Heterotrinuclear Angular Aggregates of Rhodium, Iridium, Palladium and Group 11 Metals. X-Ray Structure of the Complex $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ (cod = cycloocta-1,5-diene)*

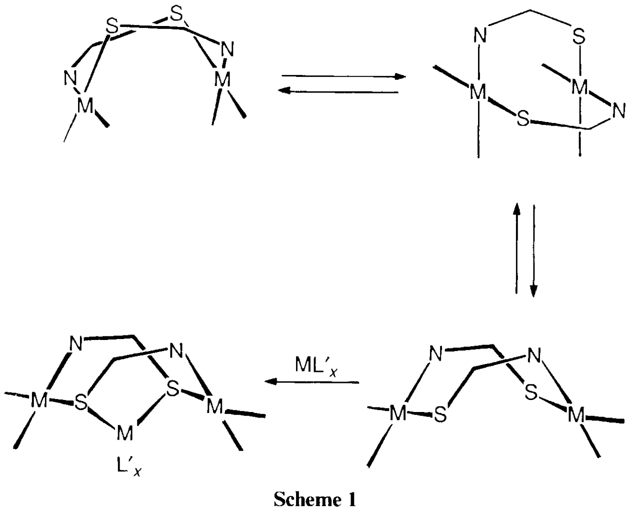
Miguel A. Ciriano,[a] **Jesús J. Pérez-Torrente,**[a] **Luis A. Oro,**[a] **Antonio Tiripicchio**[b] **and Marisa Tiripicchio-Camellini**[b]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain*

[b] *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100-Parma, Italy*

The binuclear complexes $[\{Ir(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ **1** (cod = cycloocta-1,5-diene) and $[\{Pd(\mu\text{-}C_7H_4NS_2)(\eta^3\text{-}C_3H_5)\}_2]$ **2** are isolated from the reaction of the chloro-bridged compounds $[\{M(\mu\text{-}Cl)L_2\}_2]$ (M = Ir, L_2 = cod; M = Pd, L_2 = allyl) and lithium benzothiazole-2-thiolate. Reactions of **1** and **2** with the appropriate species $[ML_2(Me_2CO)_2]^+$ afford the homotrinuclear angular aggregates $[M_3(\mu_3\text{-}C_7H_4NS_2)_2(L_2)_3]^+$. Starting from $[\{Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)\}_2]$ and $[\{M'(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ (M′ = Rh or Ir), this method is highly useful to prepare the heterotrinuclear aggregates $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2ML_2]^+$ $[ML_2$ = Ir(cod) or Pd(allyl)], $[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2AgX]^{n+}$ (n = 0, X = ClO_4, Cl, NO_3 or BF_4; n = 1, X = PPh_3 or pyridine) and $[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2M''Cl]$ (M″ = Cu or Au). They have been characterized by ^1H, ^{31}P NMR and IR spectroscopy and $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ **8** by X-ray diffraction methods. Crystals of **8** are orthorhombic, space group *Pbcn*, with a = 7.635(5), b = 27.564(11), c = 15.564(8) Å, Z = 4. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.062 for 1863 observed reflections. The complex, having an imposed C_2 symmetry, shows two Rh and one Ag atoms in a bent arrangement with two molecules of benzothiazole-2-thiolate interacting with all three metals. Each ligand is bonded to one Rh atom through the nitrogen and asymmetrically bridges one Rh and one Ag atom through the sulphur. The Rh atoms complete their co-ordination with a cod ligand interacting through the two olefinic bonds, while the Ag atom completes the co-ordination with two oxygen atoms from a perchlorate anion, which has been found disordered and distributed in two positions of equal occupancy factor with three oxygen atoms in common.

The construction of polynuclear complexes in a controlled way is a topic of current interest.[1] This can be accomplished by the use of ligands designed for such a purpose. For example, Balch *et al.* and we have shown that the small-bite tridentate ligands bis(diphenylphosphinomethyl)phenylphosphine[2] and 1,8-naphthyridin-2-onate[3] can generate trinuclear linear aggregates of rhodium in which the three metal atoms interact. Another synthetic approach consists in the incorporation of metal fragments into metalloligands, such as the thio complexes $[WS_4]^{2-}$,[4] $[\{Pt(\mu\text{-}S)(PPh_3)_2\}_2]$[5] and $[Ru_3(\mu\text{-}S)(\mu\text{-}CO)(CO)_9]$[6] in recent preparative studies through bridge-assisted reactions.[7] In this context, several years ago we explored the ability of the non-phosphorus-containing ligands pyridine-2-thiolate $(SC_5H_4N^-)$[8] and benzothiazole-2-thiolate $(C_7H_4NS_2^-)$[9] (S–N in general) to agglomerate three rhodium atoms in close proximity. Recently[10] we have given evidence that the way in which these trinuclear complexes are formed is that described in Scheme 1 (where M = Rh), *i.e.* the binuclear complexes $[\{Rh(\mu\text{-}S\text{–}N)L_2\}_2]$ co-ordinate a metal fragment RhL'_2 giving rise to a single isomer of predetermined structure. We describe here an extension of this reaction for the synthesis of other homo- or hetero-trimetallic aggregates of the $[M_3]^{n+}$ (n = 3 or 6), $[Rh_2M]^{n+}$ (n = 3 or 4) and $[M'_2M'']^{3+}$ (M = Ir or Pd; M′ = Rh or Ir; M″ = Cu, Ag or Au) cores. Part of this work has been published as preliminary communications.[9,11]



Scheme 1

Results and Discussion

Binuclear Complexes.—The binuclear complexes $[\{M(\mu\text{-}S\text{–}N)L_2\}_2]$ (M = Ir or Pd) were the first target as intermediates

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* μ_3-Benzothiazole-1κ*N*-2-thiolato-2:3κ^2*S*-μ_3-benzothiazole-3κ*N*-thiolato-1:2κ^2*S*-bis[1,3(η^4)-cycloocta-1,5-diene]perchlorato-2κ^2*O*,*O*′-1,3-dirhodium-2-silver (2*Rh–Ag*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii—xxii.

