Trinuclear Aggregates of Rhodium and Iridium supported by Thiolate Bridges: Synthesis and Crystal Structure *

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A high-yield synthesis of the complexes $[\{M(\mu\text{-SPh})(\text{diolefin})\}_2]$ [M = Rh or Ir; diolefin = cycloocta-1,5-diene (cod), norborna-1,4-diene (nbd), or tetrafluorobenzobarrelene (tfbb)] has been developed. Addition of the solvated species $[M(\text{diolefin})(Me_2CO)_x]^+$ to the binuclear complexes $[\{M(\mu\text{-SPh})(\text{diolefin})\}_2]$ affords the homotrinuclear aggregates $[M_3(\mu_3\text{-SPh})_2(\text{diolefin})_3]^+$ (M = Rh, diolefin = cod, nbd, or tfbb, M = Ir, diolefin = cod) in quantitative yield. This type of reaction can be used for the synthesis of the cations $[M_3(\mu_3\text{-SPh})_2(\text{diolefin})_2(\text{diolefin}')]^+$, having different diolefins, and $[M_2M'(\mu_3\text{-SPh})_2(\text{diolefin})_3]^+$, containing different metal atoms and diolefins. In this way, homo- and hetero-trinuclear complexes of the Rh_3^{3+}, Ir_3^{3+}, $IrRh_2^{3+}$ and Ir_2Rh^{3+} cores have been isolated. Reaction of $[M_3(\mu_3\text{-SPh})_2(\text{diolefin})_3]^+$ (M = Rh or Ir) with carbon monoxide leads to breakdown of the aggregates to give $[\{M(\mu\text{-SPh})(CO)_2\}_2]$. The new compounds have been characterized by analytical, spectroscopic (^{1}H NMR) and, particularly $[Rh_3(\mu_3\text{-SPh})_2(\text{cod})_3][ClO_4]$, by X-ray diffraction techniques. Crystals of the latter are orthorhombic, space group *Pbca* (no. 61), a = 14.818(1), b = 17.084(1), c = 27.443(1) Å, Z = 8, R = 0.0326 and R' = 0.0344 for 2908 unique reflections with $F \geq 6.0\sigma(F)$. The cation $[Rh_3(\mu_3\text{-SPh})_2(\text{cod})_3]^+$ shows a triangular arrangement of rhodium atoms capped on each side by triply bridging phenylthio groups. Each rhodium atom completes a square-planar co-ordination being bonded to a cod molecule. The metal atoms are separated by non-bonding distances, 2.9797(8), 3.3697(7) and 3.4937(8) Å.

Parallel with the interest being shown in transition-metal sulfur chemistry, numerous compounds with thiolate ligands (RS^-) have been synthesized[1] and structurally characterized[2] in the past years. This interest stems in part from the relevance of such compounds as models of biologically redox-active metalloproteins,[3] of active catalysts of the hydrodesulfurization processes in the homogeneous phase[4] and in the study of sulfur poisoning of solid catalysts.[5]

Thiolates, as HS^- and S^{2-}, have been found to be versatile ligands, co-ordinating to one, two or three metals. The triple bridge co-ordinating mode (μ_3) is relatively rare and occurs in cages and clusters, which are formed in a spontaneous and uncontrolled way.[1,2] Two examples of a controlled synthesis recently found rely on the oxidative addition of a thiol (RSH) to a preformed triangular face in the clusters $[Pt_3(\mu_3\text{-CO})(\text{dppm})_3][PF_6]_2$[6] and $[Ru_3(CO)_{10}(\text{dppm})]$[7] [dppm = bis(diphenylphosphino)methane]; further cleavage of the C–S bond leads to the sulfido compounds $[Pt_3H(\mu_3\text{-S})(\text{dppm})_3][PF_6]$ and $[Ru_3(\mu_3\text{-S})(CO)_8(\text{dppm})]$. In a different approach, we have prepared trinuclear rhodium and iridium complexes using one lone electron pair on the sulfur in binuclear complexes bridged by N,S ligands to co-ordinate a third metallic fragment.[8] Trinuclear μ_3-bridged thiolate complexes could be built up in a controlled way using the ability of sulfur and its organic compounds to agglomerate metal atoms and the involvement of the five electrons of the thiolate ligand in co-ordination. Although there is a rich chemistry of binuclear thiolate complexes of rhodium and iridium[9] and some of them are outstanding catalysts for hydroformylation of olefins,[10] this is a promising and unexplored possibility in view of the few examples of trinuclear rhodium and iridium compounds containing sulfur.[11,12] Furthermore, one of the under-investigated fields is that of rhodium and iridium cluster compounds with ligands other than carbon monoxide.[13] We describe here the synthesis and structure of diolefin trinuclear complexes of rhodium and iridium with μ_3-bridged thiolate ligands.

Results and Discussion

Previous preparations of olefin rhodiumthiolate complexes involve either the replacement of carbonyl ligands in the complexes $[\{Rh(\mu\text{-SR})(CO)_2\}_2]$ by diolefins[14] or the reaction of $[\{Rh(\mu\text{-Cl})(\text{olefin})_2\}_2]$ with the appropriate thiol (RSH).[15,16] Higher yields are attained if the thallium salt of the thiol is used instead.[17] In this context, we have found that the complexes $[\{Rh(\mu\text{-SPh})(\text{diolefin})\}_2]$ {diolefin = cycloocta-1,5-diene (cod), norborna-1,4-diene (nbd) or tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene) (tfbb)} are isolated in almost quantitative yield by treating the appropriate compound $[\{Rh(\mu\text{-Cl})(\text{diolefin})\}_2]$ with the lithium salt of the thiol prepared *in situ*. The iridium compound $[\{Ir(\mu\text{-SPh})(\text{cod})\}_2]$ is also obtained in this way[18] although an alternative route for it has been described recently.[19]

