddd, J = 4.8,3.4,1.2, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.9 (d, J = 27.3 Hz), 137.8 (d, J = 8.1 Hz), 136.3 (d, J = 26.4 hz), 133.0 (d, J = 19.7 Hz), 132.0 (s), 128.6 (d, J = 37.9 Hz), 128.4 (s), 128.0 (d, J = 8.0 Hz). $^{31}P\{^1H\}$ NMR: δ −20.9 (s). These data differ somewhat from those reported.[13] The identity of **1** was checked by the preparation of [$Ph_2MePC_4H_3S$)]I by reaction of it with methyl iodide in methanol. Addition of diethyl ether gave colorless crystals of the phosphonium iodide (0.158 g, 48%). Anal. Calcd for $C_{17}H_{16}IPS$: C, 49.77; H, 3.93; P, 7.55; S, 7.81. Found: C, 50.24; H, 3.81; P, 7.70; S, 7.64. ^1H NMR: δ 8.16 (dt, J = 0.9, 4.7 Hz, 1H), 8.01 (ddd, J = 0.9, 3.8, 8.1 Hz, 1H), 7.82−7.77 (m, 6H), 7.70−7.66 (m, 4H), 7.46 (ddd, J = 2.1, 3.8, 4.7 Hz, 1H), 3.21 (d, J = 13.4 Hz, 3H).

Reaction of [$Ru_3(CO)_{12}$] with 1. A solution of [$Ru_3(CO)_{12}$] (0.0503 g, 7.87 × 10^{-5} mol) and the tertiary phosphine **1** (0.0215 g, 8.02 × 10^{-5} mol) in toluene (12.5 mL) was refluxed under nitrogen for 30 min to give a dark orange solution. Removal of the solvent and preparative TLC workup [SiO_2, eluent dichloromethane−light petroleum (bp 30−40 °C) (v/v = 1:20)] gave the cluster [$Ru_3H(Ph_2PC_4H_2S)(CO)_9$] (**2**) as orange crystals (0.0383 g, 4.65 × 10^{-5} mol, 59%), recovered

$[Ru_3(CO)_{12}]$ (0.0028 g, 4.38 × 10^{-6} mol), and $[Ru_3H(Ph_2PC_4H_2S)(CO)_8(Ph_2PC_5H_3S)]$ (**3**) (0.0081 g, 7.61 × 10^{-6} mol, 10%). Compound **2**: parent molecular ion observed in the FAB mass spectrum; ^1H NMR (27 °C) δ 7.27 (dd, J = 5.0, 1.6 Hz, 1H), 7.35 (d, J = 5.0Hz, 1H), broad signals at 7.55 (4H), 7.96 (2H) and 7.25 (4H), −17.65 (d, J = 18.4 Hz, 1H); (toluene-d_8, −20 °C): δ 7.83 (dd, J = 7.6, 11.4 Hz,2H), 7.13 (dd, J = 7.9, 11.2 Hz, 2H), 7.05−7.01 (m, 2H), 6.90−6.69 (m, 5H), 6.39 (d, J = 0.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (toluene-d_8, −70 °C) δ 175.5 (d, J = 32.1 Hz), 143.5 (d, J = 13.9 Hz), 134.9 (d, J = 35.0 Hz), 134.3 (d, J = 61.2 Hz), 133.8 (s), 133.2 (d, J = 11.5 Hz), 131.6 (d, J = 10.2 Hz), 131.1 (d, J = 8.2 Hz), 81.5 (d, J = 53.4); $^{31}P\{^1H\}$ NMR δ 44.0 (s); ν(CO) (cm^{-1}) (cyclohexane) 2086 s, 2058 s, 2032 vs, 2021 s, 2005 m, 1998 s, 1972 m. Compound **3**: Anal. Calcd for $C_{40}H_{26}O_8P_2Ru_3S_2$: C, 45.16; H, 2.46; P, 5.82; S, 6.03. Found: C, 43.94; H, 2.28; P, 6.08; S, 5.79. The parent molecular ion was observed in the FAB mass spectrum. ^1H NMR: δ 7.90 (m, 2H), 7.63 (m, 1H), 7.48 (m, 2H), 7.40 (m, 1H), 7.21 (m, 3H), 7.15−7.00 (m, 8H), 6.98 (d, J = 5.1 Hz, 1H), 6.92 (m, 2H), 6.75−6.66 (m, 4H), 6.44 (d, J = 3.7 Hz, 1H), −17.19 (dd, J = 20.1,10.0 Hz, 1H). $^{31}P\{^1H\}$ NMR: δ 31.4 (dd, J_{PP} = 24.8, J_{PH} = 5.8 Hz), 39.9 (dd, J_{PP} = 24.9, J_{PH} = 12.0 Hz) (residual coupling to the hydride ligand was observed). ν(CO) (cm^{-1}) (cyclohexane): 2071 s, 2067 sh, 2032 vs, 2018 s, 2000 m, 1991 m, 1968 m.