Table 1 Analytical and physical data for the new complexes

Compound	Colour	Yield (%)	Analysis (%)[a] C	H	N	Λ_M[b]	*M*[c]
1 $[\{Ir(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$	Red	95	39.10	3.85	2.90		960
			(38.60)	(3.45)	(3.00)		(933)
2 $[\{Pd(\mu\text{-}C_7H_4NS_2)(\eta\text{-}C_3H_5)\}_2]$	Yellow	80	39.05	3.05	4.45		635
			(38.30)	(3.00)	(4.45)		(627)
3 $[Ir_3(\mu_3\text{-}C_7H_4NS_2)_2(cod)_3][ClO_4]$	Red-brown	90	33.05	3.25	1.95	130	
			(33.20)	(3.25)	(1.90)		
4 $[Pd_3(\mu_3\text{-}C_7H_4NS_2)_2(\eta\text{-}C_3H_5)_3][PF_6]$	Pale yellow	87	30.10	2.45	3.15	81	
			(30.05)	(2.50)	(3.05)		
5 $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ir(cod)][ClO_4]$	Green	83	47.00	3.35	1.70	125	
			(47.45)	(3.30)	(1.85)		
6 $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Pd(\eta\text{-}C_3H_5)][ClO_4]$	Orange-brown	85	47.75	3.60	2.00	131	
			(48.35)	(3.15)	(2.05)		
7 $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag_2(OClO_3)_2]$	Yellow	86	40.10	2.55	1.80	228	
			(40.70)	(2.50)	(1.80)		
8 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$	Yellow	90	37.45	3.35	2.90		
			(36.95)	(3.35)	(2.95)		
9 $[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$	Yellow	90	31.10	2.90	2.30		
			(31.60)	(2.80)	(2.45)		
10 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2AgCl]$	Yellow	87	39.55	3.85	3.00		
			(40.10)	(3.60)	(3.10)		
11 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2NO)]$	Yellow	88	38.85	3.50	4.55		
			(38.75)	(3.25)	(4.55)		
12 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(F_2BF_2)]$	Yellow	80	37.80	3.60	2.75		
			(37.95)	(3.35)	(2.95)		
13 $[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2AgCl]$	Yellow	90	32.65	2.90	2.50		
			(33.45)	(3.00)	(2.60)		
14 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(PPh_3)][ClO_4]$	Orange	86	46.20	3.25	2.00	113	
			(47.10)	(3.85)	(2.30)		
15 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(py)][ClO_4]$	Yellow	93	40.70	3.30	4.45	130	
			(40.35)	(3.60)	(4.05)		
16 $[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(PPh_3)][ClO_4]$	Brown	75	40.85	3.60	2.05	*d*	
			(41.10)	(3.35)	(2.00)		
17 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2CuCl]$	Orange	85	42.35	3.65	3.40		854
			(42.20)	(3.75)	(3.30)		(853)
18 $[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2CuCl]$	Orange	85	34.50	3.20	2.75		1075
			(34.90)	(3.10)	(2.70)		(1032)
19 $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2AuCl]$	Yellow	65	36.35	3.10	2.70		861
			(36.50)	(3.25)	(2.85)		(987)
20 $[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2AuCl]$	Red	67	31.20	2.85	2.25		1151
			(30.90)	(2.75)	(2.40)		(1165)

[a] Calculated values are given in parentheses. [b] In S cm^2 mol^{-1} in acetone. [c] In chloroform. [d] Decomposes in solution.

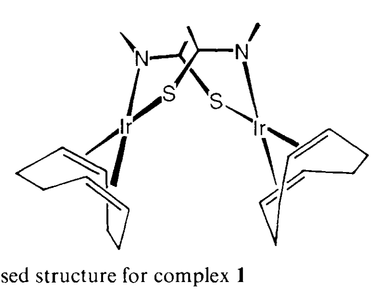


Fig. 1 Proposed structure for complex **1**

in the synthesis of trinuclear aggregates. Protonation of the methoxo ligand in the complex $[\{Ir(\mu\text{-}MeO)(cod)\}_2]$ (cod = cycloocta-1,5-diene) with 2-mercaptobenzothiazole in diethyl ether renders the compound $[\{Ir(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ **1** as a microcrystalline solid in good yield. Alternatively, this compound and $[\{Pd(\mu\text{-}C_7H_4NS_2)(\eta^3\text{-}C_3H_5)\}_2]$ **2** are obtained in excellent yield by reaction of the appropriate chloro-bridged complex $[\{M(\mu\text{-}Cl)L_2\}_2]$ with $Li(C_7H_4NS_2)$. Their formulation as binuclear complexes is consistent with their molecular weights in chloroform solution (Table 1). Complex **1** exists in solution as a single isomer, probably that of C_2 symmetry having bridging ligands in a head-to-tail fashion (Fig. 1). As required for this structure, both cod ligands and benzothiazole-2-thiolate bridges are equivalent in the ^1H and ^{13}C NMR spectra (Table 2 and Experimental section). Furthermore, the four olefinic carbons and protons in one cod ligand are not related by this C_2 axis, giving rise to four resonances in the ^{13}C and ^1H NMR spectra respectively. The origin of the chemical shift differences of these signals arises from the disposition of the active nuclei *trans* to the N and S atoms and from their orientation inside and outside of the 'pocket' of the complex. Recent structural NMR and X-ray reports[12] on the related compounds $[\{M'(\mu\text{-}Opy)(cod)\}_2]$ (M′ = Rh or Ir; OPy = 2-pyridonate), which have the proposed structure, discuss the origin and assignment of the cod resonances. For complex **1**, the absence of fine structure of these resonances in the ^1H NMR spectrum up to the freezing temperature of the solvent precludes their assignment, but suggests that a fluxional movement retaining the symmetry of the complex occurs. As the carbon resonances are sharp at low temperature, such a low-energy process should be associated with the modification of the conformation of the '$M(\mu\text{-}N\text{-}S)_2M$' ring shown in Scheme 1. This motion opening the 'pocket' of the binuclear complex is basic for the formation of the trinuclear complexes because it allows the binding of a third metal fragment ML'_2 to the already co-ordinated sulphur atoms as shown below.

Trinuclear Complexes.—Addition of the solvated species

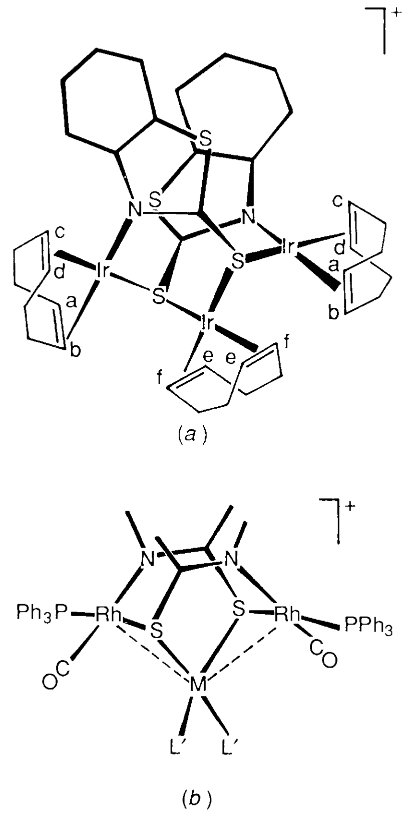
Table 2 Proton NMR data (δ) for the new complexes in CDCl$_3$ at 20 °C