The double-bridged thiolate binuclear complexes $[\{M(\mu\text{-SR})L_2\}_2]$ (M = Rh or Ir; L = monodentate ligand) can exist as *syn* and *anti* isomers (Fig. 1) because the M_2S_2 ring is not planar. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of the compound $[\{Rh(\mu\text{-SPh})(\text{cod})\}_2]$ (see Experimental section) is consistent with a *syn* isomer since both phenyl rings are equivalent. Its non-rigidity in solution, usual for these kind of compounds,[20] is associated with an inversion of the butterfly core M_2S_2 which makes the olefinic carbons equivalent. Dissociation of the diolefin does not occur in this movement since the coupling $^1J(C\text{–}Rh)$ is retained. These compounds containing diolefins as ancillary ligands are either the *syn-endo*[14,19] or the *syn-exo* isomer for polyfluorinated thiolate bridges[21] in the solid state. For our purpose, each sulfur atom in these structures has an

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

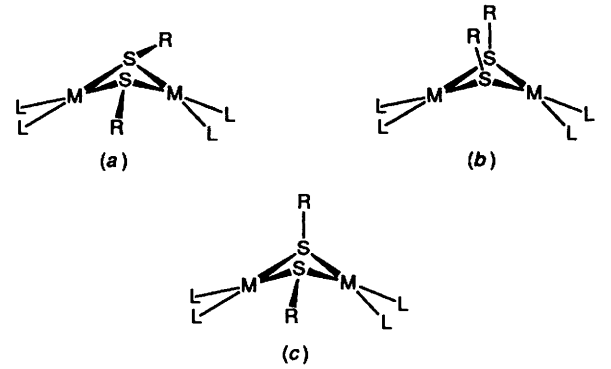

Fig. 1 Isomers for the binuclear thiolate complexes: (*a*) *syn-endo*, (*b*) *syn-exo* and (*c*) *anti*

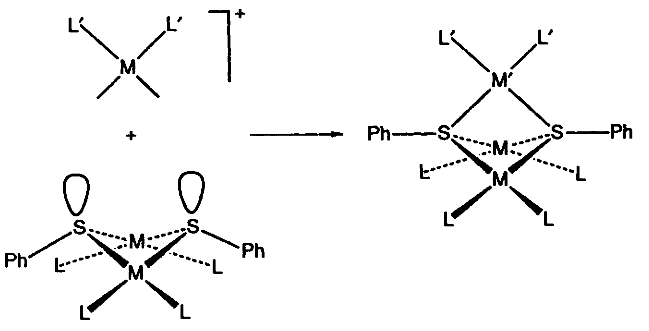

Fig. 2 Proposed mechanism of formation for the trinuclear complexes

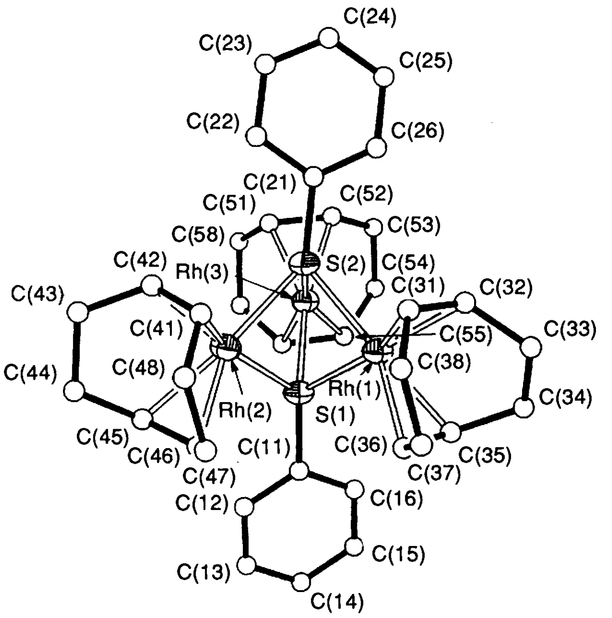

Fig. 3 Molecular representation of the cation of complex **1**, showing the atom numbering scheme

occupied orbital suitable for co-ordination. In particular, these two orbitals should be pointing to a position between the two sulfur atoms in the *syn-endo* structures, so that a metal fragment having two easily available *cis* positions can enter to form trinuclear complexes (Fig. 2). In this way, addition of the solvated species $[Rh(diolefin)(Me_2CO)_x]^+$ to the appropriate binuclear complex $[\{Rh(\mu\text{-}SPh)(diolefin)\}_2]$ in acetone gives yellow-orange solutions of the complexes $[Rh_3(\mu_3\text{-}SPh)_2(diolefin)_3]^+$ (diolefin = cod **1**, nbd **2** or tfbb **3**).

Whilst the rhodium solvent species $[Rh(diolefin)(Me_2CO)_x]^+$ can be easily prepared and handled, the corresponding iridium complex is oxidized by air. We have found that the solvated species $[M(diolefin)(Me_2CO)_x]^+$ (M = Rh or Ir), particularly the iridium complex, can be safely generated *in situ* by addition of the stoichiometric amount of tetrafluoroboric acid to an acetone solution of $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$. This reaction affords the 'Ir(diolefin)$^+$' moiety allowing the preparation of homo- and hetero-trinuclear complexes of iridium and rhodium described below. So, addition of $[Ir(cod)(Me_2CO)_x]^+$ to a solution of $[\{Ir(\mu\text{-}SPh)(cod)_2\}_2]$ gives the homotrinuclear complex $[Ir_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ **4**. Complexes **1**–**4** are isolated from these solutions as the perchlorate or tetrafluoroborate salts in good yields. Their formulation as trinuclear complexes is in accordance with microanalytical data and conductivity measurements in acetone or nitromethane (see Table 1), which are in the range described for 1:1 electrolytes. In order to confirm their formation and to compare their structures with those of other trinuclear clusters of rhodium, compound **1** was studied by single-crystal X-ray methods.

Diffraction-quality crystals of $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$ **1** were obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the compound. The crystal structure of **1** consists of the packing of discrete anions and cations separated by normal van der Waals contacts. A perspective view of the $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ cation is shown in Fig. 3. Significant bond distances and angles are listed in Table 2.

