High-yield Syntheses of Sulphido Triruthenium Carbonyl Cluster Complexes containing Bis(diphenylphosphino)methane†

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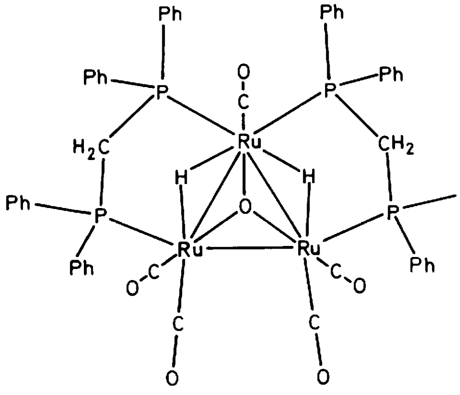
Reaction of thiophenol with $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ [dppm = bis(diphenylphosphino)methane] in toluene at 85 °C leads to the thiolato hydrido cluster complex $[Ru_3(\mu\text{-H})(\mu\text{-SPh})(CO)_8(\mu\text{-dppm})]$ in 75% yield. Prolonged heating under the same conditions gives the sulphido complex $[Ru_3(\mu_3\text{-S})(CO)_8(\mu\text{-dppm})]$ in 95% yield. This complex reacts with hydrogen to yield the hydrido species $[Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_7(\mu\text{-dppm})]$. The above sequence of reactions was repeated with $[Ru_3(CO)_8(\mu\text{-dppm})_2]$, leading directly to $[Ru_3(\mu_3\text{-S})(CO)_6(\mu\text{-dppm})_2]$ in 80% yield. Subsequent formation of $[Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_5(\mu\text{-dppm})_2]$ is achieved in the presence of hydrogen. These reactions show that co-ordination of thiophenol to dppm-substituted triruthenium clusters inhibits the oxidative cleavage of P–C bonds, while subsequent S–C bond cleavage gives sulphido–triruthenium complexes in high yield. The *X*-ray structure of the intermediate complex $[Ru_3(\mu\text{-H})(\mu\text{-SPh})(CO)_8(\mu\text{-dppm})]$ has been determined: triclinic, space group $P\bar{1}$, a = 12.361(1), b = 15.315(2), c = 11.591(2) Å, α = 92.04(1), β = 105.62(1), γ = 112.70(1)°, and Z = 2. The intensities of 5 629 reflections ($2 < 2\theta < 46°$) were measured, giving 4 701 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Final R' and R values were 0.032 and 0.041, respectively. The structure shows that the dppm ligand and the thiolato group span different edges of the cluster with the hydrido ligand bridging the same edge as the thiolato group. The Ru–Ru bond distances are 2.867(1), 2.837(1), and 2.835(1) Å.

Recent observations in the chemistry of various substituted ruthenium clusters involving bis(diphenylphosphino)methane (dppm) revealed that these complexes undergo facile conversions to phosphido-bridged species *via* cleavage of phosphorus–carbon bonds.[1] The relevance of reactions of this type to homogeneous catalyst deactivation has been stressed in a recent review article.[2]

In further studies of substituted trinuclear ruthenium complexes, we found that degradation of the dppm ligand is prevented whenever a face-bridging heteroatom is present. Typically, dppm ligands do not experience P–C bond cleavage in chemical reactions of the oxotriruthenium cluster $[Ru_3(\mu\text{-H})_2(\mu_3\text{-O})(CO)_5(dppm)_2]$ (**1**), even under drastic conditions.[3]



(**1**)

In parallel studies,[4] complex (**1**) proved to be an efficient catalyst precursor in test reactions such as the isomerisation of hexane (under ambient conditions) or the hydrogenation of cyclohexene. For comparative purposes, we were led to synthesize relevant complexes involving a different face-bridging heteroatom and a variable number of dppm ligands. We present here the syntheses and characterization of those complexes which involve sulphur as a face-bridging heteroatom. Thermal reaction of thiophenol with dppm-substituted ruthenium cluster complexes is shown to be a direct and high-yield route to such species. The *X*-ray structure of one intermediate thiolatotriruthenium carbonyl hydride cluster is also reported.

