A One Step Synthesis of Phosphine Substituted Sulphur Capped Clusters from Phosphine Sulphides: *X*-Ray Crystal Structures of $[Fe_3(CO)_8(\mu_2\text{-}CO)(\mu_3\text{-}S)(Ph_2PC_2Pr^i)]$ and $[Ru_3(CO)_8(\mu_3\text{-}S)_2(Ph_2PC_2Bu^t)]$

Graeme Hogarth,[a] Nicholas J. Taylor,[a] Arthur J. Carty,[a] and Andre Meyer[b]

[a] *Guelph-Waterloo Centre, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

[b] *Laboratoire de Chimie Organométallique, L'Université de Rennes, Campus de Beaulieu, Rennes 35042, Cedex, France*

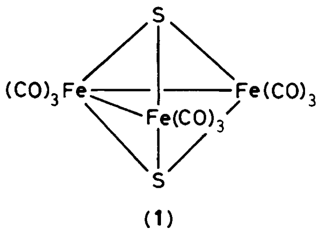
Reactions of phosphine sulphides with $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ occur *via* phosphorus–sulphur bond cleavage producing sulphido-capped trinuclear clusters; *X*-ray crystal structures of $[Fe_3(CO)_8(\mu_2\text{-}CO)(\mu_3\text{-}S)(Ph_2PC_2Pr^i)]$ and $[Ru_3(CO)_8(\mu_3\text{-}S)_2(Ph_2PC_2Bu^t)]$ are described.

Sulphido carbonyl clusters continue to attract considerable attention not only on account of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis.[1] Features of the chemistry of these molecules which are currently of interest include the mechanisms and sites of substitution as well as the modification of reactivity accompanying carbonyl replacement by donor ligands.

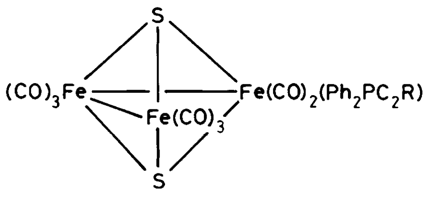
Phosphine substituted sulphido clusters have generally been prepared by reactions of phosphines with preformed sulphido clusters. We describe herein a direct route to these molecules involving the desulphurisation of readily available phosphine sulphides. This method offers a number of advantages including the synthesis of clusters previously accessible only in small yields, and in some cases, site specificity of carbonyl substitution.

Recently we described the synthesis of the first μ-phosphido-oxo (μ-$Ph_2P{=}O$) complexes of iron and ruthenium utilising the phosphine oxides, $Ph_2P(O)C_2R$.[2] During efforts to prepare the corresponding μ-$Ph_2P{=}S$ species, reactions of the phosphine sulphides, $Ph_2P(S)C_2R$ (R = Ph, Bu^t, and Pr^i), with $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ were carried out.

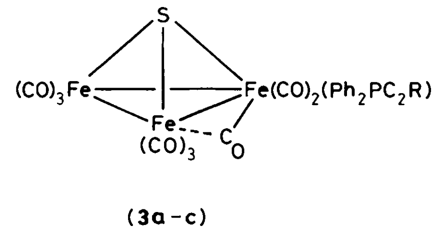
Treatment of $Fe_2(CO)_9$ with $Ph_2P(S)C_2R$ at room temperature led, after 3 h, to the isolation of three products: $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (**1**)[3] (21—48%), $[Fe_3(CO)_8(\mu_3\text{-}S)_2(Ph_2PC_2R)]$ (**2a—c**) (17—39%), and $[Fe_3(CO)_8(\mu_2\text{-}CO)$-



(1)



(2a-c)



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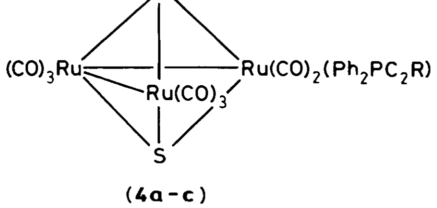
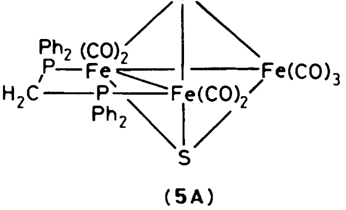
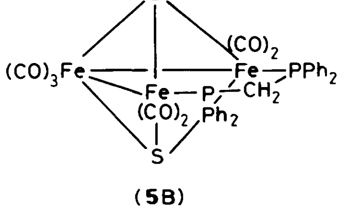