Compound	
1	8.56 (d, 2 H, H^4), 7.38 (td, 2 H, H^5 or H^6), 7.25–7.08 (m, 4 H, H^7 and H^5 or H^6), 4.6 (m, 2 H, =CH of cod), 4.1 (m, 4 H, =CH of cod), 3.4 (m, 2 H, =CH of cod), 2.6–2.1 (m, 8 H, CH$_2$ of cod), 1.8–1.3 (m, 8 H, CH$_2$ of cod)
2	7.91 (d, 2 H, H^4), 7.27 (m, 4 H, H^7 and H^5 or H^6), 7.10 (td, 2 H, H^5 or H^6), 5.53 (m, 2 H, CH allyl), 4.05 (m, 4 H, *syn*-allyl), 3.14 (m, 4 H, *anti*-allyl)
3	8.36 (d, 2 H, H^4), 7.37 (dd of d, 2 H, H^5), 7.14 (d of d, 2 H, H^7), 6.99 (dd of d, 2 H, H^6), 5.41 (m, 2 H, =CH of cod), 5.22 (m, 2 H, =CH of cod), 4.28 (m, 2 H, =CH of cod), 3.96 (m, 2 H, =CH of cod), 3.34 (m, 4 H, =CH of cod), 4.03–3.7 (m, 6 H, CH$_2$ of cod), 3.6–3.3 (m, 6 H, CH$_2$ of cod), 3.3–2.9 (m, 6 H, CH$_2$ of cod), 2.7–2.2 (m, 6 H, CH$_2$ of cod)
4	7.90 (d, 2 H, H^4), 7.4–7.0 (m, 6 H, H^5 or H^6 and H^7), 5.62 (m, 3 H, CH of allyl), 4.24 (m, 6 H, *syn*-allyl), 3.14 (m, 6 H, *anti*-allyl)
5	7.84 (d, 2 H, H^4), 7.50 (m, 12 H, PPh$_3$), 7.32 (m, 18 H, PPh$_3$), 6.86 (dd of d, 2 H, H^5), 6.70 (dd of d, 2 H, H^6), 6.58 (d of d, 2 H, H^7), 4.42 (m, 2 H, =CH of cod), 3.62 (m, 2 H, =CH of cod), 2.14 (m, 2 H, CH$_2$ of cod), 1.60 (m, 6 H, CH$_2$ of cod)
6	8.00 (d, 1 H, H^4). 7.88 (d, 1 H, H^4), 7.40 (m, 12 H, PPh$_3$), 7.24 (m, 18 H, PPh$_3$), 7.00 (m, 2 H, H^5), 6.82 (dd of d, 2 H, H^6), 6.64 (d, of d, 2 H, H^7), 5.62 (spt, 1 H, allyl), 4.64 (d, 1 H, *syn*-allyl), 4.44 (d, 1 H, *syn*-allyl), 3.66 (d, 1 H, *anti*-allyl), 3.30 (d, 1 H, *anti*-allyl)
7	8.24 (d, 2 H, H^4), 7.40 (m, 14 H, PPh$_3$ and H^5 or H^6), 7.30 (m, 18 H, PPh$_3$), 7.00 (m, 2 H, H^5 or H^6), 6.84 (m, 2 H, H^7)
17 *	8.64 (d, 2 H, H^4), 7.40 (dd of d, 2 H, H^5), 7.03 (dd of d, 2 H, H^6), 6.97 (d, 2 H, H^7), 5.10 (m, 2 H, =CH of cod), 4.62 (m, 2 H, =CH of cod), 4.35 (m, 2 H =CH of cod), 3.56 (m, 2 H, =CH of cod), 3.30 (m, 2 H, CH$_2$ of cod), 3.00 (m, 2 H, CH$_2$ of cod), 2.7–2.4 (m, 4 H, CH$_2$ of cod), 2.3–1.9 (m, 4 H, CH$_2$ of cod), 1.8–1.6 (m, 4 H, CH$_2$ of cod)
19	9.21 (d, 2 H, H^4), 7.49 (m, 4 H, H^5 and H^6), 7.27 (d of d, 2 H, H^7), 4.60 (m, 2 H, =CH of cod), 4.41 (m, 2 H, =CH of cod), 3.58 (m, 2 H, =CH of cod), 3.20 (m, 2 H, =CH of cod), 2.7–2.4 (m, 5 H, =CH of cod), 2.1–1.7 (m, 7 H, CH of cod), 1.6–1.3 (m, 4 H, CH$_2$ of cod)

d = Doublet, t = triplet, spt = septet, m = multiplet. The protons of the heterocyclic ligand are numbered according to the IUPAC rules starting from the heterocyclic sulphur. * At −20 °C.

[Ir(cod)(Me$_2$CO)$_2$]$^+$ and [Pd(η^3-C$_3$H$_5$)(Me$_2$CO)$_2$]$^+$ to the appropriate binuclear complex [{M(μ-C$_7$H$_4$NS$_2$)L$_2$}$_2$] leads to the trinuclear aggregates [M$_3$(μ$_3$-C$_7$H$_4$NS$_2$)$_2$(L$_2$)$_3$]$^+$ (M = Ir, L$_2$ = cod, **3**; M = Pd, L$_2$ = η^3-C$_3$H$_5$, **4**). They are isolated as the perchlorate or PF$_6^-$ salts and behave as 1:1 electrolytes in acetone solution in accordance with their formulation. The broad bands due to the η^3-allyl group in the ^{1}H and ^{13}C NMR spectra of the palladium complex **4** are not helpful to establish its structure by spectroscopic methods, as described by Deeming *et al.*[13] for the related species [Pd$_3$(μ$_3$-SC$_5$H$_4$N)$_2$(η^3-C$_3$H$_4$Me)$_3$]$^+$. On the contrary, the structure of the iridium complex **3** [Fig. 2(*a*)] is unequivocally supported by ^{1}H NMR data.

Formation of compounds **3** and **4** and those described below occurs as depicted in Scheme 1 *i.e.* the binuclear complex acts as a chelate metallo ligand through the sulphur atoms. In this way, the resulting trinuclear aggregates have a predetermined structure. Nevertheless, to demonstrate this point requires that the third metal fragment added in the synthesis (ML'$_2$) be different to those already present in the binuclear complex either because of the ancillary ligands, as we have already described for rhodium complexes,[10] or because of the metal atom. Conversely, this allows the preparation of heterotrinuclear aggregates in a designed way.



5 ML'$_2$ = Ir (cod)
6 ML'$_2$ = Pd (η^3-C$_3$H$_5$)

Fig. 2 Structures of (*a*) complex **3**, (*b*) **5** and **6**

Thus, addition of the species [Ir(cod)(Me$_2$CO)$_2$]$^+$ and [Pd(η^3-C$_3$H$_5$)(Me$_2$CO)$_2$]$^+$ to the binuclear complex [{Rh(μ-C$_7$H$_4$NS$_2$)(CO)(PPh$_3$)}$_2$] (now [{M(μ-S-N)L$_2$}$_2$] in Scheme 1) leads immediately to deep-coloured solutions of the cations [{Rh(μ$_3$-C$_7$H$_4$NS$_2$)(CO)(PPh$_3$)}$_2$ML'$_2$]$^+$ [ML'$_2$ = Ir(cod), **5**; or Pd(η^3-C$_3$H$_5$), **6**]. A single isomer is formed in these reactions as deduced from the ^{31}P NMR spectra of the solutions from which complexes **5** and **6** are isolated in almost quantitative yield. Our attempts to isolate heterotrimetallic aggregates of the [Ir$_2$M]$^{3+}$ core were not successful since the addition of the fragment ML'$_2$ = Rh(cod) or Pd(η^3-C$_3$H$_5$) to [{Ir(μ-C$_7$H$_4$NS$_2$)(cod)}$_2$] lead to complex mixtures.