Results and Discussion

Syntheses.—The ability of transition metal clusters to cleave C–S bonds,[5,6] discovered some time ago, is of importance to the desulphurization of fossil fuels.[7]

We used thiophenol as a source of sulphur to generate trinuclear sulphidoruthenium complexes from $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_8(\mu\text{-dppm})_2]$. Earlier reports showed that in the case of $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os), the scope of such a reaction is limited by the following problems. (*i*) Typically, the formation of arenethiolatotrimetal carbonyl hydride complexes $[M_3(\mu\text{-H})(\mu\text{-SR})(CO)_{10}]$ or $[M_3(\mu\text{-H})(\mu_3\text{-SR})(CO)_9]$ is not quantitative, also leading to mononuclear, dinuclear, or polymeric complexes.[8–12] (*ii*) Subsequent elimination of benzene from these species is poorly selective. For instance, the thermal decomposition of the arenethiolato–osmium carbonyl hydride cluster $[Os_3(\mu\text{-H})(\mu\text{-SR})(CO)_{10}]$ provides a variety of higher nuclearity sulphido–osmium carbonyl clusters,[13] and thus, photochemical elimination of benzene has been proposed as an alternative route to sulphido–trimetal complexes.[14]

Although in the case of phosphine-substituted ruthenium clusters, P–C bond cleavage might be expected to compete with S–C bond cleavage, we found that the presence of thiophenol

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

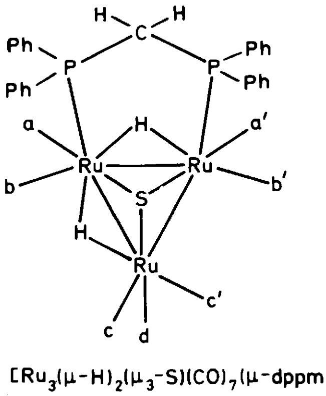
inhibits such cleavage, a feature also recently mentioned in a brief communication.[15]

Thermal reaction of thiophenol with $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ proceeded cleanly in toluene to afford $[Ru_3(\mu\text{-H})(\mu\text{-SPh})(CO)_8(\mu\text{-dppm})]$ (**2**) selectively. This is in sharp contrast with the related reaction of 7-thiabicyclo[4.1.0]heptane with $[Ru_3(CO)_{12}]$, which gave $[\{Ru(CO)_3(\mu\text{-SC}_6H_{10})\}_n]$.[16] Clearly, the dppm ligand is highly efficient in preserving the trinuclear metal framework. The subsequent step of the reaction, *i.e.* the thermal elimination of benzene, proceeded even more cleanly to afford the sulphido complex $[Ru_3(\mu_3\text{-S})(CO)_8(\mu\text{-dppm})]$ (**3**) in 95% yield. It should be noted that oxidative cleavage of the C–S bond has occurred without CO evolution. As already observed in the case of P–C bond cleavage,[1] the S–C bond cleavage reaction does not seem to require ligand dissociation. Although the possibility that CO would dissociate at an intermediate step cannot be excluded, we believe that such a process would not be quantitatively reversible.

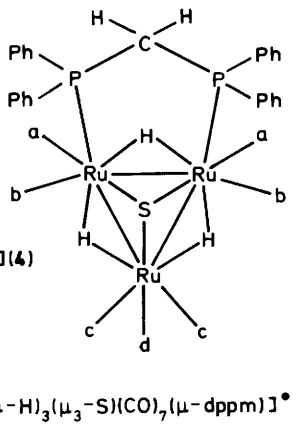
Reaction of either (**2**) or (**3**) with hydrogen gave the new hydrido sulphido cluster complex $[Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_7(\mu\text{-dppm})]$ (**4**); the unsubstituted analogues of (**4**) were previously prepared by direct reaction of $[Ru_3(CO)_{12}]$ with H_2S.[17,18]

The sequence of reactions described above was repeated with $[Ru_3(CO)_8(\mu\text{-dppm})_2]$. The intermediate thiolato complex was not detected in this case, and the sulphido carbonyl complex $[Ru_3(\mu_3\text{-S})(CO)_6(\mu\text{-dppm})_2]$ (**5**) was obtained directly in essentially quantitative yield. Subsequent reaction with hydrogen gave $[Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_5(\mu\text{-dppm})_2]$ (**6**).