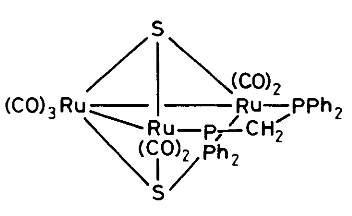
(4a-c)



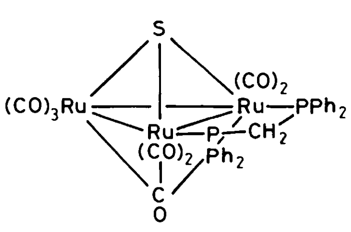
(5A)



(5B)



(6)



(7)

a; R = Ph
b; R = Bu^t
c; R = Pr^i

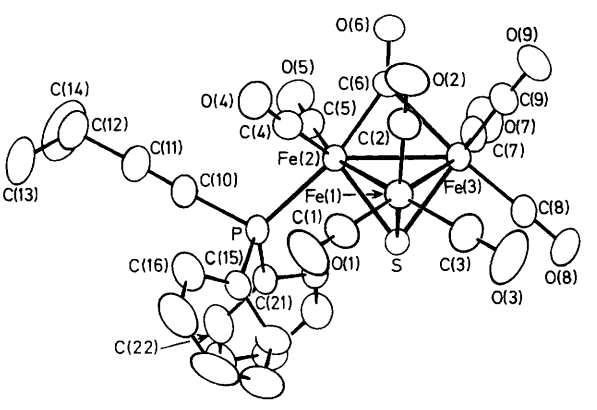


Figure 1. Molecular structure of (**3c**). Important bond lengths (Å) and angles (°) include: Fe(1)–Fe(2) 2.620(1), Fe(1)–Fe(3) 2.582(1), Fe(2)–Fe(3) 2.591(1), Fe(1)–S 2.179(1), Fe(2)–S 2.196(1), Fe(3)–S 2.201(1), Fe(2)–P 2.238(2), Fe(2)–C(6) 1.895(5), Fe(3)–C(6) 2.142(6), P–C(10) 1.744(6), P–C(15) 1.816(5), P–C(21) 1.806(5); P–Fe(2)–C(6) 166.6(2), Fe(2)–Fe(3)–C(6) 46.0(2), Fe(3)–Fe(2)–C(6) 54.4(2).

$(\mu_3\text{-S})(\text{Ph}_2\text{PC}_2\text{R})]$ (**3a**—**c**) (15—46% yield).† The first two of these contain the relatively common $\text{Fe}_3(\mu_3\text{-S})_2$ core. Selective substitution of an 'open' metal site is found for complexes (**2a**—**c**) with the isolation of a single isomeric form. In contrast, the $\text{Fe}_3(\mu_3\text{-S})$ framework found in (**3a**—**c**) is rare, the only example previously reported being the 'parent' complex $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})]$, and this in low yield (*ca.* 5%).[4]

In order to confirm the nature of complexes (**3a**—**c**) and to elucidate the site of substitution, the molecular structure of $[\text{Fe}_3(\text{CO})_8(\mu_2\text{-CO})(\mu_3\text{-S})(\text{Ph}_2\text{PC}_2\text{Pr}^i)]$ (**3c**) was determined by an *X*-ray diffraction study, the results of which are summarised in Figure 1.‡ The structure indeed consists of a 'closed' triangle of metal atoms capped symmetrically by a single sulphur atom. However, unlike its parent molecule $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})]$, the remaining triangular face is not capped by a carbonyl, but rather is open, with the odd CO now semi-bridging a metal–metal bond [Fe(2)–C(6) 1.895(5), Fe(3)–C(6) 2.142(6) Å]. The phosphine ligand lies approximately *trans* to one arm of the semi-bridging carbonyl [P–Fe(2)–C(6) 166.6(2)°], presumably for steric reasons, and perhaps, significantly, it is this edge which is the shorter of the two. Thus, although the complexes (**3a**—**c**) are formally simple substitution products of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})]$, their structures more closely resemble those of the isoelectronic phosphinidine clusters which also contain a semi-bridging carbonyl moiety.[5]