The cage structure of the complexes **3**, **5** and **6** [Fig. 2(*a*) and 2(*b*), where one of the two enantiomers is shown] is fully consistent with their spectroscopic data (Table 2). Complexes **3** and **5** have equivalent benzothiazole-2-thiolate bridging ligands (resonances between δ 8.4 and 6.8 in their ^{1}H NMR spectra) and **5** has equivalent phosphine ligands because they are related by the C_2 symmetry axis of the cation which contains the central metal atom. Furthermore, this C_2 axis groups the olefinic protons of the cod ligands in complex **3** into six sets of two equivalent protons [labelled a–f in Fig. 2(*a*)], which give rise to six resonances between δ 5.5 and 3.0 in its ^{1}H NMR spectrum (Fig. 3). In contrast, the structure of the rhodiumpalladium complex **6** lacks elements of symmetry, which is evidenced by the presence of two close doublets of equal intensity in its ^{31}P NMR spectrum. As the coupling constants ^1J(P–Rh) are similar, both rhodium atoms are in identical chemical environments and hence the palladium atom is bonded to the sulphur atoms. The lack of the C_2 axis in complex **6** comes from the trihapto co-ordination of the allyl group. The chemical shift differences for the *syn*- and *anti*-protons, close to the origin of the asymmetry, are more pronounced than those for the inequivalent bridging ligands in the ^{1}H NMR spectrum of **6**.

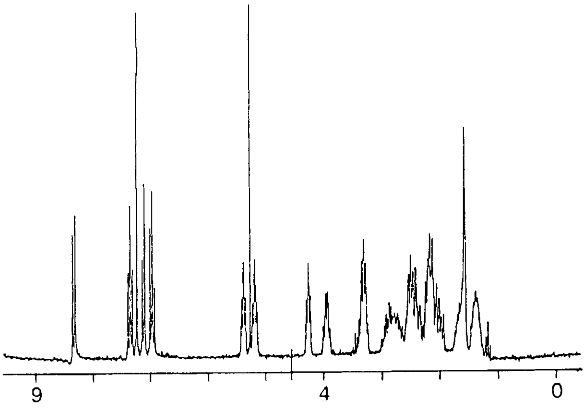


Fig. 3 Proton NMR spectrum of complex **3**

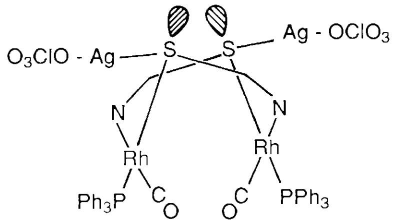


Fig. 4 Proposed array of the metal atoms in complex **7**

Silver salts have been widely used as chemical oxidants for one-electron processes,[14] which is particularly useful for preparative studies of paramagnetic binuclear rhodium complexes.[15] In other instances, where reduction to silver metal does not occur, the silver cation acts as a Lewis acid giving either mixed-metal clusters[16] or heteropolynuclear complexes.[17] The latter case was the result of the addition of silver perchlorate to the compound $[\{Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)\}_2]$ and the yellow 2:1 adduct $[\{Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)\}_2]\cdot 2Ag[ClO_4]$ **7** was isolated. In the solid state the co-ordination of the perchlorate group to silver through its oxygen atoms is clearly evidenced by the splitting of its stretching and bending vibrations (at 1100 and 620 cm^{-1} in T_d symmetry) at 1140, 1120, 1100, 905, 625 and 615 cm^{-1} due to a lowering of the local symmetry to C_{3v} or C_{2v}.[18] However in acetone solutions compound **7** behaves as a 2:1 electrolyte due to replacement of the weak co-ordinating anion by the donor solvent. This is associated with a change in colour of the solution from yellow to red. In non-donor solvents such as chloroform, where the solutions are yellow, the structure of compound **7** has a C_2 symmetry axis that makes equivalent both the triphenylphosphine ligands and the benzothiazole-2-thiolate bridges in the ^{31}P and ^1H NMR spectra respectively. In the light of these data, compound **7** should be reformulated as $[\{(Ph_3P)(OC)Rh(\mu_3\text{-}C_7H_4NS_2)Ag(OClO_3)\}_2]$ with the silver atoms co-ordinated to the bridging thiolate sulphurs and one perchlorate group as depicted in Fig. 4. Upon co-ordination of the silver cations to the binuclear complex there is a shift of ν(CO) to higher frequencies (*ca.* 30 cm^{-1}) and a decrease of the coupling constant ^1J(P–Rh) as a consequence of the reduction of the electron density on the rhodium atoms, which does not correspond with a formal oxidation.

Reaction of silver perchlorate with the complexes $[\{M'(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ gives 1:1 adducts of formula $[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(ClO_4)]$ (M′ = Rh, **8**; or Ir, **9**) independently of the molar ratio of the reagents. The co-ordination of the perchlorate group in the solid state is again deduced from the splitting of bands (at 1160, 1120, 1085, 915, 628, 625 and 604 cm^{-1}) but the scarce solubility in most organic solvents precludes further characterization. The structure of the rhodium complex **8**, determined by X-ray diffraction, confirms that for its formation $[\{Rh(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ behaves as a bidentate and chelating ligand, binding the 'AgO_2ClO_2' fragment through the thiolate sulphurs.

Table 3 Selected bond distances (Å) and angles (°) in complex **8***

Ag–Rh	2.796(3)	C(4)–C(5)	1.363(19)
Ag–S(1)	2.609(4)	C(5)–C(6)	1.413(19)
Ag–O(1)	2.532(17)	C(6)–C(7)	1.404(19)
Rh–S(1′)	2.358(4)	C(2)–C(7)	1.397(17)
Rh–N	2.080(9)	C(8)–C(9)	1.37(2)
Rh–C(8)	2.108(15)	C(9)–C(10)	1.57(2)
Rh–C(9)	2.131(15)	C(10)–C(11)	1.53(2)
Rh–C(12)	2.131(15)	C(11)–C(12)	1.55(2)
Rh–C(13)	2.166(14)	C(12)–C(13)	1.36(2)
S(1)–C(1)	1.757(14)	C(13)–C(14)	1.55(2)
N–C(1)	1.298(16)	C(14)–C(15)	1.57(2)
N–C(2)	1.418(16)	C(8)–C(15)	1.52(2)
S(2)–C(1)	1.729(14)	Cl–O(1)	1.34(2)
S(2)–C(3)	1.714(11)	Cl–O(2)	1.29(3)
C(2)–C(3)	1.395(17)	Cl–O(3)	1.33(3)
C(3)–C(4)	1.368(16)		

Rh–Ag–Rh′	110.5(1)	Ag–S(1)–C(1)	102.7(4)
S(1)–Ag–S(1′)	104.1(1)	S(1)–C(1)–N	127.1(10)
S(1)–Ag–O(1)	101.9(4)	S(1)–C(1)–S(2)	117.0(7)
S(1′)–Ag–O(1)	154.0(4)	N–C(1)–S(2)	116.0(10)
O(1)–Ag–O(1′)	52.2(5)	C(1)–S(2)–C(3)	90.6(6)
Rh–Ag–S(1)	85.4(1)	C(2)–C(3)–S(2)	108.6(9)
Rh–Ag–O(1)	132.5(4)	N–C(2)–C(7)	123.4(12)
N–Rh–S(1′)	93.8(3)	C(1)–N–C(2)	109.1(10)
Ag–Rh–N	90.2(3)	Rh–N–C(1)	128.9(8)
Ag–Rh–S(1′)	60.1(1)	Rh–N–C(2)	122.1(8)
M(1)–Rh–M(2)	88.8(6)	C(15)–C(8)–C(9)	126.6(15)
N–Rh–M(1)	88.9(5)	C(8)–C(9)–C(10)	124.6(15)
N–Rh–M(2)	174.4(5)	C(9)–C(10)–C(11)	112.8(14)
M(1)–Rh–S(1′)	172.1(5)	C(10)–C(11)–C(12)	111.1(13)
M(2)–Rh–S(1′)	89.3(4)	C(11)–C(12)–C(13)	129.9(13)
Ag–Rh–M(1)	112.5(5)	C(12)–C(13)–C(14)	120.5(13)
Ag–Rh–M(2)	95.5(4)	C(13)–C(14)–C(15)	112.1(13)
Ag–S(1)–Rh′	68.3(1)	C(8)–C(15)–C(14)	110.6(13)
Rh′–S(1)–C(1)	104.7(4)		

* M(1) and M(2) are the midpoints of the olefinic C(8)–C(9) and C(12)–C(13) bonds. Primed atoms are related to unprimed ones by the transformation $-x,y,\frac{1}{2}-z$.