Spectroscopic Characterization of the Complexes.—For complex (**2**), n.m.r. spectra provided experimental evidence that the thiolato group and the dppm ligand are spanning different edges of the metal triangle. This was inferred from the inequivalence of phosphorus nuclei (which also ruled out the possibility of a face-bridging thiolato group[12]) and subsequently confirmed by the *X*-ray structure (see below). Complexes (**3**) and (**5**) are substituted analogues of $[M_3(\mu_3\text{-S})(CO)_{10}]$ (M = Fe,[19] Ru,[12] or Os[14]). Our spectroscopic data are consistent with the structure established for such complexes. Notably, the i.r. spectrum of complex (**3**) exhibits a splitting of the bridging ν(CO) band, a feature previously noticed for $[Fe_3(\mu_3\text{-S})(CO)_{10}]$,[19] and related to the existence of valence isomeric forms involving μ_3-CO and μ-CO in equilibrium. Complex (**5**) is isostructural with $[Ru_3(\mu_3\text{-O})(CO)_6(\mu\text{-dppm})_2]$.[20]



$[Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_7(\mu\text{-dppm})]$(**4**)



$[Ru_3(\mu\text{-H})_3(\mu_3\text{-S})(CO)_7(\mu\text{-dppm})]^+$

Complexes (**4**) and (**6**) are substituted analogues of $[M_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_9]$ (M = Ru[18,21] or Os[14]). A detailed n.m.r. study of (**4**) was made. At low temperature, the ^1H spectrum showed two independent hydride signals, one corresponding to a hydride in a *trans* position relative to a phosphorus atom [*J*(P–H) = 34 Hz], and the second corresponding to a hydride in a *cis* position [*J*(P–H) *ca.* 3 Hz]. The magnetic inequivalence of the carbonyl groups a and a′, b and b′, c and c′ respectively observed in the low-temperature ^{13}C spectrum is attributed to the position of the hydrides, disturbing the mirror-plane symmetry of the molecule. (The four doublets are attributed to carbonyl groups a, a′, b, and b′, in *cis* positions relative to phosphorus atoms, while the three singlets are assigned to c, c′, and d, attached to the unique ruthenium atom.) The occurrence of an additional hydride ligand in the acidified product $[Ru_3(\mu\text{-H})_3(\mu_3\text{-S})(CO)_7(dppm)]^+$ restores the equivalence of the above mentioned carbonyls, which then give four signals with multiplicities of 2 (a), 2 (b), 2 (c), and 1 (d). At ambient temperature, the ^1H spectrum of (**4**) shows coalescence of the hydride signals, indicating the mobility of these ligands on the metal triangle.

Description of the Structure of $[Ru_3(\mu\text{-H})(\mu\text{-SPh})(CO)_8(\mu\text{-dppm})]$ (**2**).—The geometry of complex (**2**) is shown in the Figure. Selected interatomic distances and bond angles are listed in Tables 1 and 2 respectively. The structure shows that the dppm ligand and the thiolato group are spanning two different edges of the cluster. Although the dppm ligand occupies equatorial co-ordination sites in the parent complex $[Ru_3(CO)_{10}(dppm)]$,[22] a shift of the phosphorus atom P(1) towards a semi-axial position is observed here. This may be attributed to a stereochemical effect of the adjacent sulphido bridge. The hydride ligand, directly located in this structure, occupies the same edge as the thiolato group, and is approximately *trans* to both P(1)–Ru(1) and C(8)–Ru(3). The corresponding metal–metal bond Ru(1)–Ru(3) [2.867(1) Å] is only slightly elongated with respect to Ru(1)–Ru(2) [2.837(1) Å] and Ru(2)–Ru(3) [2.835(1) Å], as seen in related species.[11,23] The *exo* conformation of the phenyl group about sulphur disfavours any interaction between the phenyl ring and the metal centre Ru(2). This would support the idea that

