Binuclear rhodium(I) compounds bridged by the bifunctional 2-mercaptothiazolinate anion

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(Received December 7th, 1987)
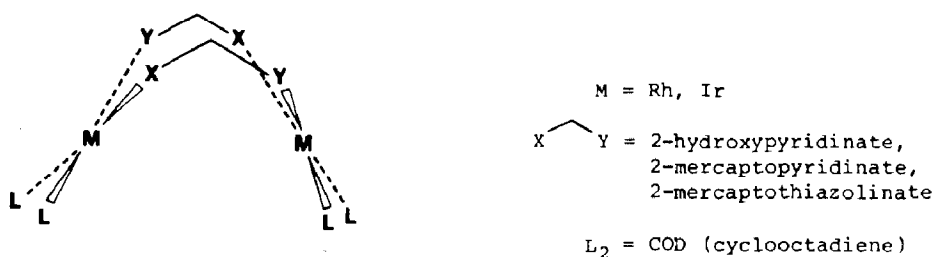
Abstract

Reaction of $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (1) with carbon monoxide yields the wine-red species $[Rh(\mu\text{-}S_2NC_3N_4)(CO)_2]_2$ (2). Addition of phosphine or phosphite ligands to solutions of 2 results in replacement of one carbonyl group on each metal to give $[Rh(\mu\text{-}S_2NC_3H_4)(CO)(L)]_2$ (L = PPh$_3$ (3), PMe$_3$ (4), P(OPh)$_3$ (5), P(OMe)$_3$ (6)). Only the *trans* isomers of these compounds are observed. The structures of 3 and 4 have been determined by X-ray crystallography. Compound 3 crystallizes with two equivalents of THF in the triclinic space group $P\bar{1}$ with a 10.973(1) Å, b 12.142(2) Å, c 20.611(3) Å, α 76.62(1)°, β 80.41(1)°, γ 80.78(1)°, V 2613.0 Å^3 and $Z = 2$. On the basis of 7098 independent observations and 570 parameters varied the structure has refined to $R = 0.035$ and $R_w = 0.057$. In 3 the two square planar rhodium(I) centers are bridged in a head-to-tail arrangement by the two 2-mercaptothiazolinate groups, which are bound to the metals through the exocyclic sulfur and the nitrogen. The square planes are tilted to each other by 38.5° and the Rh–Rh separation is 3.2435(3) Å. Compound 4 crystallizes in the orthorhombic space group $Pbca$ with a 10.032(2) Å, b 28.335(5) Å, c 17.126(2) Å, V 4868.1 Å^3 and $Z = 8$ and has refined to $R = 0.031$ and $R_w = 0.046$ on the basis of 3682 independent observations and 235 parameters varied. The structure of 4 closely resembles that of 3 except that the tilt of the square planes is 30.0° and the Rh–Rh separation has decreased to 3.0524(4) Å.

Introduction

In a previous paper we described the synthesis and characterization of a series of binuclear complexes of rhodium and iridium bridged by some bifunctional anionic groups [1], as diagrammed below. One aspect of interest concerned the influence of

these bridging groups on the tilt of the two metal coordination planes and on the resulting metal–metal separation, particularly as related to the photochemical

M = Rh, Ir

X⌒Y = 2-hydroxypyridinate,
2-mercaptopyridinate,
2-mercaptothiazolinate

L_2 = COD (cyclooctadiene)

activation of such species toward 2-center oxidative addition reactions. In the two structurally characterized complexes, $[M_2(\mu\text{-}L)_2(COD)_2]$ (M = Rh, Ir; L = 2-mercaptothiazolinate) the metal–metal separations (3.7154(5) and 3.5434(4) Å, respectively) were too large to suggest a significant degree of direct metal–metal interaction, due probably to non-bonded contacts between the two COD ligands [1]. However, it seemed apparent that with the other smaller ligands, significantly shorter M $\cdots$ M separations should be possible, and it was these complexes that were of interest to us for the possible binuclear photoactivation of substrate molecules. Recent studies by other groups have indeed shown some interesting photochemistry of related complexes [2,3,4].