Description of Crystal Structure of $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ **8**.—The structure of the heterotrinuclear complex, having an imposed crystallographic C_2 symmetry, is shown in Fig. 5; selected bond distances and angles are given in Table 3. The two Rh and the unique Ag atoms are in a bent arrangement [Rh–Ag–Rh′ 110.5(1)°] with two molecules of benzothiazole-2-thiolate interacting with all three metals. Each ligand is bonded to one Rh atom through the nitrogen atom [Rh–N 2.080(9) Å] and asymmetrically bridges one Rh and one Ag atom through the sulphur [Ag–S(1) 2.609(4) and Rh–S(1′) 2.358(4) Å]. The Rh atoms complete their co-ordination with a cod ligand interacting in a η^2 fashion through the two double bonds [Rh–C 2.108(15)–2.166(14), Rh–M(1) 2.005(14) and Rh–M(2) 2.038(14) Å, where M(1) and M(2) are the midpoints of the two C(8)–C(9) and C(12)–C(13) bonds]. The co-ordination around the Ag atom involves also two oxygen atoms from a perchlorate anion acting as a chelating ligand. The perchlorate anion is disordered and distributed in two positions of equal occupancy with three oxygen atoms in common.

The separation between the Rh and Ag atoms is rather short, 2.796(3) Å, and one may question if this is indicative of a direct metal–metal bond or simply an attractive interaction. A short metal–metal separation alone is not a sign of metal–metal bonding, especially when bridging ligands are present as already pointed out by Mehrotra and Hoffmann.[19] The separation in compound **8** is longer than that expected for a single metal–metal bond (*ca.* 2.591 Å)[20] and those found in the almost linear

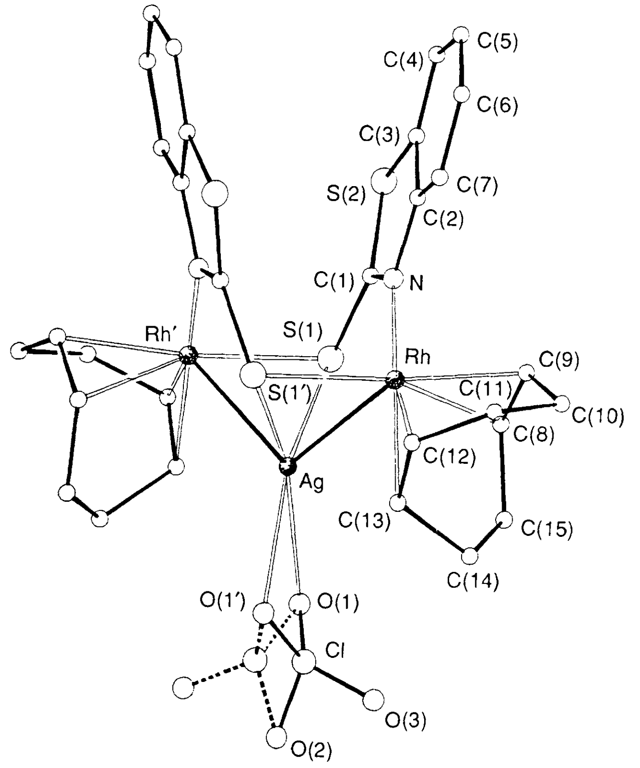


Fig. 5 View of the structure of the complex $[(cod)_2Rh_2(\mu_3-C_7H_4NS_2)_2Ag(O_2ClO_2)]$ **8** with the atomic numbering scheme

cationic complex $[Ag\{Rh(\eta-C_5H_5)(CO)(PPh_3)\}_2]^+$ [2.651(1) and 2.636(1) Å, with a Rh–Ag–Rh angle of 171.0(1)°][20] and in the very similar triangular complexes $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(\mu-dppm)(AgOPF_2O)]$ (dppm = $Ph_2PCH_2PPh_2$), 2.689(2) Å,[21a] $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(\mu-dppm)(AgO_2CMe)]$, 2.730(1) Å,[21b] and $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(\mu-dppm)(AgO_2CCF_3)]$, 2.719(1) Å,[16b] in which a metal–metal bond must be invoked as the Ag–Rh separations are not supported by a bridge. In the cationic complex $[Rh_3Ag_3H_9\{MeC(CH_2PPh_2)_3\}_3]^{3+}$ the Rh–Ag separations bridged by a single hydride were in the range 2.884(4)–2.933(4) Å and the ones doubly bridged by hydrides in the range 2.795(4)–2.807(4) Å.[17b]

Furthermore, the Rh–Ag metal–metal bond is not necessary for the description of the bonding in compound **8**. Indeed if the Ag–Rh separations, supported by benzothiazole-2-thiolate bridges, are not taken into account, each Rh atom adopts a slightly distorted square-planar co-ordination involving one N and one S atom from different bridging ligands and the midpoints of the double bonds of the cod ligand [N, S(1′), M(1), M(2) and Rh deviate from the mean plane through them by −0.048(8), 0.008(3), 0.251(16), −0.129(4) and −0.003(2) Å respectively] and the Ag atom is in a tetrahedral arrangement, determined by two S atoms from different benzothiazole-2-thiolate ligands and two O atoms of the perchlorate anion. This tetrahedral co-ordination is severely distorted because of the short 'bite' O(1) ··· O(1′) [2.23(3) Å] determining a very narrow O(1)–Ag–O(1′) angle [52.2(5)°]. The rather long Ag–O bond distances [2.532(17) Å] and the narrow O–Ag–O angle in **8** are comparable to those found in $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(\mu-dppm)(AgO_2CMe)]$, 2.432(7) Å and 51.0(3)°,[21b] and in $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(\mu-dppm)(AgO_2CCF_3)]$, 2.522(9) Å and 48.6(3)°,[16b] where a carboxylate group, with a short 'bite' O ··· O, acts a chelating ligand. Reported values for Ag–S bond distances fall in a large range depending on the metal co-ordination geometry and on the bonding mode of the sulphur (terminal or bridging). The values found in **8** are comparable to some reported for tetrahedral and bridging Ag–S bonds in silver–thiosemicarbazide complexes.[22]