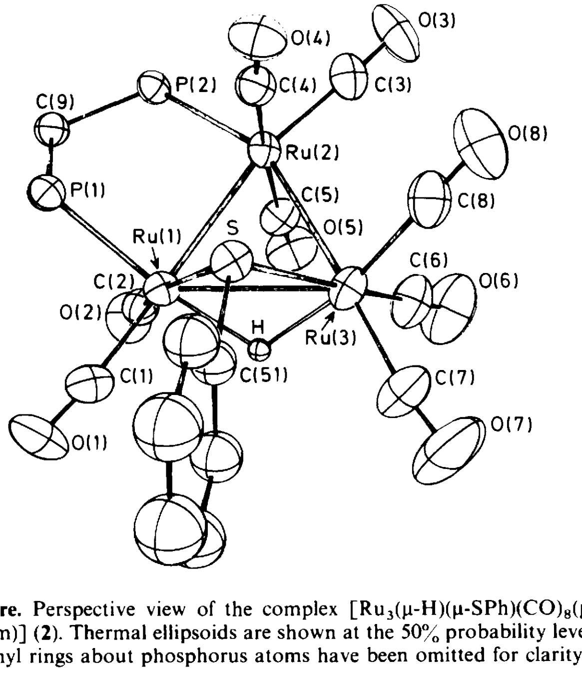


Figure. Perspective view of the complex $[Ru_3(\mu\text{-H})(\mu\text{-SPh})(CO)_8(\mu\text{-dppm})]$ (**2**). Thermal ellipsoids are shown at the 50% probability level. Phenyl rings about phosphorus atoms have been omitted for clarity

Table 1. Selected interatomic distances (Å) for $[Ru_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(\mu\text{-}dppm)]$ (**2**) with e.s.d.s in parentheses

Ru(1)–Ru(2)	2.837(1)	Ru(1)–Ru(3)	2.867(1)
Ru(2)–Ru(3)	2.835(1)		
Ru(1)–P(1)	2.309(1)	Ru(2)–P(2)	2.331(1)
Ru(1)–S	2.395(1)	Ru(3)–S	2.387(1)
Ru(1)–H	1.84(3)	Ru(3)–H	1.86(3)
P(1)–C(9)	1.834(4)	P(2)–C(9)	1.845(4)
P(1)–C(11)	1.827(4)	P(2)–C(31)	1.835(4)
P(1)–C(21)	1.833(4)	P(2)–C(41)	1.831(4)
Ru(1)–C(1)	1.907(5)	Ru(1)–C(2)	1.873(4)
Ru(2)–C(3)	1.892(5)	Ru(2)–C(4)	1.944(4)
Ru(2)–C(5)	1.925(4)	Ru(3)–C(6)	1.896(5)
Ru(3)–C(7)	1.916(5)	Ru(3)–C(8)	1.892(5)
C(1)–O(1)	1.135(5)	C(5)–O(5)	1.134(4)
C(2)–O(2)	1.147(4)	C(6)–O(6)	1.134(5)
C(3)–O(3)	1.135(5)	C(7)–O(7)	1.136(5)
C(4)–O(4)	1.132(4)	C(8)–O(8)	1.134(5)

Table 2. Selected bond angles (°) for $[Ru_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(\mu\text{-}dppm)]$ (**2**)