In this paper we present our data on the substitution of the COD ligands in $[Rh_2(\mu\text{-}L)_2(COD)_2]$ (L = 2-mercaptothiazolinate) by carbon monoxide and phosphine ligands, and describe the structural characterization of two derivatives, one containing the large PPh$_3$ group and the other containing the smaller PMe$_3$ ligand.

Experimental

General comments. All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen and all operations were routinely carried out under Schlenk conditions utilizing a dinitrogen atmosphere. The compounds, 2-mercaptothiazoline, trimethylphosphite, triphenylphosphite, triphenylphosphine, and 1,5-cyclooctadiene (COD) were obtained from Aldrich; trimethylphosphine was obtained from Strem and hydrated rhodium trichloride was received from Englehard. Sodium hydride as a 60% oil emulsion was obtained from Aldrich and stored under dinitrogen; before use it was washed with toluene and hexane to remove the oil. The complexes, $[Rh(\mu\text{-}Cl)(COD)]_2$ [5] and $[RhCl(CO)(PPh_3)_2]$ [6] were prepared by the reported procedures. IR spectra were recorded on either Nicolet 7199 or Mattson Polaris FT spectrometers with use of Nujol mulls on KBr plates or in solution in NaCl cells. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were run on a Bruker WH-400 instrument and elemental analyses were performed within the department.

Preparation of complexes. *(a) [Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PPh$_3$)]$_2$ · 2THF (3).* Method A. A solution of sodium 2-mercaptothiazolinate in THF (10 ml), prepared by stirring 87 mg (0.73 mmol) 2-mercaptothiazoline and 17.5 mg (0.73 mmol) NaH for 1 h at room temperature, was slowly added to a solution of 480 mg (0.69 mmol) $[RhCl(CO)(PPh_3)_2]$ in THF (40 ml), resulting in an immediate color change from yellow to orange. The reaction mixture was allowed to stir for 5 h and on removal of

Table 1

Spectroscopic data for the compounds [Rh(μ-S$_2$NC$_3$H$_4$)(CO)(L)]$_2$

L	IR (cm^{-1})		NMR ^{a} (ppm)	
	solid	solution ^{b}	^{31}P{^{1}H} ^{b,c}	^{1}H
CO (2)		2094(s), 2058(m), 2045(w,sh), 2018(s) ^{d}		
PPh$_3$ (3)	1966, 1974(s)	1981(s) ^{e}	39.81 (d, J(Rh–P) 163.6) ^{f}	7.38–7.81 (m, 30H), 3.83 (m, 2H), 3.19 (m, 2H), 2.81 (m, 2H), 2.05 (m, 2H) ^{f}
PMe$_3$ (4)	1954(sh), 1963(s)	1962(sh), 1973(s) ^{e}	0.82 (d, J(Rh–P) 148.4) ^{e}	3.90 (m, 4H), 3.29 (m, 4H), 1.50 (dd, J(P–H) 9.9 Hz, J(Rh–H) 1.2 Hz, 18H) ^{g}
P(OPh)$_3$ (5)	1958(sh), 1998(s)	2005(sh), 2015(s) ^{d}	112.8 (d, J(Rh–P) 271.2) ^{h}	
P(OMe)$_3$ (6)	1972(sh), 1985(s)	1985(sh), 1994(s) ^{e}	132.5 (d, J(Rh–P) 252.2) ^{e}	3.89 (m, 4H), 3.71 (d, J(P–H) 12.3 Hz, 18H), 3.30 (m, 4H) ^{g}

^{a} Temperatures at $-40\,^{\circ}$C, except for **3** which was obtained at $20\,^{\circ}$C. ^{b} Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; d, doublet; m, multiplet; dd, doublet of doublets. ^{c} Coupling given in Hz. ^{d} THF. ^{e} CH$_2$Cl$_2$. ^{f} CDCl$_3$. ^{g} CD$_2$Cl$_2$. ^{h} THF-d_8.