The cation is formed by a triangular arrangement of rhodium atoms capped on each side by two triply bridging phenylthio groups; each metal is additionally bound to two double bonds of a cycloocta-1,5-diene molecule. If one considers the centres of the double bonds of each cod ligand and the S atoms of the thiolate groups, each Rh atom is in a distorted square-planar environment. The highest deviations from the least-squares planes are 0.048(5) Å for Rh(1), 0.088(5) Å for Rh(2) and 0.193(6) Å for Rh(3). The cage skeleton, Rh_3S_2, suffers several distortions, resulting in loss of the ideal D_{3h} symmetry, due to the presence of two significantly longer Rh $\cdots$ Rh distances, Rh(1) $\cdots$ Rh(3) 3.3697(7) and Rh(2) $\cdots$ Rh(3) 3.4937(8) Å, compared to the third distance Rh(1) $\cdots$ Rh(2) 2.9797(8) Å, which is very similar to that [2.948(1) Å] observed in the related neutral dinuclear complex $[Rh_2(\mu\text{-}SMe)_2(cod)_2]$.[22] The real symmetry of the whole cation, including the cod molecules and the phenyl groups, is approximately C_{2v}. All the intermetallic distances are well over the range described for Rh–Rh bonds.[23] Only the Rh(1) $\cdots$ Rh(2) separation is indicative of a weak metal–metal interaction.[24]

Bearing in mind the structural aspects discussed above, the lack of metal–metal bonds and the square-planar metal environment, the cation could be described as an aggregate formed by three square-planar rhodium(I) units sharing the common edge defined by the bridging S atoms.

All the six Rh–S distances are significantly different, ranging from 2.322(2) to 2.400(2) Å. They compare well with those observed in related complexes of general formula $[Rh_2(\mu\text{-}SR)_2(cod)_2]$ [R = C_6F_5, 2.407; C_6HF_4, 2.398(1);[21] or Me, 2.349 Å[22]]. For these distances as for the intermetallic distances, the atom Rh(3) exhibits a peculiar behaviour, showing shorter Rh(3)–S distances, average 2.331(2) Å. compared to those observed for Rh(1) and Rh(2), average 2.369(2) and 2.392(2) Å, respectively. Considering the chemical preparation of **1**, starting from the neutral dinuclear complex $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$, all these structural parameters are consistent with the idea that the Rh(3)(cod) moiety corresponds to the fragment added to the starting material in the synthetic procedure. The stereochemistry of the sulfur atoms is tetrahedral, with a severe distortion arising from the bridging character of the S atom [mean Rh–S–Rh 88.2(1) and C–S–Rh 126.5(1)°]. Similar distorted-tetrahedral geometries for the μ_3-SR ligand have been observed for the trinuclear complex $[Ir_3(\mu_3\text{-}SBu^t)(\mu\text{-}SBu^t)(\eta\text{-}C_4F_6)(CO)_5(\eta\text{-}C_4F_6)]$,[25] and in the ruthenium clusters $[Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)]$[26] or $[Ru_3(\mu_3\text{-}SBu^t)(\mu_3\text{-}\eta^7\text{-}C_7H_7)(CO)_6]$.[27]

The planes of the phenyl rings are nearly perpendicular [85.0(2) and 81.4(2)°] to the Rh_3 triangle, and are not eclipsed

Table 1 Analytical and physical properties for the new complexes

Compound	Colour	Yield (%)	Analysis (%)[a] C	Analysis (%)[a] H	Λ_M/S cm^2 mol^{-1}
1 $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$	Orange	85	46.05 (45.45)	4.75 (4.85)	134[b]
2 $[Rh_3(\mu_3\text{-}SPh)_2(nbd)_3][ClO_4]$	Yellow	90	43.35 (43.90)	4.30 (3.80)	132[b]
3 $[Rh_3(\mu_3\text{-}SPh)_2(tfbb)_3][ClO_4]$	Yellow	80	44.00 (44.15)	2.45 (2.15)	87[c]
4 $[Ir_3(\mu_3\text{-}SPh)_2(cod)_3][BF_4]$	Red	85	35.75 (35.85)	4.00 (3.85)	130[b]
5 $[(cod)_2Rh_2(\mu_3\text{-}SPh)_2Rh(nbd)][ClO_4]$	Orange	82	44.40 (44.95)	4.85 (4.50)	95[c]
6 $[(cod)_2Rh_2(\mu_3\text{-}SPh)_2Rh(tfbb)][ClO_4]$	Yellow	80	44.30 (44.95)	3.70 (3.75)	137[b]
7 $[(nbd)_2Rh_2(\mu_3\text{-}SPh)_2Ir(cod)][BF_4]$	Red-brown	88	41.05 (41.00)	4.01 (3.85)	131[b]
8 $[(cod)_2Ir_2(\mu_3\text{-}SPh)_2Rh(tfbb)][BF_4]$	Orange-red	83	38.70 (38.90)	3.60 (3.25)	92[c]

[a] Calculated values are given in parentheses. [b] In acetone. [c] In nitromethane.

Table 2 Selected bond distances (Å) and angles* (°) for the complex $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$ **1**