Ru(2)–Ru(1)–Ru(3)	59.61(1)	Ru(1)–Ru(2)–Ru(3)	60.73(1)
Ru(2)–Ru(3)–Ru(1)	59.66(1)		
Ru(3)–Ru(1)–P(1)	136.63(3)	Ru(3)–Ru(2)–P(2)	158.86(3)
Ru(1)–Ru(2)–P(2)	93.22(3)	Ru(2)–Ru(1)–P(1)	86.23(3)
Ru(2)–Ru(1)–C(1)	175.3(1)	Ru(3)–Ru(2)–C(5)	83.4(1)
Ru(3)–Ru(1)–C(1)	119.0(1)	Ru(1)–Ru(2)–C(5)	83.4(1)
Ru(2)–Ru(1)–C(2)	90.5(1)	Ru(1)–Ru(3)–C(6)	116.1(1)
Ru(3)–Ru(1)–C(2)	113.4(1)	Ru(2)–Ru(3)–C(6)	89.9(1)
Ru(3)–Ru(2)–C(3)	107.5(1)	Ru(1)–Ru(3)–C(7)	117.7(1)
Ru(1)–Ru(2)–C(3)	167.6(1)	Ru(2)–Ru(3)–C(7)	176.7(1)
Ru(3)–Ru(2)–C(4)	87.9(1)	Ru(1)–Ru(3)–C(8)	131.1(1)
Ru(1)–Ru(2)–C(4)	92.8(1)	Ru(2)–Ru(3)–C(8)	84.1(1)
C(1)–Ru(1)–C(2)	94.2(2)		
C(3)–Ru(2)–C(4)	90.5(2)	C(6)–Ru(3)–C(7)	93.2(2)
C(3)–Ru(2)–C(5)	91.6(2)	C(6)–Ru(3)–C(8)	93.5(2)
C(4)–Ru(2)–C(5)	171.3(2)	C(7)–Ru(3)–C(8)	96.9(2)
C(1)–Ru(1)–P(1)	92.7(1)	C(2)–Ru(1)–P(1)	90.9(1)
C(3)–Ru(2)–P(2)	98.3(2)	C(4)–Ru(2)–P(2)	96.2(1)
C(5)–Ru(2)–P(2)	91.9(1)		
C(1)–Ru(1)–S	94.7(1)	C(2)–Ru(1)–S	166.4(1)
C(6)–Ru(3)–S	168.7(1)	C(7)–Ru(3)–S	95.7(1)
C(8)–Ru(3)–S	92.3(1)		
Ru(1)–P(1)–C(9)	111.7(1)	Ru(2)–P(2)–C(9)	112.9(1)
Ru(1)–P(1)–C(11)	116.6(1)	Ru(2)–P(2)–C(31)	113.8(1)
Ru(1)–P(1)–C(21)	114.8(1)	Ru(2)–P(2)–C(41)	120.4(1)

orthometallation is not an intermediate step for the subsequent S–C bond-cleavage reaction.

In summary, the addition of thiophenol to dppm-substituted triruthenium clusters has a net inhibitor effect on the oxidative cleavage of P–C bonds. Alternatively, S–C bond cleavage is seen to occur selectively and quantitatively to bring about sulphido–triruthenium complexes. In these species, both the sulphido bridge and the intact dppm ligand play an important role in preserving the integrity of the metal core under the reported experimental conditions.

Experimental

General.—All reactions were carried out under a nitrogen atmosphere, using Schlenk line techniques. All organic solvents were freshly distilled prior to use. $[Ru_3(CO)_{12}]$,[24] $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$,[25] and $[Ru_3(CO)_8(\mu\text{-}dppm)_2]$[26] were prepared according to published procedures. Infrared spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrophotometer. These spectra were calibrated against water vapour absorptions. N.m.r. spectra were recorded on a Bruker WM 250 instrument; ^1H and ^{13}C chemical shifts (δ/p.p.m.) are downfield from external $SiMe_4$, ^{31}P chemical shifts (δ/p.p.m.) downfield from external H_3PO_4.

Synthesis of $[Ru_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(\mu\text{-}dppm)]$ (**2**).—$[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ (200 mg, 0.21 mmol) and a slight excess of thiophenol (21 μl) were dissolved in toluene (30 cm^3). The solution was heated at 95 °C for 40 min. The solvent was then evaporated to dryness under vacuum. The solid residue was chromatographed on silica gel (Kieselgel 60, Merck, art. 7734). Elution with heptane separated traces of $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$; further elution with toluene gave the orange complex (**2**) (160 mg, 75%) (Found: C, 44.8; H, 2.35. $C_{39}H_{28}O_8P_2Ru_3S$ requires C, 45.8; H, 2.75%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 065vs, 2 022s, 1 995vs, br, 1 962m, and 1 935 (sh) cm^{-1}. N.m.r.: δ_H (250 MHz, CD_2Cl_2) 7.8—7.1 (25 H, m, Ph), 4.51 (2 H, ABXY pattern, CH_2), and −14.37 [1 H, dd, $^2J(P^1\text{–}H) = 34.4$, $^3J(P^2\text{–}H) = 3.4$ Hz]; δ_P (101.270 MHz, CD_2Cl_2) 23.7 [P^1, d, $J(P\text{–}P) = 44.1$ Hz], and 16.4 (P^2, d).