THF an orange solid remained which was washed with hexane (3 × 5 ml). Dissolution in THF (30 ml) was followed by filtration and concentration to ca. 10 ml, after which 10 ml hexane was slowly layered on top. Refrigeration afforded the product as orange crystals; yield 295 mg (73%). Anal. Found: C, 53.49; H, 4.83; N, 2.37. C$_{52}$H$_{54}$N$_2$O$_4$P$_2$Rh$_2$S$_4$ calcd.: C, 53.52; H, 4.66; N, 2.40%. See Table 1 for spectroscopic details for this and other compounds.

Method B. A solution of sodium 2-mercaptothiazolinate in THF (10 ml), prepared by using 68 mg (0.57 mmol) of 2-mercaptothiazoline and 13.7 mg (0.57 mmol) NaH, was slowly added to a solution of 135 mg (0.27 mmol) [Rh(μ-Cl)(COD)]$_2$ in THF (10 ml). An orange color, due to [Rh(μ-S$_2$NC$_3$H$_4$)(COD)]$_2$ (1) [1], developed within 1 h and the reaction mixture was stirred overnight to ensure completion. The solution was filtered, transfered to a 100 ml flask and filled to a volume of 50 ml with THF. Passing a slow stream of CO through the solution resulted in a color change to wine red within 5 min, indicating the presence of [Rh(μ-S$_2$NC$_3$H$_4$)(CO)$_2$]$_2$ (2) (vide infra). Addition of 160 mg (0.61 mmol) PPh$_3$ in 5 ml THF caused the color to change to orange red with gas evolution. After 5 h the solution was concentrated to 5 ml and 5 ml hexane was slowly layered on top. Refrigeration afforded the compound as red orange crystals, shown to be identical to that obtained by Method A (yield 180 mg, 57%).

(b) [Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PMe$_3$)]$_2$ (4). This species was prepared as described in Method B for compound **3** starting with 250 mg (0.51 mmol) [Rh(μ-Cl)(COD)]$_2$ and 97 mg (1.27 mmol, 130 μl) PMe$_3$. Addition of the PMe$_3$ to the wine-red solution of [Rh(μ-S$_2$NC$_3$H$_4$)(CO)$_2$]$_2$ (2) resulted in a color change to orange, accompanied

by gas evolution. After 5 h the solvent was removed and the resulting orange solid was washed with hexane (2×20 ml). After drying in vacuo the product was obtained as an orange powder (282 mg, 85%). Recrystallization from THF/hexane yielded dark red crystals suitable for an X-ray study in 40% yield. Anal. Found: C, 26.10; H, 4.07; N, 4.42. $C_{14}H_{26}N_2O_2P_2Rh_2S_4$ calcd.: C, 25.85; H, 4.03; N, 4.31%.

(c) [Rh(\mu-S$_2$NC$_3$H$_4$)(CO)(P(OPh)$_3$)]$_2 \cdot 2THF$ (5). To a wine-red THF solution (50 ml) of [Rh(μ-S$_2$NC$_3$H$_4$)(CO)$_2$]$_2$ (2), prepared as described above by using 295 mg (0.60 mmol) [Rh(μ-Cl)(COD)]$_2$, was added 410 mg (1.32 mmol, 346 μl) P(OPh)$_3$ resulting in gas evolution and a color change to orange. The solvent was removed after 2 h and the resulting red-brown solid was washed with hexane (2×20 ml) and dried in vacuo. Recrystallization from THF/hexane yielded a red-brown powder in 80% yield. Anal. Found: C, 50.17; H, 4.17; N, 2.02. $C_{52}H_{54}N_2O_{10}P_2Rh_2S_4$ calcd.: C, 49.45; H, 4.31; N, 2.22%.