Rh(1) ··· Rh(2)	2.9797(8)		
Rh(1) ··· Rh(3)	3.3697(7)	Rh(2) ··· Rh(3)	3.4937(8)
Rh(1)–S(1)	2.369(2)	Rh(1)–S(2)	2.369(3)
Rh(2)–S(1)	2.385(3)	Rh(2)–S(2)	2.400(2)
Rh(3)–S(1)	2.322(2)	Rh(3)–S(2)	2.339(2)
S(1)–C(11)	1.785(6)	S(2)–C(21)	1.776(6)
Rh(1)–C(31)	2.142(7)	Rh(2)–C(45)	2.155(7)
Rh(1)–C(32)	2.179(6)	Rh(2)–C(46)	2.141(7)
Rh(1)–C(35)	2.148(6)	Rh(3)–C(51)	2.136(8)
Rh(1)–C(36)	2.132(7)	Rh(3)–C(52)	2.153(7)
Rh(2)–C(41)	2.147(8)	Rh(3)–C(55)	2.157(8)
Rh(2)–C(42)	2.159(8)	Rh(3)–C(56)	2.147(7)
C(31)–C(32)	1.375(10)	C(45)–C(46)	1.397(11)
C(35)–C(36)	1.393(10)	C(51)–C(52)	1.370(11)
C(41)–C(42)	1.386(12)	C(55)–C(56)	1.383(12)
S(1)–Rh(1)–S(2)	72.1(1)	S(1)–Rh(2)–S(2)	71.3(1)
S(1)–Rh(1)–M(1)	170.0(2)	S(1)–Rh(2)–M(3)	168.6(1)
S(1)–Rh(1)–M(2)	98.4(2)	S(1)–Rh(2)–M(4)	99.2(2)
S(2)–Rh(1)–M(1)	101.7(2)	S(2)–Rh(2)–M(3)	101.8(1)
S(2)–Rh(1)–M(2)	169.4(1)	S(2)–Rh(2)–M(4)	170.0(2)
M(1)–Rh(1)–M(2)	87.1(2)	M(3)–Rh(2)–M(4)	87.0(2)
S(1)–Rh(3)–S(2)	73.5(1)	S(2)–Rh(3)–M(5)	99.5(2)
S(1)–Rh(3)–M(5)	170.5(2)	S(2)–Rh(3)–M(6)	172.1(2)
S(1)–Rh(3)–M(6)	100.1(2)	M(5)–Rh(3)–M(6)	87.4(2)
Rh(1)–S(1)–Rh(2)	77.6(1)	Rh(1)–S(2)–Rh(2)	77.3(1)
Rh(1)–S(1)–Rh(3)	91.9(1)	Rh(1)–S(2)–Rh(3)	91.4(1)
Rh(1)–S(1)–C(11)	126.0(2)	Rh(1)–S(2)–C(21)	127.4(2)
Rh(2)–S(1)–Rh(3)	95.9(1)	Rh(2)–S(2)–Rh(3)	95.0(1)
Rh(2)–S(1)–C(11)	129.4(2)	Rh(2)–S(2)–C(21)	132.5(2)
Rh(3)–S(1)–C(11)	123.1(2)	Rh(3)–S(2)–C(21)	120.3(2)
S(1)–C(11)–C(12)	120.4(5)	S(1)–C(21)–C(22)	120.3(5)
S(1)–C(11)–C(16)	117.9(5)	S(1)–C(21)–C(26)	118.7(5)
C(12)–C(11)–C(16)	121.6(6)	C(22)–C(21)–C(26)	120.8(6)
C(32)–C(31)–C(38)	125.6(7)	C(44)–C(45)–C(46)	123.4(7)
C(31)–C(32)–C(33)	124.8(6)	C(45)–C(46)–C(47)	126.8(7)
C(34)–C(35)–C(36)	125.3(7)	C(52)–C(51)–C(58)	121.8(7)
C(35)–C(36)–C(37)	123.5(7)	C(51)–C(52)–C(53)	125.4(7)
C(42)–C(41)–C(48)	124.3(7)	C(54)–C(55)–C(56)	122.9(7)
C(41)–C(42)–C(43)	123.5(8)	C(55)–C(56)–C(57)	124.7(7)

* M(1) to M(6) represent the midpoints of the olefinic double bonds of the cod ligands.

with any of the rhodium co-ordination planes, but slightly rotated, giving rise to a pseudo-staggered conformation (see Fig. 4). The smallest dihedral angle characterizing this rotation is with the Rh(2) plane, 27.6(2) and 38.7(2)°. An analogous situation has been described in the related platinum complex $[(PtMe_3)_4(\mu_3\text{-}SPh)_4]$,[28] where the phenyl groups of the four μ_3-SPh bridging ligands are rotated with respect to the metal co-ordination planes [mean 8.5(1)°].

Each of the cyclooctadiene rings has a boat configuration with a mean carbon–carbon double-bond length of 1.384(5) Å. Interestingly, within the accuracy obtained, the asymmetry observed in the central Rh_3S_2 skeleton does not affect the co-ordination of the diolefinic molecules: the mean Rh–C(olefinic) bond distances are 2.150(4), 2.151(4) and 2.148(4) Å for Rh(1), Rh(2) and Rh(3) respectively, and the olefinic double bonds exhibit equivalent distances in the narrow range 1.370–1.397(12) Å. These distances involving cyclooctadiene co-ordination compare well with those observed in the dinuclear thiolate-bridged complexes $[Rh_2(\mu\text{-}SMe)_2(cod)]$[22] [2.130(3) Å] and $[Rh_2(\mu\text{-}SC_6HF_4)_2(cod)_2]$[21] [2.138(2) Å], or in trinuclear μ_3-sulfido complexes $[Rh_3H(\mu_3\text{-}S)_2(cod)_3]$[29] [2.169(5) Å] and $[Rh_3H(\mu_3\text{-}S)_2(cod)_2(PMe_3)_3]$[11] [2.142(5) Å], where, in all cases, the alkene bonds are co-ordinated in a rhodium square-planar arrangement opposite to two S atoms.

In solution, the integrity of the aggregates **1**–**4** is maintained. Their ^1H NMR spectra (Table 3) are similar to those of the corresponding binuclear complexes $[\{Rh(\mu\text{-}SPh)(diolefin)\}_2]$ except in the chemical shifts, which are at lower field. As the three diolefin ligands are equivalent, which is not expected from the X-ray structure, and the fine structure of the resonance for the olefinic protons is lacking, some kind of non-rigidity giving an averaged highly symmetrical species is operating. Inversion at the sulfur cannot be invoked since all the tetrahedral electron pairs are engaged in co-ordination. Besides, no dissociation of the diolefin occurs as the coupling ^1J(C–Rh) for the olefinic carbons is observed (for example, in the ^{13}C-$\{^1H\}$ NMR spectrum of the complex $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$). As this spectrum does not change at low temperature, the simplest low-energy fluxional process to account for the equivalence of the olefinic protons and carbons is a free rotation of the phenyl rings followed by wandering of the sulfurs around the centre of the metal triangle.