Synthesis of $[Ru_3(\mu_3\text{-}S)(CO)_8(\mu\text{-}dppm)]$ (**3**).—Thermolysis of (**2**) (200 mg, 0.20 mmol) took place at 85 °C in toluene solution (30 cm^3) for 2 h. After evaporation of the solvent under vacuum, the solid residue was chromatographed on silica gel, and the new complex (**3**) eluted with dichloromethane, in essentially quantitative yield (176 mg, 95%) (Found: C, 45.35; H, 2.65. $C_{33}H_{22}O_8P_2Ru_3S$ requires C, 45.85; H, 2.35%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 070s, 2 023vs, 2 000m, 1 975 (sh), 1 710br, and 1 675 (sh) cm^{-1}. N.m.r.: δ_H (250.13 MHz, CD_2Cl_2) 7.9—7.1 (20 H, m, Ph) and 4.51 [2 H, ABX_2 pattern, CH_2, $\Delta\nu = 125$ Hz, $J(H\text{–}H) = 13.7$, $J(P\text{–}H) = 23.5$ Hz]; δ_P (101.270 MHz, CD_2Cl_2) 30.16 (2 P, s, dppm).

Synthesis of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$ (**4**).—*Method* (*a*). Hydrogen was bubbled through a toluene solution (30 cm^3) of (**3**) (200 mg, 0.21 mmol) for 5 h at 85 °C. Chromatographic work-up of the reaction product resulted in a yellow fraction which eluted with toluene. The complex was subsequently characterized as $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$ (**4**) (111 mg, 57%).

Method (*b*). Reaction of (**2**) (200 mg) with hydrogen under analogous experimental conditions gave (**4**) in comparable yield (108 mg, 60%) (Found: C, 41.2; H, 3.85. $C_{32}H_{24}O_7P_2Ru_3S$ requires C, 41.9; H, 3.65%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 065s, 2 035s, 1 995vs, 1 985 (sh), and 1 940 (sh) cm^{-1}. N.m.r.: δ_H (250.13 MHz, CD_2Cl_2, 213 K) 7.8—7.2 (20 H, m, Ph), 4.51 [2 H, ABX_2 pattern, CH_2, $\Delta\nu = 165$ Hz, $J(H\text{–}H) = 13.7$, $J(P\text{–}H) = 23.5$ Hz], −17.5 (1 H, s, br, hydride), and −17.9 [1 H, d, $J(P\text{–}H) = 34$ Hz] (coalescence of the hydride signals occurs at ambient temperature); δ_P (101.270 MHz, CD_2Cl_2) 30.16 (2 P, s, dppm); $\delta_C(CO)$ (62.9 MHz, CD_2Cl_2, 183 K) 202.8 (1 C, s), 200.9 (1 C, s), 198.3 (1 C, s), 195.1 (1 C, d), 194.1 (1 C, d), 189.3 (1 C, d), and 188.2 (1 C, d). Complex (**4**) was acidified with CF_3COOH to give $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]^+$ whose ^1H and ^{13}C spectra were recorded: δ_H (250.13 MHz, CD_2Cl_2, 203 K) −17.99 (2 H, s, hydride), and −18.12 (1 H, s, hydride); $\delta_C(CO)$ (62.9 MHz, CD_2Cl_2, 203 K) 190.2 (2 C, s), 187.7 (2 C, s), 186.7 (1 C, s), and 182.6 (2 C, s).

Synthesis of $[Ru_3(\mu_3\text{-}S)(CO)_6(\mu\text{-}dppm)_2]$ (**5**).—$[Ru_3(CO)_8(\mu\text{-}dppm)_2]$ (300 mg, 0.23 mmol) and excess of