(e) [Rh(\mu-S$_2$NC$_3$H$_4$)(CO)(P(OMe)$_3$)]$_2$ (6). To a wine-red THF solution (50 ml) of [Rh(μ-S$_2$NC$_3$H$_4$)(CO)$_2$]$_2$ (2) (prepared as above by using 275 mg (0.56 mmol) [Rh(μ-Cl)(COD)]$_2$) was added 152.5 mg (1.23 mmol, 145 μl) P(OMe)$_3$ resulting in a color change to orange and gas evolution. The solvent was removed after 2 h and the resulting light brown solid was washed with hexane (2×20 ml), dried in vacuo and recrystallized from THF/hexane; yield 368 mg (88%). Anal. Found: C, 22.87; H, 3.66; N, 3.55. $C_{14}H_{26}N_2O_8P_2Rh_2S_4$ calcd.: C, 22.53; H, 3.51; N, 3.75%.

X-Ray data collection. Suitable crystals of **3** and **4** were obtained as described earlier. Compound **3** was mounted in air on a glass fiber using epoxy resin, whereas **4** was mounted in a N$_2$-filled capillary as a precaution against air oxidation. Data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation. The automatic peak search and reflection indexing programs, in conjunction with a cell reduction program, established the crystal systems. For compound **3** the lack of absences and the $\bar{1}$ Laue symmetry of the diffraction pattern established the space group as either $P1$ or $P\bar{1}$; the latter was confirmed by the successful refinement. For **4** the *mmm* diffraction symmetry and the systematic absences ($0kl$; k odd; $h0l$, l odd; $hk0$, h odd) unambiguously defined the space group as *Pbca*. Cell constants for both compounds were obtained from a least-squares refinement of the setting angles (centered in both positive and negative theta) of 25 reflections having 2θ between 22.02 and 25.78 for **3** and between 20.10 and 25.84 for **4**.

The intensity data were collected by using a $\theta/2\theta$ scan with variable speeds chosen to give $\sigma(I)/I \leqslant 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the $\alpha_1-\alpha_2$ wavelength dispersion, and backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. For compound **3** the intensity fell by 10(2)% over the data collection so a linear correction was applied; for **4** no significant variation in the standards was observed so no correction was applied. See Table 2 for crystal data and details of intensity collection. The data were corrected for Lorenz and polarization effects and for absorption by the method of Walker and Stuart [7]. Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections [8].

Table 2

Crystal data and details of intensity collection for compounds **3** and **4**

	[Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PPh$_3$)]$_2$· 2THF (3)	[Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PMe$_3$)]$_2$ (4)
mol formula	C$_{52}$H$_{54}$N$_2$O$_4$P$_2$Rh$_2$S$_4$	C$_{14}$H$_{26}$N$_2$O$_2$P$_2$Rh$_2$S$_4$
FW	1167.04	650.39
crystal shape	parallelipiped	orthorhombic prism (14 sides)
crystal size, mm	0.31×0.24×0.36	0.26×0.38×0.47
systematic absences	none	$0kl$ (k odd), $h0l$ (l odd), $hk0$ (h odd)
space group	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)
temperature, °C	22	22
radiation (λ, Å)	Mo (0.71073)	Mo (0.71073)
unit cell parameters		
a, Å	10.973(1)	10.032(2)
b, Å	12.142(2)	28.335(5)
c, Å	20.611(3)	17.126(2)
α, deg	76.62(1)	90.00
β, deg	80.41(1)	90.00
γ, deg	80.78(1)	90.00
V, Å^3	2613.0	4868.1
Z	2	8
ρ_{calcd}, g cm^{-3}	1.483	1.775
linear absorp coeff. μ, cm^{-1}	8.789	18.075
max 2θ, deg	50.00	55.00
takeoff angle, deg	3.00	3.00
detector aperture, mm	(3.00 + tan θ)×4.00	(3.00 + tan θ)×4.00
cryst. to detector dist, mm	173	173
scan type	$\theta/2\theta$	$\theta/2\theta$
scan rate, deg min^{-1}	variable between 1.25 and 6.67	variable between 1.33 and 6.67
scan width, deg	0.70 + 0.347 tan θ	0.60 + 0.347 tan θ
total no. of reflections collected	9667 (h, ± k, ± l)	6194 (h, k, l)
No. indep. reflections	9137	6194
no. of obserns (*NO*) ($I \geqslant 3\sigma(I)$)	7098	3682
no. of variables (*NV*)	570	235
R^a	0.035	0.031
R_w^a	0.057	0.046
GOF^a	1.983	1.497