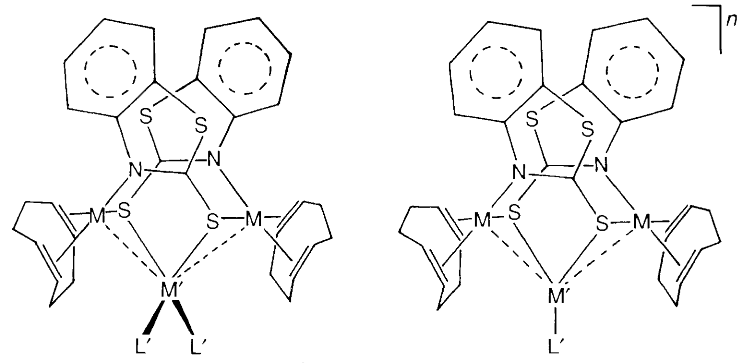
The structure of compound **8** is comparable to those of the homotrinuclear cationic complexes $[Rh_3(\mu_3-SC_5H_4N)_2(CO)_6]^+$ (SC_5H_4N = pyridine-2-thiolate) and $[Rh_3(\mu_3-C_7H_4NS_2)_2(CO)_2(PPh_3)_2(tfbb)]^+$ [tfbb = tetrafluorobenzobarrelene (tetrafluoro[5,6]bicyclo[2.2.2]octa-2,5,7-triene)], in which both pyridine-2-thiolate and benzothiazole-2-thiolate ligands behave as five-electron donors in the same manner, and from which **8** can be derived by substituting a RhL_2 fragment by $Ag(O_2ClO_2)$.[10] The main differences concern the symmetric sulphur bridges in the homotrinuclear complexes and the larger Rh ··· Rh separations (*ca.* 2.90 and 3.00 Å) compared to the Rh ··· Ag ones with the Rh atoms displaying square-planar co-ordinations. The similarities between these homo- and hetero-trinuclear complexes give a further confirmation that the short Rh–Ag separations in **8** must be considered attractive interactions rather than true direct metal–metal bonds.[10]

The structure of compound **8** contrasts with that of the 2:1 adduct **7** formed in the similar reaction of $Ag[ClO_4]$ with $[\{Rh(\mu-C_7H_4NS_2)(CO)(PPh_3)\}_2]$. As electronic, steric, and solubility effects can be adduced to account for such a different behaviour, several metal fragments AgX and AgL^+ were tested.

Addition of silver chloride, $Ag[NO_3]$, and $Ag[BF_4]$ to the complexes $[\{M'(\mu-C_7H_4NS_2)(cod)\}_2]$ gives 1:1 adducts as solids of general formula $[(cod)_2M'_2(\mu_3-C_7H_4NS_2)_2AgX]$ (M′ = Rh, X = Cl, **10**, NO_3, **11**, or BF_4, **12**; M′ = Ir, X = Cl, **13**). Once isolated, complexes **10**–**13** are scarcely soluble in most of the common organic solvents. In the solid state, co-ordination of the group X to silver can be detected from the IR spectra of the solids by ν(Ag–Cl) bands (at 265 cm^{-1} for **10** and 260 cm^{-1} for **13**), splitting of the characteristic band of the BF_4^- anion in the 1100–1050 cm^{-1} region[23] (bands at 1095, 1065 and 955 cm^{-1} for complex **12**), and bands assigned to the bidentate nitrate ligand[24] [$\nu_1(A_1)$ 1450, $\nu_5(B_2)$ 1285 and $\nu_2(A_1)$ 1025 cm^{-1}] for complex **11**. The structure of these compounds is drawn in Fig. 6.

Reaction of silver salts having anions able to act as bidentate bridges such as AgO_2CMe and AgSCN with the complex $[\{Rh(\mu-C_7H_4NS_2)(cod)\}_2]$ lead to compounds $[\{Rh(\mu-X)(cod)\}_2]$ (X = O_2CMe or SCN) through a redistribution of the ligands. The reaction is driven by the immediate formation of the white insoluble solid $[Ag(C_7H_4NS_2)]_x$. This compound can easily be prepared by reaction of $Li(C_7H_4NS_2)$ and silver perchlorate in tetrahydrofuran. Presumably the reaction starts with the formation of the heterotrinuclear complex $[(cod)_2Rh_2(\mu_3-C_7H_4NS_2)_2AgX]$, as occurs with silver chloride, or even the tetranuclear complex $[(cod)_2Rh_2(\mu_3-C_7H_4NS_2)_2Ag_2X_2]$. In contrast with chloride, the ability of thiocyanate and acetate to act as bidentate ligands leads to the final products by migration of these ligands from silver to rhodium in the heteropolynuclear intermediate complex.

The insolubility of complexes **8**–**13** is not the origin of their stability. In this context, soluble heterotrinuclear aggregates of formula $[(cod)_2M'_2(\mu_3-C_7H_4NS_2)_2AgL][ClO_4]$ (L = PPh_3; M′ = Rh, **14**, or Ir, **16**), are prepared by reaction of $[Ag(PPh_3)(Me_2CO)_x][ClO_4]$ with the appropriate complex $[\{M'(\mu-C_7H_4NS_2)(cod)\}_2]$. The heterotrinuclear complex is formed independently of the molar ratio of the reagents used. These compounds and **15** (M′ = Rh, L = pyridine) are also obtained by replacement of the poorly co-ordinating perchlorate ligand by triphenylphosphine or pyridine in **8** and **9**. However, addition of an excess of triphenylphosphine leads to breakdown of the aggregate giving $[\{Rh(\mu-C_7H_4NS_2)(cod)\}_2]$ and $[Ir(\mu-C_7H_4NS_2)(cod)(PPh_3)]$ respectively and $[Ag(PPh_3)_x][ClO_4]$. Complexes **14**–**16** behave as 1:1 electrolytes in acetone and their IR spectra shown the typical bands of unco-ordinated perchlorate at 1100 and 620 cm^{-1} in the solid state. Co-ordination of the triphenylphosphine to silver is evident from the ^{31}P NMR spectra of complexes **14** and **16** which consists of two sharp doublets at −40 °C due to coupling of the phosphorus nucleus with the active ^{107}Ag and ^{109}Ag nuclei. The ratio of the coupling constants satisfies the gyromagnetic ratio $[^1J(^{31}P-^{109}Ag) = {}^1J(^{31}P-^{107}Ag)(\gamma^{109}Ag/\gamma^{107}Ag)]$ although



M = Rh or Ir

$M'L'_2$ = Ag (O_2ClO_2) or Ag (O_2NO)
8, **9**, **11**, **12**

n = 0 M′L′ = AgCl, CuCl or AuCl
n = 1 M′L′ = Ag(PPh_3)
10, **13** – **20**

Fig. 6 Structure of complexes **8** **20**

the values of the coupling constants (see Experimental section) are slightly outside the range found[25] for silver phosphine compounds (200–500 Hz). These, in turn, depend on the co-ordination number of the silver atom and the nature of the ancillary ligands. Coupling with the ^{103}Rh atoms is not observed.

Metals of Group 11 other than silver also add to the binuclear complexes [{M′(μ-$C_7H_4NS_2$)(cod)}$_2$] following the pattern described in Scheme 1. The heterotrinuclear aggregates [(cod)$_2$M′$_2$(μ$_3$-$C_7H_4NS_2$)$_2$M″Cl] (M″ = Cu, M′ = Rh, **17**, or Ir, **18**; M″ = Au, M′ = Rh, **19**, or Ir, **20**) are obtained in good yield by reaction of copper(I) chloride and [AuCl(tht)] (tht = tetrahydrothiophene) respectively to the binuclear complexes. Compounds **17**–**20** are soluble in organic solvents and their molecular weights are in accordance with the proposed formulation.