Table 3. Final positional parameters with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Ru(1)	−0.030 06(4)	0.171 13(3)	0.283 25(4)	C(15)	−0.117 9(6)	0.471 6(4)	0.253 8(6)
Ru(2)	0.225 63(3)	0.291 33(3)	0.362 97(4)	C(16)	−0.121 1(5)	0.383 2(4)	0.217 9(5)
Ru(3)	0.107 70(4)	0.209 43(3)	0.535 55(4)	C(21)	−0.179 4(4)	0.198 2(3)	−0.006 8(4)
S	−0.027 3(1)	0.280 18(9)	0.438 4(1)	C(22)	−0.200 4(5)	0.110 0(4)	−0.065 2(5)
P(1)	−0.042 7(1)	0.258 28(9)	0.125 5(1)	C(23)	−0.306 2(5)	0.059 4(4)	−0.161 8(5)
P(2)	0.232 6(1)	0.313 27(9)	0.166 7(1)	C(24)	−0.390 4(5)	0.096 4(4)	−0.200 0(5)
C(1)	−0.204 1(5)	0.098 8(4)	0.235 1(5)	C(25)	−0.371 7(6)	0.182 7(4)	−0.146 9(6)
O(1)	−0.308 1(3)	0.058 9(3)	0.196 7(4)	C(26)	−0.266 1(5)	0.235 1(4)	−0.052 1(5)
C(2)	−0.002 4(5)	0.083 4(3)	0.191 2(5)	C(31)	0.306 3(4)	0.246 4(3)	0.106 9(5)
O(2)	0.011 3(4)	0.027 8(3)	0.134 5(4)	C(32)	0.253 7(5)	0.184 8(4)	−0.001 5(5)
C(3)	0.395 8(5)	0.358 4(4)	0.446 1(5)	C(33)	0.317 9(6)	0.136 6(5)	−0.036 7(6)
O(3)	0.498 8(4)	0.398 3(3)	0.492 1(4)	C(34)	0.428 7(6)	0.147 7(5)	0.035 2(6)
C(4)	0.198 0(4)	0.404 6(4)	0.398 9(5)	C(35)	0.483 3(6)	0.208 4(5)	0.140 7(6)
O(4)	0.194 3(3)	0.474 9(2)	0.425 7(4)	C(36)	0.422 9(5)	0.259 4(4)	0.177 4(5)
C(5)	0.242 2(5)	0.172 0(4)	0.346 7(5)	C(41)	0.316 3(4)	0.432 6(3)	0.134 2(5)
O(5)	0.260 6(4)	0.105 2(3)	0.340 1(4)	C(42)	0.318 1(5)	0.444 7(4)	0.015 9(5)
C(6)	0.216 2(6)	0.147 9(4)	0.581 6(5)	C(43)	0.381 3(5)	0.533 6(4)	−0.009 9(5)
O(6)	0.281 4(4)	0.112 0(3)	0.614 0(5)	C(44)	0.443 1(5)	0.611 3(4)	0.080 9(5)
C(7)	0.019 8(6)	0.155 3(4)	0.646 9(6)	C(45)	0.442 3(6)	0.600 7(4)	0.196 1(6)
O(7)	−0.021 4(5)	0.131 5(4)	0.723 0(4)	C(46)	0.378 3(5)	0.511 0(4)	0.224 2(5)
C(8)	0.220 2(5)	0.325 9(4)	0.638 6(5)	C(51)	−0.169 8(5)	0.234 8(4)	0.472 9(5)
O(8)	0.284 1(4)	0.396 2(3)	0.700 8(4)	C(52)	−0.234 6(5)	0.138 1(4)	0.478 8(5)
C(9)	0.078 3(4)	0.273 4(4)	0.055 0(4)	C(53)	−0.347 4(6)	0.111 5(5)	0.501 6(6)
C(11)	−0.039 3(4)	0.376 7(3)	0.161 0(4)	C(54)	−0.392 4(7)	0.178 0(5)	0.517 2(7)
C(12)	0.045 8(5)	0.459 8(4)	0.138 6(5)	C(55)	−0.327 3(6)	0.272 4(5)	0.513 5(6)
C(13)	0.049 3(6)	0.548 2(4)	0.177 3(6)	C(56)	−0.215 0(5)	0.302 1(4)	0.491 6(5)
C(14)	−0.032 0(6)	0.552 7(4)	0.233 5(6)	H	0.009(4)	0.108(3)	0.409(4)

thiophenol (60 µl, 0.975 mmol) were dissolved in octane (30 cm^3) with stirring. The solution was heated at 95 °C for 3 h and a yellow precipitate appeared. The solvent was then evaporated to dryness under vacuum. The solid residue was chromatographed on silica gel. Elution with dichloromethane gave the yellow complex (**5**) (236 mg, 80%) (Found: C, 52.75; H, 3.60. $C_{56}H_{44}O_6P_4Ru_3S$ requires C, 52.85; H, 3.50%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 010vs, 1 978m, 1 900s, and 1 710w cm^{-1}. N.m.r.: δ_H [250.13 MHz, $(CD_3)_2CO$] 7.7—6.9 (40 H, m, Ph), and 3.74 [4 H, quartet with superimposed phosphorus coupling, CH_2, $\Delta\nu$ 77.5 Hz, J(H–H) = 14.0 Hz]; δ_P (101.270 MHz, CD_2Cl_2) 29.15 [4 P, AA′XX′ pattern, $\Delta\nu$ = 590 Hz, J(A–A′) = 103.2, J(A–X) = J(A′–X′) = 164.5, J(A–X′) = 30.6, J(X–X′) = 38.1 Hz].