^{a} $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2}$; GOF $= [\Sigma w(|F_0| - |F_c|)^2/(NO - NV)]^{1/2}$.

Structure solution and refinement. Both structures were solved by using Patterson techniques to locate the rhodium atoms, and subsequent least-squares and difference Fourier calculations [9] to obtain the other atom positions. All hydrogens (except those on the THF molecules of **1**) were located and were input in their idealized positions using C–H distances of 0.95 Å; their thermal parameters were fixed at 1.2 times those of the attached carbon atoms. Hydrogen positions were not refined but were allowed to "ride" on their attached carbon. One of the two THF molecules in **3** was badly disordered such that the oxygen and carbon atoms could not be unambiguously distinguished, so all five atoms were refined as carbon atoms.

Table 3

Positional and isotropic thermal parameters for $[Rh(\mu\text{-}S_2NC_3H_4)(CO)(PPh_3)]_2 \cdot 2THF$ (**3**)

Atom	x	y	z	B (Å^2) [a]
Rh(1)	0.25674(3)	0.12009(3)	0.23787(2)	3.215(7)
Rh(2)	0.15933(3)	−0.12716(3)	0.26503(2)	3.043(7)
S(1)	0.2726(1)	0.0508(1)	0.35425(6)	4.90(3)
S(2)	0.4305(1)	−0.1531(1)	0.42050(7)	5.44(3)
S(3)	0.3309(1)	−0.1398(1)	0.17860(6)	4.56(3)
S(4)	0.5991(1)	−0.1379(1)	0.18512(9)	6.49(4)
P(1)	0.2614(1)	0.22237(9)	0.12995(5)	3.17(2)
P(2)	−0.0022(1)	−0.16610(9)	0.34742(5)	3.14(2)
O(1)	0.0239(4)	0.2642(3)	0.2753(2)	6.7(1)
O(2)	−0.0127(4)	−0.1055(3)	0.1663(2)	6.6(1)
O(3) [b]	0.346(1)	0.5963(7)	0.8004(5)	19.5(4)
N(1)	0.2862(3)	−0.1624(3)	0.3355(2)	3.49(8)
N(2)	0.4282(3)	0.0204(3)	0.2177(2)	3.67(8)
C(1)	0.3197(4)	−0.0913(4)	0.3640(2)	3.8(1)
C(2)	0.3977(5)	−0.2926(5)	0.4188(3)	5.7(1)
C(3)	0.3515(4)	−0.2784(4)	0.3523(3)	4.6(1)
C(4)	0.4444(4)	−0.0744(4)	0.1977(2)	3.9(1)
C(5)	0.6519(5)	−0.0144(7)	0.2010(4)	8.6(2)
C(6)	0.5442(4)	0.0524(5)	0.2313(3)	5.5(1)
C(7)	0.1143(4)	0.2084(4)	0.2602(2)	4.2(1)
C(8)	0.0539(4)	−0.1112(4)	0.2043(2)	4.1(1)
C(11)	0.1597(4)	0.1892(3)	0.0774(2)	3.55(9)
C(12)	0.0410(5)	0.1679(5)	0.1050(3)	5.5(1)
C(13)	−0.0403(5)	0.1456(5)	0.0658(3)	6.2(1)
C(14)	−0.0031(5)	0.1422(4)	0.0000(3)	5.6(1)
C(15)	0.1142(5)	0.1629(5)	−0.0284(3)	6.1(1)
C(16)	0.1964(5)	0.1866(5)	0.0100(3)	5.3(1)