In order to look for structural changes in the environment of the rhodium atoms on formation of the trinuclear complexes, we have compared the crystal structures of the binuclear complex *syn-endo*-$[\{Ir(\mu\text{-}SPh)(cod)\}_2]$ and the binuclear fragment $[\{Rh(\mu\text{-}SPh)(cod)\}_2]^+$ resulting from the removal of the Rh(3)(cod) moiety supposed to be the added fragment; the covalent radii of rhodium and iridium are identical.[30] As depicted in Fig. 5, two changes concerning to the molecular frame can be detected in the transformation $M_2(\mu\text{-}SPh)_2$

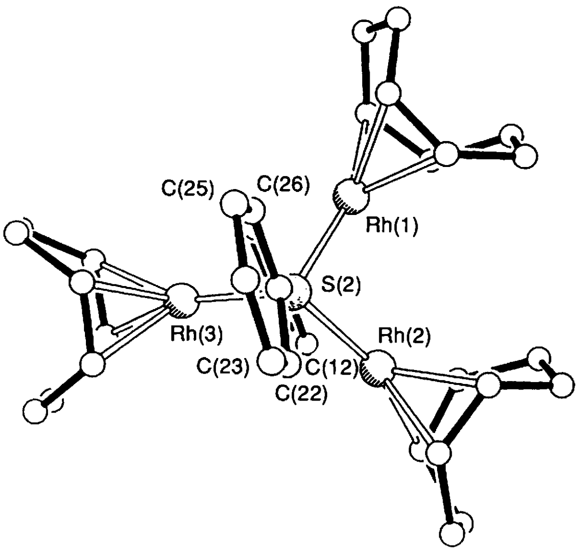

Fig. 4 Perspective view of the cation $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ perpendicular to the Rh_3 plane, showing phenyl dispositions

Table 3 Proton NMR spectral data for the trinuclear complexes

Compound	δ
1	7.36 (m, 6 H, H_m and H_p, SPh^-), 7.00 (m, 4 H, H_o, SPh^-), 4.66 (s, 12 H, =CH, cod), 2.60 (m, 12 H, CH_2, cod), 2.13 (m, 12 H, CH_2, cod)
2	7.26 (m, 6 H, H_m and H_p, SPh^-), 6.77 (m, 4 H, H_o, SPh^-), 4.41 (s, 12 H, =CH, nbd), 4.08 (s, 6 H, CH, nbd), 1.39 (s, 6 H, CH_2, nbd)
3	7.36 (m, 6 H, H_m and H_p, SPh^-), 7.22 (m, 4 H, H_o, SPh^-), 6.06 (m, 6 H, CH, tfbb), 4.62 (m, 12 H, =CH, tfbb)
4	7.47 (m, 6 H, H_m and H_p, SPh^-), 7.17 (m, 4 H, H_o, SPh^-), 4.57 (m, 12 H, =CH, cod), 2.39 (m, 12 H, CH_2, cod), 2.04 (m, 12 H, CH_2, cod)
5	7.40 (m, 6 H, H_m and H_p, SPh^-), 7.0–6.7 (m, 4 H, H_o, SPh^-), 4.66 (m, 6 H, =CH, cod and nbd), 4.44 (m, 6 H, =CH, cod and nbd), 4.12 (m, 2 H, CH, nbd), 2.60 (m, 8 H, CH_2, cod), 2.12 (m, 8 H, CH_2, cod), 1.50 (s, 1 H, CH_2, nbd), 1.42 (s, 1 H, CH_2, nbd)
6	7.31 (m, 6 H, H_m and H_p, SPh^-), 6.92 (m, 4 H, H_o, SPh^-), 5.87 (m, 2 H, CH, tfbb), 4.56 (m, 12 H, =CH, cod and tfbb), 2.63 (m, 8 H, CH_2, cod), 2.12 (m, 8 H, CH_2, cod)
7	7.4–7.2 (m, 6 H, H_m and H_p, SPh^-), 7.0–6.6 (m, 4 H, H_o, SPh^-), 4.7–4.2 (m, 12 H, =CH, cod and nbd), 4.07 (s, 4 H, CH, nbd), 2.37 (m, 4 H, CH_2, cod), 1.94 (m, 4 H, CH_2, cod), 1.45 (s, 4 H, CH_2, nbd)
8	7.5–7.3 (m, 6 H, H_m and H_p, SPh^-), 7.2–7.1 (m, 4 H, H_o, SPh^-), 5.86 (m, 2 H, CH, tfbb), 4.62 (m, 12 H, =CH, cod and tfbb), 2.48 (m, 8 H, CH_2, cod), 2.08 (m, 8 H, CH_2, cod)

[a] In $CDCl_3$ at 20 °C. H_o, H_m, H_p = *ortho*-, *meta*- and *para*-protons of the thiophenolate ligands.

$\longrightarrow M_3(\mu_3\text{-}SPh)_2$. (*a*) Closure of the angles centred on the sulfur (M–S–M) by *ca.* 8° on approach to the third metal fragment. As a consequence, the C–S bonds of both thiolate ligands which form an angle of 153.4° in the binuclear complex became almost aligned (168.8°) in the trinuclear complex. A similar decrease in the M–S–M angle (12°) takes place on formation of the metal–metal bond by oxidative addition of iodine to $[\{Ir(\mu\text{-}SPh)(cod)\}_2]$ but there is a simultaneous change to the *anti* isomer.[19] In the trinuclear complex the closure of the angles M–S–M leads to shorter metal–metal separations. (*b*) Rotation of the phenyl rings, to give a position of least steric hindrance with the diolefins. From this picture it seems also that the formation of the trinuclear complexes is better described as a co-ordination of the fragment Rh(cod) to the sulfur atoms than to the formation of metal–metal bonds.