The cage structures of the rhodium complexes **17** and **19**, Fig. 6, are the only ones compatible with their ^{1}H NMR spectra (Table 2) where both benzothiazole-2-thiolate and cod ligands are equivalent. The iridium complexes **18** and **20** are fluxional and their ^{1}H NMR spectra are not informative about their structure which should be similar to those of the rhodium complexes. These structures involve three-co-ordinate copper and gold. This co-ordination number is usual for copper but is not commonly found in gold complexes although [{Au(PEt_3)}$_2$-MoS_4][26] and [{Au($PMePh_2$)}$_2$$WS_4$][27] are well known representative examples.

Complex **17** is one of the scarce heterotrinuclear complexes of rhodium and copper, [CuRh_2(μ-CO)$_2$(η-C_5Me_5)][28] and [Cu_2Rh_6(CO)$_{15}$C(NCMe)$_2$][29] being characterized by X-ray diffraction studies. These compounds and [(η-C_5H_5)$_2$Rh(μ-CO)(μ-dppm)CuI][16b] result from the addition of the fragments Cu(C_5Me_5), Cu(NCMe)$^+$, and CuI to a Rh–Rh bond giving Rh–Cu bonds. As discussed in connection with the X-ray structure of the rhodiumsilver complex **8**, the bonding situation in our complexes is better described as if the electrophilic fragments CuCl and AuCl find electronic density in the already co-ordinated thiolate sulphur atoms of the binuclear complex to which they bind.

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.

The starting materials [{Ir(μ-Cl)(cod)}$_2$],[30] [{Pd(μ-Cl)-(allyl)}$_2$],[31] [Ag(PPh_3)($OClO_3$)],[32] [{Rh(μ-$C_7H_4NS_2$)-(cod)}$_2$][33] and [{Rh(μ-$C_7H_4NS_2$)(CO)(PPh_3)}$_2$][33] were prepared according to reported methods.

Proton, ^{13}C and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 50.309 and 80.984 MHz respectively; chemical shifts are reported relative to tetramethylsilane and 85% phosphoric acid as external references. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in NaCl windows. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Conductivities were measured in *ca.* 5 × 10^{-4} mol dm^{-3} acetone solutions using a Phillips 9501/01 conductimeter.

Preparation of the Complexes.—[{M(μ-$C_7H_4NS_2$)(L_2)}$_2$] (M = Ir, L_2 = cod, **1**; M = Pd, L_2 = η^3-C_3H_5, **2**). *Method A.* To a solution of lithium benzothiazole-2-thiolate (0.2 mmol) in diethyl ether [prepared by addition of butyllithium (0.14 cm^3, 1.38 mol dm^{-3}, 0.2 mmol) to a solution of benzothiazole-2-thiolate in diethyl ether (10 cm^3)] was added to the appropriate solid compound [{M(μ-Cl)(L_2)}$_2$] (0.1 mmol) and allowed to react for 30 min. The solvent was pumped off and the residue washed with acetone–water (4:1, 5 cm^3) to give the required compounds as microcrystalline solids which were separated by filtration, washed with acetone–water, and vacuum dried.

Method B. Solid 2-mercaptobenzothiazole (66.9 mg, 0.4 mmol) was added to a suspension of [{Ir(μ-OMe)(cod)}$_2$] (133 mg, 0.2 mmol) in diethyl ether (10 cm^3) to give a red suspension in a few minutes. The solid was separated by filtration, washed with diethyl ether, and vacuum dried. Yield: 95%. ^{13}C NMR ($CDCl_3$, −50 °C): δ 178.2 (C=S), 150.8, 134.5, 125.9, 124.3, 120.3, 119.9 ($C_7H_4NS_2$), 66.1, 65.4, 63.9, 62.6 (olefinic cod), 32.2, 32.0, 31.8 and 31.3 (CH_2 of cod).

Complex **3**. An acetone solution of [Ir(cod)(Me_2CO)$_x$]-[ClO_4] (prepared by treating [{Ir(μ-Cl)(cod)}$_2$] (33.6 mg, 0.05 mmol) with Ag[ClO_4] (20.73 mg, 0.1 mmol) in acetone (10 cm^3) for 15 min and filtering off the AgCl formed) was added slowly to a solution of the compound [{Ir(μ-$C_7H_4NS_2$)(cod)}$_2$] (93.2 mg, 0.1 mmol) in dichloromethane (5 cm^3). The red-brown solution was evaporated under vacuum to 1 cm^3. Slow addition of diethyl ether (5 cm^3) gave compound **3** as a crystalline solid which was filtered off, washed with diethyl ether and dried under vacuum.

Complex **4**. An acetone solution of [Pd(η^3-C_3H_5)(Me_2CO)$_x$]-[PF_6] (prepared by treating [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] (29.25 mg, 0.08 mmol) with Tl[PF_6] (55.67 mg, 0.16 mmol) in acetone (10 cm^3) for 30 min and filtering off the TlCl formed) was added slowly to a solution of the compound [{Pd(μ-$C_7H_4NS_2$)(η^3-

$C_3H_5)\}_2]$ (100 mg, 0.16 mmol) in dichloromethane to give a yellow solution of complex **4**. Evaporation of the solution under vacuum to 1 cm^3 and addition of diethyl ether (5 cm^3) gave the complex as a microcrystalline solid which was filtered off, washed with diethyl ether and dried under vacuum.

$[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2ML'_2][ClO_4]$ [ML'_2 = Ir(cod), **5**, or Pd(η^3-C_3H_5), **6**]. Solutions of the appropriate species $[ML_2(Me_2CO)_x][ClO_4]$ (0.071 mmol) (M = Ir, L_2 = cod; M = Pd, L_2 = η^3-C_3H_5) in acetone (10 cm^3) (prepared as described above) were added slowly to an orange solution of the complex $[\{Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)\}_2]$ (80 mg, 0.071 mmol) in dichloromethane (5 cm^3). The solutions turned green, **5** or red, **6**. Concentration to *ca.* 1 cm^3 and slow addition of diethyl ether (10 cm^3) rendered the complexes as crystalline solids, which were filtered off, washed with diethyl ether, and vacuum dried: **5**, ν(CO) (CH_2Cl_2) 2000 s (br) cm^{-1}, $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$) δ 41.5 [d, ^1J(Rh–P) = 170 Hz]; **6**, ν(CO) (CH_2Cl_2) 2000 s (br) cm^{-1}, $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$) δ 42.5 [d, ^1J(Rh–P) = 167] and 41.3 [d, ^1J(Rh–P) = 169 Hz].

Complex **7**. Solid $AgClO_4$ (40.7 mg, 0.2 mmol) was added to a solution of the complex $[\{Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)\}_2]$ (118.9 mg, 0.1 mmol) in acetone (15 cm^3) to give a red solution. Evaporation to 1 cm^3 and slow addition of diethyl ether (10 cm^3) gave complex **7** as a yellow solid which was filtered off, washed with diethyl ether, and dried under vacuum: $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$) δ 39.6 [d, ^1J(Rh–P) = 154 Hz], ν(CO) (in CH_2Cl_2) 2010s(br) cm^{-1}.