C(21)	0.4124(4)	0.2217(4)	0.0772(2)	3.33(9)
C(22)	0.4708(4)	0.1201(4)	0.0603(2)	4.4(1)
C(23)	0.5853(5)	0.1155(5)	0.0193(3)	5.1(1)
C(24)	0.6417(5)	0.2121(5)	−0.0050(3)	5.9(1)
C(25)	0.5843(5)	0.3149(5)	0.0116(3)	6.4(2)
C(26)	0.4707(5)	0.3181(4)	0.0523(3)	4.9(1)
C(31)	0.2136(4)	0.3751(3)	0.1266(2)	3.54(9)
C(32)	0.2581(5)	0.4244(4)	0.1706(3)	4.8(1)
C(33)	0.2249(6)	0.5418(4)	0.1699(3)	5.9(1)
C(34)	0.1471(6)	0.6068(4)	0.1251(3)	5.1(1)
C(35)	0.1027(6)	0.5573(5)	0.0829(3)	6.7(2)
C(36)	0.1379(5)	0.4418(4)	0.0823(3)	5.2(1)
C(41)	−0.1288(4)	−0.0525(4)	0.3601(2)	4.0(1)
C(42)	−0.1377(5)	0.0461(4)	0.3110(3)	5.6(1)
C(43)	−0.2376(6)	0.1309(5)	0.3193(4)	8.0(2)
C(44)	−0.3234(6)	0.1155(5)	0.3748(4)	10.9(2)
C(45)	−0.3169(5)	0.0197(5)	0.4249(4)	8.6(2)
C(46)	−0.2162(5)	−0.0661(5)	0.4177(3)	6.1(1)
C(51)	−0.0791(4)	−0.2791(4)	0.3324(2)	3.50(9)
C(52)	−0.2083(4)	−0.2814(4)	0.3443(3)	5.1(1)
C(53)	−0.2561(5)	−0.3702(5)	0.3304(3)	6.7(1)
C(54)	−0.1836(5)	−0.4566(4)	0.3044(3)	5.4(1)
C(55)	−0.0578(5)	−0.4544(4)	0.2919(3)	5.6(1)
C(56)	−0.0051(4)	−0.3646(4)	0.3051(3)	4.7(1)
C(61)	0.0389(4)	−0.2210(4)	0.4326(2)	3.43(9)
C(62)	0.0595(5)	−0.1443(4)	0.4693(2)	4.6(1)

Table 3 (continued)

Atom	x	y	z	B (Å^2) [a]
C(63)	0.0933(5)	−0.1812(5)	0.5326(2)	5.2(1)
C(64)	0.1053(5)	−0.2949(5)	0.5619(3)	5.6(1)
C(65)	0.0876(6)	−0.3734(5)	0.5255(3)	6.1(1)
C(66)	0.0538(5)	−0.3358(4)	0.4614(2)	4.6(1)
C(71) [b]	0.413(1)	0.486(1)	0.8179(7)	16.8(5)
C(72)	0.355(2)	0.440(1)	0.8713(7)	20.7(6)
C(73)	0.257(1)	0.478(1)	0.8855(8)	21.1(6)
C(74)	0.237(1)	0.593(1)	0.8499(6)	18.1(4)
C(81) [c]	0.447(1)	0.407(1)	0.3654(6)	14.3(4) *
C(82)	0.425(1)	0.387(1)	0.4353(7)	17.1(5) *
C(83)	0.323(2)	0.336(1)	0.4576(8)	20.4(6) *
C(84)	0.257(1)	0.342(1)	0.4044(7)	17.5(5) *
C(85)	0.336(1)	0.386(1)	0.3464(6)	15.5(4) *

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + (ab \cos \gamma)B_{12} + (ac \cos \beta)B_{13} + (bc \cos \alpha)B_{23}]$. Starred atoms were refined isotropically. [b] Atoms O(3), C(71), C(72), C(73), C(74) are THF solvent molecule 1. [c] Atoms C(81), C(82), C(83), C(84), C(85) are the rotationally disordered THF molecule 2 in which all atoms were refined as carbon atoms.