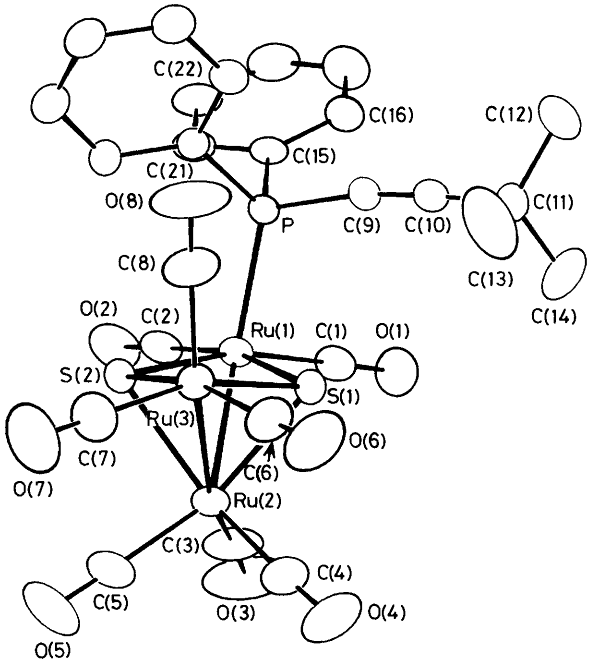


Figure 2. Molecular structure of (**4b**). Important bond lengths (Å) and angles (°) include: Ru(1)–Ru(2) 2.8275(5), Ru(2)–Ru(3) 2.7316(5), Ru(1)–S(1) 2.365(1), Ru(2)–S(1) 2.402(1), Ru(3)–S(1) 2.379(1), Ru(1)–S(2) 2.368(1), Ru(2)–S(2) 2.412(1), Ru(3)–S(2) 2.376(1), Ru(1)–P 2.284(1), P–C(9) 1.744(5), P–C(15) 1.821(5), P–C(21) 1.832(5); Ru(2)–Ru(1)–P 143.31(3).

Reaction of the phosphine sulphides with $\text{Ru}_3(\text{CO})_{12}$ (70 °C, $\text{NaPh}_2\text{CO}^\bullet$) led to the isolation of the complexes $[\text{Ru}_3(\text{CO})_8(\mu_3\text{-S})_2(\text{Ph}_2\text{PC}_2\text{R})]$ (**4a**—**c**) as the major product (36—56%),§ each of which was shown by ^{31}P n.m.r. spectroscopy to exist as a mixture of two isomers (ratio of approx. 6:1) inseparable by chromatography [(**4b**) δ 21.08 (major) and 9.56 (minor) p.p.m.]. However, the major isomer

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† The new complexes were characterised by elemental analyses and i.r. and n.m.r. (^{1}H and ^{31}P) spectra. *Selected data* for (**2a**): yellow crystals; ν(CO) (cyclohexane) 2076s, 2047m, 2040vs, 2016s, 2007m, 1992m, 1978m, and 1948w cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 8.28—6.74m; ^{31}P {^{1}H} n.m.r. (C_6D_6) δ 48.40 p.p.m. For (**3c**): brown crystals; ν(CO) (cyclohexane) 2069m, 2030sh, 2022s, 2006s, 2000sh, 1982m, 1968m, 1958sh, and 1866w cm^{-1}; ^{1}H n.m.r. (CDCl_3) δ 7.76—7.24 m (10H), 2.88 (doublet of septets, *J* 7.0 and 3.3 Hz, 1H), and 1.32 (d, *J* 7.0 Hz, 6H); ^{31}P{^{1}H} n.m.r. (CDCl_3) δ 40.52 p.p.m. For (**4b**): orange crystals; ν(CO) (cyclohexane) 2078s, 2046vs, 2028s, 2009s, 1992m, and 1981m cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 7.83—7.24m (10H) and 1.38s (9H); ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 21.08 (major) and 9.56 (minor) p.p.m. For (**5**): purple crystals; ν(CO) (cyclohexane) 2047s, 2004s, 1994m, 1977sh, and 1949m cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 8.01—6.85m, 4.01 (dd, *J* 11.6 and 7.6 Hz) (**5A**), and 2.72 (t, *J* 10.8 Hz) (**5B**); ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 76.01 (s) (**5B**), 66.52 (d, *J* 62.4 Hz) (**5A**), and 33.28 (d, *J* 62.4 Hz) (**5A**). For (**6**): orange crystals; ν(CO) (cyclohexane) 2055s, 2028sh, 2019s, 1992m, 1977m, and 1958m cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 7.26—6.73m (20H) and 3.79 (t, *J* 11.0 Hz, (2H); ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 61.53 p.p.m.