Substitution of 2 by Tertiary Phosphine 1. A solution of the nonacarbonyl cluster **2** (0.0488 g, 5.93 × 10^{-5} mol) and ligand **1** (0.0193 g, 7.19 × 10^{-5} mol) in hexane (25 mL) was refluxed under nitrogen for 1 h leading to a color change from orange to red. Removal of the solvent and preparative TLC workup [SiO_2, eluent dichloromethane−light petroleum (bp 30−40 °C) (v/v, 1:5)] gave one main orange band which yielded the product **3** as orange crystals (0.0417 g, 3.92 × 10^{-5} mol, 66%), characterized analytically and spectroscopically as the same compound described above.

Treatment of Cluster 2 with CO. A solution of the cluster **2** (0.0840 g, 1.02 × 10^{-4} mol) in heptane (20 mL) was saturated with CO gas (1 atm) and sealed in a glass tube which was heated at 80 °C for 42 h. The tube was opened, the solvent removed, and the residue treated by preparative TLC [SiO_2, eluent dichloromethane−light petroleum (bp 30−40 °C) (v/v, 1:20)] to give one main orange band which gave a red oil on removal of the solvent. This was characterized by IR, ^1H NMR, and MS as $[Ru_3(CO)_{11}(Ph_2PC_4H_3S)]$ (**4**) (0.0706 g, 8.03 × 10^{-5} mol, 79%). ν(CO) (cm^{-1}) (cyclohexane): 2098 s, 2048 s, 2033 m, 2026 m, 2017 vs, 2005 w, 1998 w, 1988 w, 1973 w. ^1H NMR: δ 7.64 (m, 1H), 7.48−7.39 (m, 10H), 7.35 (s, 1H) and 7.17 (m, 1H). $^{31}P\{^1H\}$ NMR: δ 21.0 (s). Compound **4** is moderately unstable in solution and in refluxing heptane under nitrogen converted quantitatively to cluster **2** in less than 20 min. There was no indication of any other product.

Thermolysis of Cluster 2. Cluster **2** was prepared *in situ* from $[Ru_3(CO)_{12}]$ (0.258 g, 4.03 × 10^{-4} mol) and ligand **1** (0.109 g, 4.06 × 10^{-4} mol) in toluene (75 mL) as described above, and the reflux was extended to 19 h. The solvent was removed and the mixture separated by column chromatography [SiO_2, eluent dichloromethane−light petroleum (bp 30−40 °C) (v/v 1:7.5 and then 1:2.5)]. The main bands were further separated by TLC [SiO_2, eluent dichloromethane−light petroleum (bp 30−40 °C) (v/v 1:20)] to give four compounds: red crystals of $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_2S)(CO)_{11}]$ (**5**) (0.0127 g, 1.41 × 10^{-5} mol, 4%), red crystals of $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_6H_4)(CO)_{11}]$ (**6**) (0.0208 g, 2.32 × 10^{-5} mol, 6%), cluster **2** (0.031 g, 3.76 × 10^{-5} mol, 9%), and a partially characterized compound (0.0243 g). Cluster **5**: Anal. Calcd for $C_{21}H_7O_{11}PRu_4S$: C, 27.95; H, 0.78; P, 3.43. Found: C, 28.02; H, 0.93; P, 3.15. ^1H NMR: δ 7.27 (d, J = 5.0 Hz, 1H), 7.21−7.14 (m, 3H), 6.97 (d, J = 5.0 Hz, 1H), 6.59 (dd, J = 6.7, 14.8 Hz, 2H). $^{31}P\{^1H\}$ NMR: δ −47.4 (s). ν(CO) (cm^{-1}) (cyclohexane): 2085 w, 2052 s, 2040 vs, 2031 s, 2021 w, 2003 m, 1985 m, 1851 w. Cluster **6**: ^1H NMR: δ 7.50−7.41 (m, 5H), 6.93 (m, 2H), 6.33 (m, 2H). $^{13}C\{^1H\}$ NMR: δ ca. 200 (broad singlet), 144.8 (d, J = 5.4 Hz), 132.9 (d, J = 13.9 Hz), 132.3 (s), 128.3 (m), 119.7 (d, J = 3.8 Hz). ν(CO) (cm^{-1}) (cyclohexane): 2084 w, 2050 s, 2041 vs, 2026 s, 2023 s, 2007 vw, 1996 m, 1986 w, 1979 w, 1826 w. The crystal structure was determined and shown to be essentially as reported previously. Partially characterized product: ^1H NMR δ 9.25 (dd, J = 2.1, 5.3 Hz, 1H), 7.69 (m, 2H), 7.53−7.38 (m, 8H), 6.51 (ddd, J = 2.3, 3.3, 5.4 Hz, 1H), 5.40 (dt, J = 10.3, 2.2 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 13.5 (s); ν(CO) (cm^{-1}) (cyclohexane) 2077 s, 2032 vw, 2046 vs, 2015 s, 2005 s, 1993 s, 1972 w, 1945 m.