Table 4

Positional and isotropic thermal parameters for [Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PMe$_3$)]$_2$ (4)

Atom	x	y	z	B (Å^2) [a]
Rh(1)	−0.02328(4)	0.09480(1)	−0.00749(2)	3.039(7)
Rh(2)	−0.21162(4)	0.17890(1)	0.00778(20	2.918(6)
S(1)	−0.0859(1)	0.08580(5)	0.12652(7)	3.92(3)
S(2)	−0.3568(2)	0.07156(5)	0.19456(8)	5.20(3)
S(3)	−0.3283(1)	0.13824(5)	−0.09411(7)	3.92(3)
S(4)	−0.4341(2)	0.03981(5)	−0.09569(9)	5.13(3)
P(1)	0.0445(1)	0.09043(5)	−0.13364(8)	4.19(3)
P(2)	−0.1358(1)	0.22463(5)	0.10617(8)	3.99(3)
O(1)	0.2377(4)	0.1319(2)	0.0424(3)	7.6(1)
O(2)	−0.0841(5)	0.2437(1)	−0.1037(3)	7.2(1)
N(1)	−0.3073(4)	0.1339(1)	0.0878(2)	2.90(7)
N(2)	−0.2020(4)	0.0614(1)	−0.0389(2)	3.17(7)
C(1)	−0.2500(5)	0.1019(2)	0.1291(2)	3.23(9)
C(2)	−0.4878(6)	0.1138(2)	0.1763(3)	5.4(1)
C(3)	−0.4532(5)	0.1361(2)	0.0982(3)	4.1(1)
C(4)	−0.3045(5)	0.0796(2)	−0.0723(3)	3.27(9)
C(5)	−0.3247(6)	−0.0095(2)	−0.0755(4)	5.3(1)
C(6)	−0.2201(6)	0.0108(2)	−0.0202(3)	4.61(1)
C(7)	0.1361(5)	0.1182(2)	0.0215(3)	4.5(1)
C(8)	−0.1349(6)	0.2188(2)	−0.0595(3)	4.5(1)
C(9)	0.0076(7)	0.1400(2)	−0.1965(3)	6.0(1)
C(10)	−0.0251(8)	0.0410(2)	−0.1869(3)	6.7(2)
C(11)	0.2237(6)	0.0827(3)	−0.1496(4)	7.8(2)
C(12)	−0.2088(8)	0.2143(2)	0.2005(4)	7.1(2)
C(13)	0.0409(7)	0.2239(3)	0.1261(5)	7.5(2)
C(14)	−0.1670(8)	0.2877(2)	0.0919(5)	7.4(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + (ab \cos \gamma)B_{12} + (ac \cos \beta)B_{13} + (bc \cos \alpha)B_{23}]$.

Refinement was carried out by full-matrix least-squares techniques minimizing the function $\Sigma w(|F_0| - |F_c|)^2$, with $w = 4F_0^2/\sigma^2(F_0^2)$. The neutral atom scattering factors [10,11] and anomalous dispersion terms [12] for the atoms were obtained from the usual sources. Analyses of F_0 vs. F_c showed no unusual trends. The highest ten peaks in the difference Fourier maps were between 0.37 and 0.82 e Å^{-3} for **3** (all in the vicinities of the solvent molecules) and between 0.36 and 0.42 e Å^{-3} for **4**.

The positional and isotropic thermal parameters for the two structures are given in Tables 3 and 4. Structure amplitudes, anisotropic thermal parameters, hydrogen parameters, least-squares planes, and bond lengths and angles involving the phenyl groups and solvent molecules in **3** are available from M.C. on request (Tables S1–S5 for compound **3** and Tables S6–S9 for compound **4**).