‡ *Crystal data* for (**3c**): $\text{Fe}_3\text{SPO}_9\text{C}_{26}\text{H}_{17}$, $M = 703.99$, monoclinic, $a = 17.078(4)$, $b = 10.031(2)$, $c = 18.290(5)$ Å, $\beta = 110.67(2)°$, $U = 2932(1)$ Å^3; space group $P2_1/c$; $Z = 4$; $D_c = 1.595$ g cm^{-3}; $F(000) = 1416$; $T = 294 \pm 1$ K; $\mu(\text{Mo-}K_\alpha) = 16.74$ cm^{-1}. Data were collected by the θ–2θ method from a crystal of dimensions 0.25 × 0.25 × 0.30 mm mounted on a Syntex $P2_1$ diffractometer. The structure was solved by Patterson and Fourier techniques using 2600 observed data [$I \geqslant 3\sigma(I)$] from 3863 ($2\theta \leqslant 45°$) measured reflections. The structure was refined by full-matrix least-squares methods to $R = 0.033$, $R_w = 0.035$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Crystal data* for (**4b**): $\text{Ru}_3\text{S}_2\text{PO}_8\text{C}_{26}\text{H}_{21}$, $M = 857.74$, triclinic, $a = 9.442(1)$, $b = 13.902(2)$, $c = 14.360(1)$ Å, $\alpha = 74.76(1)$, $\beta = 79.29(1)$, $\gamma = 69.08(1)°$, $U = 1591.3(3)$ Å^3; space group $P\bar{1}$; $Z = 2$; $D_c = 1.790$ g cm^{-3}; $F(000) = 836$; $T = 294 \pm 1$ K; $\mu(\text{Mo-}K_\alpha) = 15.91$ cm^{-1}. Data were collected by the θ—2θ method from a crystal of dimensions 0.22 × 0.24 × 0.25 mm mounted on a Syntex $P2_1$ diffractometer. The structure was solved by Patterson and Fourier techniques using 4406 ($I \geqslant 3\sigma(I)$] observed data (5640 measured, $2\theta \leqslant 50°$). The structure was refined by full-matrix least-squares methods to a conventional *R* of 0.029 ($R_w = 0.033$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

crystallised preferentially; thus, to elucidate the site of substitution, its structure was determined by *X*-ray diffraction (Figure 2).‡

The molecule consists of a triangle of ruthenium atoms capped above and below the plane by sulphur. Two of the ruthenium–ruthenium distances [Ru(1)–Ru(2) and Ru(2)–Ru(3)], are bonding, while the third [Ru(1)–Ru(3) 3.6293(5) Å] represents a non-bonding interaction. The site of phosphine substitution is equatorial to the tri-ruthenium plane and at an 'exterior' metal atom, Ru(1). A further feature is the significant difference in the two metal–metal bond lengths, that *trans* to phosphorus being the longer by almost 0.1 Å. A similar, though less pronounced effect, has been found in $[Os_3(CO)_8(\mu_3\text{-}S)_2(Ph_2PMe)]$[6] and is attributed to a *trans* influence strongly dominated by sigma-inductive effects.

The extrusion of sulphur from phosphine sulphides is not limited to monophosphines; both $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ react in a similar fashion with $[Ph_2P(S)]_2CH_2$. The former results in the isolation of (**1**) (10%) and its disubstituted analogue $[Fe_3(CO)_7(\mu_3\text{-}S)_2(\mu_2\text{-dppm})]$ [dppm = bis(diphenylphosphino)methane] (**5**) (35%) which exists as a 1 : 1 mixture of two isomers, one with the diphosphine spanning an Fe–Fe bond (**5A**) and the second with the desulphurised ligand bridging a non-bonding metal–metal vector (**5B**).† Interestingly, although dppm reacts directly with (**1**), exclusive formation of (**5B**) is found (56%). With $Ru_3(CO)_{12}$ two products are formed: $[Ru_3(CO)_7(\mu_3\text{-}S)_2(\mu_2\text{-dppm})]$ (**6**) (42%), solely in the form in which dppm spans the non-bonded metal–metal edge, and surprisingly, the known mono-capped complex $[Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu_2\text{-dppm})]$ (**7**)[7] (16%).

Although mechanistic details have not been explored, initial co-ordination of the ligand through a lone pair on sulphur is anticipated,[8] followed by extrusion of sulphur. In support of this hypothesis direct selenium extrusion from a Pt–Se–P system has been recently reported,[9] however, the possibility that P–S bond cleavage involves more than one metal centre cannot, as yet, be discounted. We are currently involved in extending this extrusion phenomenon to other phosphines, phosphites, arsines, and selenides while studying the reactivity of previously inaccessible clusters.

We are grateful to the S.E.R.C. (G. H.) and the National Sciences and Engineering Research Council (grants to A. J. C. and an International Scientific Exchange Award to A. M.) for financial support.

Received, 23rd December 1987; Com. 1841

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