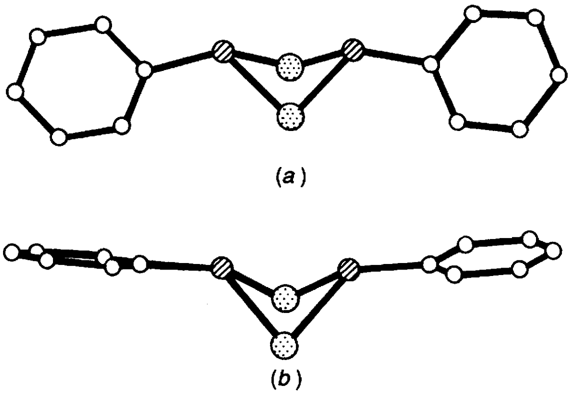

Fig. 5 Changes of the orientation of the phenyl rings and the wideness of the M–S–M angles from the binuclear (*a*) to the trinuclear complexes (*b*)

The 48-valence-electron complexes $[M_3(\mu_3\text{-}SPh)_2(\text{diolefin})^3]^+$ reported herein give the right polyhedral electron count for either a triangular M_3 or a trigonal-bipyramidal M_3S_2 core according with the polyhedral skeletal electron pair theory (PSEPT) of Wade and Mingos[31] for clusters. On the other hand, the square-planar co-ordination of the rhodium atoms if metal–metal interactions are neglected is typical of a Wernerian co-ordination complex. The decision as to whether there are or there are not metal–metal bonds is not simple when short metal–metal bond distances are bridged by ligands as pointed out by Mehrotra and Hoffmann.[32] The bonding situation in our compounds should be similar to that in the related isoelectronic anions. $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh[33] or Ir[34]) reported by Martinengo and co-workers. Therein, both the square-planar co-ordination of the rhodium atoms and the lengthening of the metal–metal separations on substitution of sulfur by selenium bridges lead to the conclusion that there are no true metal–metal bonds. Moreover, comparison with other related chalcogenide trimetallic clusters of Fe and Co shows breakage of the metal–metal bonds when one moves from the first to the second row in Groups 8 and 9 and to the right.[33]

On the other hand, Jones and co-workers have described the preparation and structures of the other 48-electron diolefin compounds known $[M_3H(\mu_3\text{-}S)_2(cod)_3]$ and $[M_3H(\mu_3\text{-}S)_2(cod)_2(PBu^t{}_2H)_2]$ (M = Rh[29] or Ir[11]). For these compounds the retention of both the metal–metal separation and the core in substitution reactions, occasionally of one ancillary ligand only, suggest the presence of two normal and one protonated metal–metal bond. Moreover, when a two-electron ligand is added one of these bonds is broken, resulting in the 50-electron trimetallic compounds $[Rh_3H(\mu_3\text{-}S)_2(cod)_2(PMe_3)_3]$ and $[Ir_3H(\mu_3\text{-}S)_2(cod)_3(PMe_3)]$.

Substitution of the diolefin for carbonyl ligands in our compounds **1** and **4** by reaction with carbon monoxide, a standard reaction for mononuclear complexes of rhodium and iridium, occurs but it causes also the rupture of the aggregate. From this reaction the binuclear complexes $[\{M(\mu\text{-}SPh)(CO)_2\}_2]$ (M = Rh or Ir) besides $[Rh(cod)_2][ClO_4]$ are isolated. In contrast, the above-mentioned diolefin clusters described by Jones and co-workers[11,29] retain their nuclearity on reaction with carbon monoxide, giving the carbonyl compounds $[M_3H(\mu\text{-}S)_2(CO)_6]$.

So it seems that the existence of metal–metal bonds in these trimetallic compounds of rhodium depends on very subtle factors. In this context, Jones *et al.*[35] have described the easy and reversible transformation of the isomer $[\{Rh(\mu\text{-}PBu^t{}_2)(CO)_2\}_2]$, containing a double metal–metal bond, into the isomer without a metal–metal bond by the action of heat. It seems that the difference between the compounds reported by Jones and those by Martinengo and co-workers and by us is a formal oxidation of the metal atoms, so that we attempted to oxidize the binuclear complex $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ with silver salts, which have been used as mild oxidants of organometallic rhodium compounds. On the other hand, the affinity of silver for sulfur could lead to the formation of heterotrinuclear silver–rhodium compounds. In fact the reaction of silver perchlorate with the rhodium complex follows a different pathway since the silver cation abstracts benzenethiolate from the binuclear complex yielding the stable cationic species $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ in good yield. This species is again obtained in the reaction of the above rhodium binuclear complex with $[Pd(\eta^3\text{-}C_3H_5)(Me_2CO)_x]^+$ instead of the heterotrinuclear complex. Furthermore, the complex $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ is formed in good yield from solutions of the binuclear complex $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ in polar solvents when non-co-ordinating anions are present. The stability of the trinuclear diolefin rhodium complex is the driving force in these reactions, which contrasts with the instability of the corresponding carbonyl complex.

The crystal structure of $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3]^+$ suggests that one of the fragments Rh(cod) is more tightly bonded to the sulfurs than the others. Nevertheless, an average situation is detected in solution, so that if dissociation of one of these moieties took place it would be a random process. A further confirmation of the absence of this type of dissociation and the proposed mechanism of formation of the trinuclear complexes is the clean synthesis of those containing different diolefins of the type $[Rh_3(\mu_3\text{-}SPh)_2(diolefin)_2(diolefin')]^+$. So, using the approach described, addition of the species $[Rh(nbd)(Me_2CO)_x]^+$ or $[Rh(tfbb)(Me_2CO)_x]^+$ to the binuclear complex $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ gives the compounds $[(cod)_2Rh_2(\mu_3\text{-}SPh)_2Rh(nbd)][ClO_4]$ **5** or $[(cod)_2Rh_2(\mu_3\text{-}SPh)_2Rh(tfbb)][ClO_4]$ **6** respectively in high yield. These complexes are 1:1 electrolytes in acetone as expected.