$[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2AgX]$ (X = ClO_4, **8**, Cl, **10**, NO_3, **11**, *or* BF_4, **12**). A solution (or suspension) of the appropriate species AgX (0.1 mmol) in acetone (5 cm^3) was added to a solution of the compound $[\{Rh(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ (75.4 mg, 0.1 mmol) in dichloromethane (5 cm^3) to give immediately yellow suspensions of the complexes **8** and **10** or orange solutions of **11** and **12**. The yellow suspensions were stirred for 30 min and then the solids were separated by filtration. Complex **11** began to precipitate after stirring for 1 h. The yellow suspension was stirred for 5 h and then diethyl ether (10 cm^3) was added to complete the precipitation. The orange solution of **12** was evaporated under vacuum to an oily residue which was stirred with diethyl ether (10 cm^3) to give a yellow solid. The solids were filtered off, washed with diethyl ether, and vacuum dried.

$[(cod)_2Ir_2(\mu_3\text{-}C_7H_4NS_2)_2AgX]$ (X = ClO_4, **9**, *or* Cl **13**). A solution (or suspension) of the appropriate AgX (0.107 mmol) in acetone (5 cm^3) was added to a solution of the compound $[\{Ir(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ (100 mg, 0.107 mmol) in dichloromethane (5 cm^3) to give immediately yellow suspensions which were stirred for 30 min. The suspensions were concentrated to *ca.* 2 cm^3 and then diethyl ether (10 cm^3) was added to complete the precipitation. The solids were separated by filtration and washed with diethyl ether.

$[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(PPh_3)][ClO_4]$ (M′ = Rh, **14**, *or* Ir, **16**). *Method A*. Solid triphenylphosphine (26.2 mg, 0.1 mmol) was added to a suspension of the compounds $[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ (0.1 mmol) in dichloromethane (10 cm^3), to give orange or red solutions. Concentration to *ca.* 1 cm^3 and slow addition of diethyl ether (10 cm^3) rendered the complexes as crystalline solids, which were filtered off, washed with diethyl ether, and vacuum dried.

Method B. Solid $[Ag(PPh_3)(OClO_3)]$ (47 mg, 0.1 mmol) was added to a solution of the complexes $[\{M'(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ (0.1 mmol) in dichloromethane (10 cm^3). The colour changed as described above and then work-up was performed as described in method A. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, −40 °C); **14**, δ 15.8 [two d, $^1J(^{109}Ag\text{-}^{31}P)$ = 660, $^1J(^{107}Ag\text{-}^{31}P)$ = 572]; **16**, δ 15.2 [two d, $^1J(^{109}Ag\text{-}^{31}P)$ = 663, $^1J(^{107}Ag\text{-}^{31}P)$ = 575 Hz].

Complex **15**. Pyridine (9 μl, 0.1 mmol) was added slowly to a suspension of $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ (96.2 mg, 0.1 mmol) in dichloromethane (10 cm^3). The yellow solution was evaporated under vacuum to 1 cm^3. Addition of diethyl ether (10 cm^3) gave complex **15** as yellow crystals which were filtered off, washed with diethyl ether, and dried under vacuum.

Table 4 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*
Ag	0	3166(1)	2500
Rh	1144(1)	3744(1)	3865(1)
S(1)	1836(4)	3748(1)	1532(2)
S(2)	2755(5)	4792(1)	1686(2)
N	1813(11)	4292(3)	3007(6)
C(1)	2072(15)	4264(5)	2184(8)
C(2)	2054(16)	4779(5)	3275(8)
C(3)	2571(16)	5103(4)	2635(7)
C(4)	2800(17)	5586(4)	2804(8)
C(5)	2558(19)	5743(5)	3626(9)
C(6)	2002(19)	5432(5)	4294(8)
C(7)	1749(18)	4938(5)	4114(7)
C(8)	3739(18)	3486(7)	3795(10)
C(9)	3656(19)	3819(6)	4446(11)
C(10)	3572(25)	3688(7)	5427(11)
C(11)	1701(22)	3653(7)	5765(10)
C(12)	456(18)	3439(5)	5077(10)
C(13)	708(18)	3062(5)	4522(9)
C(14)	2415(20)	2757(6)	4559(11)
C(15)	3820(22)	2038(6)	3891(12)
Cl	504(8)	2038(3)	2590(5)
O(1)	950(21)	2341(6)	1957(12)
O(2)	0	1596(13)	2500
O(3)	1660(35)	1846(9)	3129(18)

$[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2(CuCl)]$ (M′ = Rh, **17**, *or* Ir, **18**). Solid CuCl (9.9 mg, 0.1 mmol) was added to a solution of the complexes $[\{M'(\mu\text{-}C_7H_4NS_2)(cod)\}_2]$ (0.1 mmol) in CH_2Cl_2. The mixtures were stirred for 1 h and then the orange and dark red solutions were concentrated to *ca.* 3 cm^3. Slow addition of diethyl ether (10 cm^3) rendered the complexes as microcrystalline solids which were filtered off, washed with diethyl ether, and dried under vacuum.

$[(cod)_2M'_2(\mu_3\text{-}C_7H_4NS_2)_2(AuCl)]$ (M′ = Rh, **19**, *or* Ir, **20**). Solid [AuCl(tht)] (32.06 mg, 0.1 mmol) was added to a solution of the appropriate compound $[\{M'(\mu\text{-}C_7H_4NS_2)(cod)_2\}_2]$ (0.1 mmol) in dichloromethane (10 cm^3). The mixtures were stirred for 1 h and then filtered under nitrogen. Concentration of the filtrate to *ca.* 1 cm^3 and slow addition of diethyl ether (10 cm^3) gave yellow crystals of **19**. Complex **20** was obtained as red crystals by addition of hexane and cooling to −15 °C. The complexes were isolated by filtration, washed with cold hexane, and vacuum dried.

Crystal Structure Determination of $[(cod)_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$ **8**.—A yellow prismatic crystal of approximate dimensions 0.23 × 0.28 × 0.64 mm was used for the X-ray analysis.

Crystal data. $C_{30}H_{32}AgClN_2O_4Rh_2S_4$, M = 961.97, orthorhombic, space group *Pbcn*, a = 7.635(5), b = 27.564(11), c = 15.564(8) Å, U = 3 275(3) Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.951 g cm^{-3}, $F(000)$ = 1 904, μ(Mo-Kα) = 19.34 cm^{-1}.

Data collection and processing. Siemens AED single-crystal diffractometer (θ–2θ scan mode, niobium-filtered Mo-Kα radiation). All reflections with θ in the range 3–27° were measured; of 3586 independent reflections, 1863, having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analysed according to Lehmann and Larsen.[34] A correction for absorption effects was applied,[35] using the program ABSORB[36] (maximum and minimum transmission factors 1.3436 and 1.0000).

Structure solution and refinement. Direct and Fourier methods, full-matrix least-squares refinements with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the perchlorate anion. This was found disordered and distributed in two positions of equal occupancy with three oxygen atoms in common. All the hydrogen atoms were placed at geometrically calculated positions (C–H 1.00 Å) and introduced in the final structure-factor calculations. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.9838$ and $g = 0.0298$. Final R and R' values were 0.062 and 0.079 respectively. The SHELX 76 system of computer programs was used.[37] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 38. Final atomic coordinates for the non-hydrogen atoms are given in Table 4. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

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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