X-ray Structure Determinations: Suitable crystals of compounds **2**, **3**, and **5** were examined by similar procedures. The crystal was fixed to a glass fiber mounted on a goniometer on a Nicolet R3v/m diffractometer. Cell constants and an orientation matrix were obtained from least squares refinement of 30 reflections ($13 \le 2\theta \le 26°$) for **2**, 28 reflections ($16 \le 2\theta \le 29°$) for **3**, and 35 reflections ($13 \le 2\theta \le 29°$) for **5**. Details of the crystal data for the three compounds are in Table 4. Data were collected by the $\omega-2\theta$ method for **2** and **5** and by the ω method for **3** in the 2θ ranges $5 \le 2\theta \le 45°$ for **2** and $5 \le 2\theta \le 50°$ for the other crystals. Three standard reflections monitored every 100 reflections showed only small variations in intensity. Lorentz and polarization corrections were applied as was an empirical absorption correction (Ψ-scan method). Maximum and minimum transmission coefficients: 1.000 and 0.798 for **2**, 0.976 and 0.787 for **3**, and 0.876 and 0.838 for **5**.

Structures were solved by direct methods and refined using difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, and H-atoms bonded to carbon were included in idealized positions and allowed to ride on the C atoms with C−H distances set at 0.96 Å and isotropic thermal parameters at 0.08 Å^3. The hydride ligand in **3** but not that in **2** was located.

Some disorder was found for the 2-thienyl group of the $Ph_2PC_4H_3S$ ligand of **3** which was refined in two orientations, that shown in Figure 2 and another with a 180° rotation about the P(2)−C(5) bond. The sulfur atoms for the two orientations S(2) and S(2A) were refined isotropically, and the corresponding carbon atoms C(6) and C(6A), similarly with thermal parameters fixed to be the same as the sulfur atoms. The best refined populations, 0.658 for S(2) and C(6) and 0.342 for S(2A) and C(6A), were fixed in the final cycles of refinement.

Some disorder was also found for the C_4H_2S ligand in cluster **5** which was found with the orientation as shown in Figure 6 and the reverse orientation with atoms S and C(3) replaced by atoms C(3A) and S(A). The refined populations of these disordered orientations were 0.79(1) and 0.21(1), respectively, and these values were fixed in the final cycles of refinement. Atoms S and C(3a) were refined with the same positional and thermal parameters and likewise atoms S(A) and C(3). No hydrogen atoms were included for the disordered C_4H_3S group of **3** or the C_4H_2S group of **5**.

All calculations were carried out on a MicroVax II computer running SHELXTL-PLUS.[38] The final refinement parameters are in Table 4, selected bond lengths and angles for **2**, **3**, and **5** are in Tables 1−3, and atomic coordinates for these compounds are in Tables 5−7. Anisotropic thermal parameters and full sets of bond lengths and angles have been deposited as Supporting Information.

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Supporting Information Available: Tables of crystal data, H atom positions and *U* values, anisotropic thermal parameters, and bond distances and angles (25 pages). Ordering information is given on any current masthead page.

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[38] Sheldrick, G. M. SHELXTL-PLUS, Package for crystal structure determination, University of Göttingen, Germany, 1986.