Synthesis of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_5(\mu\text{-dppm})_2]$ (**6**).—Hydrogen was bubbled through a xylene solution (30 cm^3) of (**5**) (300 mg) for 18 h at 135 °C. Chromatographic work-up of the reaction product afforded a yellow fraction which eluted with dichloromethane. The complex was subsequently characterized as $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_5(\mu\text{-dppm})_2]$ (**6**) (205 mg, 70%) (Found: C, 53.3; H, 3.8. $C_{55}H_{46}O_5P_4Ru_3S$ requires C, 53.0; H, 3.70%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 003vs, 1 950s, br, and 1 933 (sh) cm^{-1}. N.m.r.: δ_H [250.13 MHz, $(CD_3)_2CO$, 292 K] 7.8—6.8 (40 H, m, Ph), 3.5 [4 H, quartet with superimposed phosphorus coupling, CH_2, $\Delta\nu$ = 138 Hz, J(H–H) = 12.8 Hz], and −18.0 (2 H, s, hydride); δ_P (101.270 MHz, CD_2Cl_2) 24.8 [4 P, AA′XX′ pattern, $\Delta\nu$ = 1 140 Hz, J(A–A′) = 70.0, J(A–X) = J(A′–X′) = 127.0, J(A–X′) = J(A′–X) = 10.0, J(X–X′) = 36.2 Hz].

X-*Ray Structure Analysis of* $[Ru_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(\mu\text{-dppm})]$ (**2**).—*Crystal data.* $C_{39}H_{28}O_8P_2Ru_3S$, M = 1 021.86, triclinic, space group $P\bar{1}$ (no. 2), a = 12.361(1), b = 15.315(2), c = 11.591(2) Å, α = 92.04(1), β = 105.62(1), γ = 112.70(1)°, U = 1 925 Å^3 [by least-squares refinement on diffractometer angles for 25 reflections in the range 22 < 2θ (Mo-K_α) <26° (λ = 0.710 7 Å)], Z = 2, D_c = 1.763 g cm^{-3}. Crystal dimensions (distances from faces to centre): 0.06 $(100,\bar{1}00)$ × 0.09 $(1\bar{2}0,\bar{1}20)$ × 0.14 $(\bar{1}02,10\bar{2})$ mm, µ(Mo-K_α) = 13.2 cm^{-1}, temperature 22 °C.

Data collection and processing.[1] Enraf Nonius CAD4 diffractometer, ω/θ scan mode with ω scan width (1.0 + 0.35 tanθ)°, ω scan speed 2° min^{-1}, graphite-monochromatized Mo-K_α radiation (take-off angle, 2.4°); 5 629 reflections measured (2 < 2θ < 46°), giving 4 701 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Intensities were corrected for absorption; minimum and maximum transmission factors 0.77 and 0.86. No intensity decay observed (see ref. 1 for full details of techniques used).

Structure analysis and refinement. Direct methods (location of Ru, P, and S atoms). The model was extended through a combination of Fourier-difference maps and full-matrix least-squares refinements. Carbon atoms of phenyl rings were given isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of methylene and phenyl groups were entered in idealized positions, and were not refined. The hydride ligand was located in a final Fourier-difference map, and its atomic co-ordinates were successfully refined, leading to a reasonable position. Final R' and R values were 0.032 and 0.041, respectively. Details of the programs and computer used and sources of scattering factor data are given in ref. 1. Refined atomic co-ordinates are listed in Table 3.

Acknowledgements

Financial support from C.N.R.S. is gratefully acknowledged. We also thank Johnson Matthey for the generous loan of ruthenium chloride, and G. Commenges for the careful recording of the n.m.r. spectra.

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Received 20*th January* 1986; *Paper* 6/142