This synthesis is so versatile that it allows the preparation of heterotrinuclear aggregates. In this way, addition of the solvated species $[Ir(cod)(Me_2CO)_x]^+$ to the rhodium binuclear complex $[\{Rh(\mu\text{-}SPh)(nbd)\}_2]$ gives $[IrRh_2(\mu_3\text{-}SPh)_2(cod)(nbd)_2]^+$ **7**, which was isolated as the tetrafluoroborate salt in good yield. Conversely, addition of $[Rh(tfbb)(Me_2CO)_x]^+$ to the binuclear complex $[\{Ir(\mu\text{-}SPh)(cod)\}_2]$ affords the heterotrinuclear complex $[Ir_2Rh(\mu_3\text{-}SPh)_2(cod)_2(tfbb)]^+$ **8**. Complexes **7** and **8** are 1:1 electrolytes in acetone and they show typical bands of the unco-ordinated tetrafluoroborate in the solid state.

The presence of different metal atoms or different diolefins in the trinuclear complexes **5**–**8** reduces their symmetry relative to their homotrinuclear counterparts, which is evidenced by a higher complexity in the aromatic region of their ^1H NMR spectra.

Experimental

All the reactions were carried out under a nitrogen atmosphere at room temperature using Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use.

Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 and 50.309 MHz respectively; chemical shifts are reported relative to tetramethylsilane as external reference. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solutions in NaCl windows. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} acetone or nitromethane solutions using a Phillips 9501/01 conductimeter.

The starting materials $[\{Rh(\mu\text{-}Cl)(diolefin)\}_2]$ (diolefin = cod, nbd or tfbb),[36] $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$,[37] $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$ and $[\{Rh(\mu\text{-}OMe)(tfbb)\}_2]$[38] were prepared according to reported methods.

Preparations.—$[\{Rh(\mu\text{-}SPh)(diolefin)\}_2]$ (*diolefin = cod, nbd or tfbb*). A white suspension of lithium thiophenolate (0.4 mmol) was prepared by addition of butyllithium (0.25 cm^3, 1.55 mol dm^{-3} in hexane, 0.4 mmol) to a solution of thiophenol (0.4 mmol) in diethyl ether (10 cm^3). The appropriate solid compound $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$ (0.2 mmol) was added to the above suspension and allowed to react for 30 min. The solvent was pumped off and then the residue was washed with acetone–water (4:1, 5 cm^3), filtered and washed with acetone–water. Recrystallization from dichloromethane–diethyl ether or hexane gave the complexes as microcrystalline solids in high yield (over 90%). $^{13}C\text{-}\{^1H\}$ NMR of $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ ($CDCl_3$, −40 °C): δ 135.2 (C_{ipso}), 133.8, 128.0, 126.3 (Ph), 80.0 [d, ^1J(Rh–C) 11.8 Hz, cod] and 30.9 (cod).

$[Rh_3(\mu_3\text{-}SPh)_2(diolefin)_3][ClO_4]$ **1**–**3**. An acetone solution of $[Rh(diolefin)(Me_2CO)_x][ClO_4]$ (0.2 mmol) (prepared by treating $[\{RhCl(diolefin)\}_2]$ (0.1 mmol) with $Ag[ClO_4]$ (0.2 mmol) in acetone (10 cm^3) for 30 min and filtering off the AgCl formed) was added to a solution of the appropriate compound $[\{Rh(\mu\text{-}SPh)(diolefin)\}_2]$ (0.2 mmol) in dichloromethane (5 cm^3). Evaporation of the solutions under vacuum to 1 cm^3 and addition of diethyl ether (5 cm^3) gave the complexes as microcrystalline solids which were filtered off, washed with diethyl ether and dried under vacuum. $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[Rh_3(\mu\text{-}SPh)_2(cod)_3]^+$ ($CDCl_3$): δ 130.9 (C_{ipso}), 130.2, 130.0, 123.7 (Ph), 82.7 [d, ^1J(Rh–C) 11.8 Hz, cod] and 31.0 (cod).

$[Rh_3(\mu_3\text{-}SPh)_2(cod)_2(diolefin)][ClO_4]$ **5** *and* **6**. A solution of $[Rh(diolefin)(Me_2CO)_x][ClO_4]$ (0.2 mmol) (diolefin = nbd or tfbb) (prepared as described above) was added slowly to a solution of the compound $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ (0.2 mmol) in dichloromethane (5 cm^3) to give orange solutions. Concentration of these solutions under vacuum to 1 cm^3 and slow addition of diethyl ether rendered the required complexes as crystalline solids, which were filtered off, washed with diethyl ether and then vacuum-dried.

$[(diolefin)_2M_2(\mu_3\text{-}SPh)_2M'(diolefin)][BF_4]$ **4**, **7** *and* **8**. An acetone solution of $[M'(diolefin)(Me_2CO)_x][BF_4]$ (0.4 mmol) (M′ = Ir, diolefin = cod **4**, **7**; M′ = Rh, diolefin = tfbb **8**) was prepared by reaction of $[\{M'(\mu\text{-}OMe)(diolefin)\}_2]$ (0.1 mmol) with a solution of tetrafluoroboric acid (54%) in diethyl ether (60 μl, 0.2 mmol). The addition of this solution to a suspension of the appropriate compound $[\{M(\mu\text{-}SPh)(diolefin)\}_2]$ (M = Rh, diolefin = nbd **7**; M = Ir, diolefin = cod **4**, **8**) (0.2 mmol) in acetone (5 cm^3) gave red-orange solutions. The solvent was pumped off and the residue dissolved in dichloromethane (1 cm^3). Addition of diethyl ether (20 cm^3) gave the required complexes as microcrystalline solids which were filtered off, washed with diethyl ether and vacuum-dried.

$[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$ **1** *in polar solvents.* A solution of $Na[ClO_4]\cdot H_2O$ (2.13 mmol) in acetone (7 cm^3) was added to a solution of the compound $[\{Rh(\mu\text{-}SPh)(cod)\}_2]$ (0.156 mmol) in dichloromethane (7 cm^3). The mixture was stirred under nitrogen for 48 h to give an orange-red solution. The volatiles were removed under vacuum and the residue extracted with dichloromethane. Concentration of this solution under vacuum and addition of diethyl ether gave crude complex **1** in 70% yield as an orange-brown solid which was recrystallized from acetone–diethyl ether.

Crystal Structure Determination of $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$ **1**.—*Crystal data.* $C_{36}H_{46}ClO_4Rh_3S_2$, $M = 951.05$, orthorhombic, space group *Pbca* (no. 61), $a = 14.818(1)$, $b = 17.084(1)$, $c = 27.443(1)$ Å, $U = 6947.2(7)$ Å^3, $Z = 8$, $D_c = 1.819$ Mg m^{-3}, $F(000) = 3824$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 16.19$ cm^{-1}, $T = 20$ °C.

Data collection and processing. A Siemens AED-2 diffractometer with monochromated Mo-Kα radiation was used. An orange prismatic block 0.308 × 0.080 × 0.323 mm was mounted on a glass fibre. 13 311 Intensities were registered to $2\theta_{max}$ 40°. Averaging equivalents gave 3224 unique reflections, of which 2908 with $F \geqslant 6.0\sigma(F)$ were used for all calculations

Table 4 Final atomic coordinates (× 10^4; × 10^5 for Rh atoms) for the non-hydrogen atoms of $[Rh_3(\mu_3\text{-}SPh)_2(cod)_3][ClO_4]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	8 106(3)	14 109(3)	9 159(2)
Rh(2)	−5 863(4)	12 802(3)	16 927(2)
Rh(3)	−1 246(3)	31 392(3)	12 244(2)
S(1)	−661(1)	1 952(1)	932(1)
S(2)	671(1)	2 161(1)	1 638(1)
Cl	135(2)	2 908(1)	−1 144(1)
C(11)	−1 484(4)	1 880(4)	459(2)
C(12)	−2 345(5)	1 638(4)	562(3)
C(13)	−2 990(5)	1 615(5)	182(3)
C(14)	−2 748(5)	1 847(4)	−275(3)
C(15)	−1 884(5)	2 093(4)	−377(3)
C(16)	−1 237(5)	2 114(4)	−3(2)
C(21)	1 540(4)	2 414(4)	2 055(2)
C(22)	1 363(5)	2 448(4)	2 550(3)
C(23)	2 070(5)	2 682(5)	2 869(3)
C(24)	2 880(6)	2 881(5)	2 682(3)
C(25)	3 052(6)	2 877(5)	2 199(3)
C(26)	2 373(5)	2 643(4)	1 872(3)
C(31)	1 822(4)	625(4)	1 184(3)
C(32)	2 238(4)	1 118(4)	858(2)
C(33)	2 516(5)	894(4)	346(3)
C(34)	1 800(5)	1 080(5)	−32(3)
C(35)	855(5)	1 048(4)	167(2)
C(36)	504(5)	446(4)	452(3)
C(37)	1 031(5)	−293(4)	584(3)
C(38)	1 526(5)	−202(4)	1 080(3)
C(41)	−51(5)	378(5)	2 154(3)
C(42)	−490(5)	921(5)	2 445(3)
C(43)	−1 404(5)	786(5)	2 665(3)
C(44)	−2 117(5)	516(5)	2 299(3)
C(45)	−1 911(5)	777(4)	1 774(3)
C(46)	−1 408(4)	329(4)	1 446(3)
C(47)	−946(5)	−435(4)	1 549(3)
C(48)	−420(5)	−424(4)	2 032(3)
C(51)	−37(5)	4 071(4)	1 741(3)
C(52)	702(5)	4 115(4)	1 442(3)
C(53)	827(6)	4 689(5)	1 042(3)
C(54)	173(6)	4 634(5)	639(3)
C(55)	−437(6)	3 927(4)	634(3)
C(56)	−1 184(5)	3 857(4)	933(3)
C(57)	−1 471(6)	4 454(5)	1 302(4)
C(58)	−817(6)	4 636(6)	1 696(4)
O(1)	838(5)	3 360(5)	−1 353(3)
O(2)*	529(8)	2 240(7)	−944(5)
O(3)*	−501(11)	2 787(10)	−1 479(6)
O(4)*	−187(6)	3 330(6)	−719(3)
O(12)*	−91(23)	2 202(22)	−1 448(14)
O(13)*	−747(19)	3 259(18)	−1 306(11)
O(14)*	299(48)	2 537(49)	−624(29)

* Atom corresponding to the model established for the disordered oxygens of the ClO_4^- anion.

(program system SHELX 76).[39] Cell constants were refined from setting angles of 48 reflections in the range 2θ 20–30°. A numerical absorption correction was applied based on indexed morphological faces of the crystal[40] (transmission factors 0.883–0.674). An isotropic extinction correction factor was also refined (0.000 03).

Structure solution and refinement. The structure was solved by Patterson methods and extended by difference syntheses. All atoms were first refined isotropically, and in subsequent cycles with anisotropic thermal parameters for Rh, S, Cl and C atoms of the cyclooctadiene groups. Hydrogen atoms were included in idealized positions in the last cycles of refinement using a riding model and with a common fixed thermal parameter. The oxygen atoms of the perchlorate anion were observed disordered around Cl. A model for this disorder was established with two groups of oxygen atoms with complementary occupancy factors [O(2)–O(4) 0.78; O(12)–O(14) 0.22]. The final *R* value was 0.0326, with $R' = 0.0344$. The weighting scheme was $w = k/\sigma^2(F) + gF^2$, with $k = 4.7407$ and $g = 0.000\,08$; 351 parameters; maximum $\Delta/\sigma < 0.343$, maximum $\Delta\rho$ 0.92 e Å^{-3} close to the anion. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 41. Final atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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