Results and discussion

(a) Description of structures. *(i)* *[Rh(μ-S₂NC₃H₄)(CO)(PPh₃)]₂ · 2THF (3).* The binuclear complex crystallizes together with two equivalents of THF, such that there are no unusual contacts between species. Although one of the THF molecules is rotationally disordered (vide supra), both display the expected geometry. Within the complex, shown in Fig. 1, the two Rh centers are bridged by two 2-mercaptothiazolinate groups, which are bound through the mercapto sulfur atom and the ring nitrogen in a head-to-tail arrangement, much as was observed in the precursor, [Rh(μ-S$_2$NC$_3$H$_4$)(COD)]$_2$ [1] and in related species bridged by other bifunctional ligands [2,3,13]. The coordination about each metal is completed by a carbonyl and a triphenylphosphine group to give each a slightly distorted square planar geometry. These coordination planes are staggered by an average of 30.9° in order to
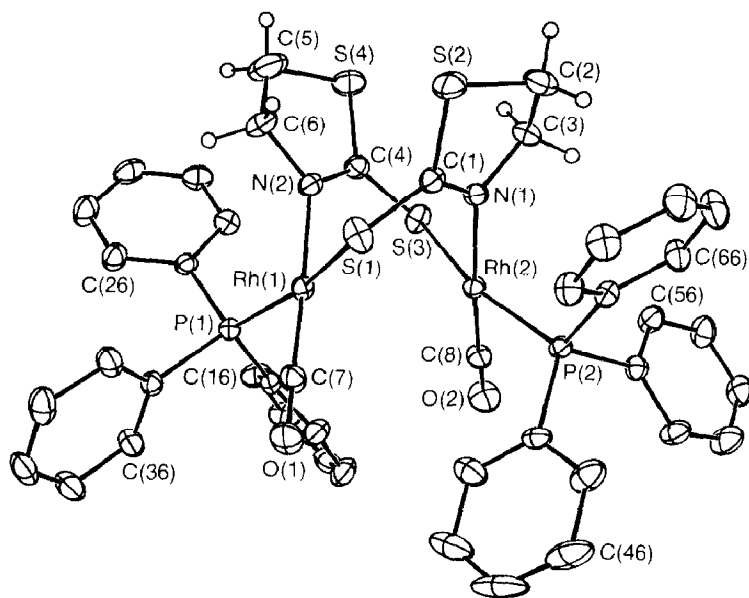

Fig. 1. A perspective drawing of [Rh(μ-S$_2$NC$_3$H$_4$)(CO)(PPh$_3$)]$_2$ (**3**) showing the numbering scheme. Thermal ellipsoids are drawn at the 20% level except for hydrogens on the 2-mercaptothiazolinate groups, which are shown artificially small. Phenyl hydrogens are not shown.

Table 5

Selected distances (Å) for compound **3** [a]

Rh(1)–S(1)	2.378(1) [b]	P(1)–C(11)	1.825(3)
Rh(1)–P(1)	2.2797(9)	P(1)–C(21)	1.824(3)
Rh(1)–N(2)	2.102(3)	P(1)–C(31)	1.833(3)
Rh(1)–C(7)	1.804(3)	P(2)–C(41)	1.826(3)
Rh(2)–S(3)	2.3787(9)	P(2)–C(51)	1.829(3)
Rh(2)–P(2)	2.2679(8)	P(2)–C(61)	1.831(3)
Rh(2)–N(1)	2.104(3)	O(1)–C(7)	1.149(4)
Rh(2)–C(8)	1.800(3)	O(2)–C(8)	1.142(4)
S(1)–C(1)	1.696(4)	N(1)–C(1)	1.278(4)
S(2)–C(1)	1.781(3)	N(1)–C(3)	1.466(4)
S(2)–C(2)	1.796(5)	N(2)–C(4)	1.287(4)
S(3)–C(4)	1.720(4)	N(2)–C(6)	1.476(4)
S(4)–C(4)	1.753(3)	C(2)–C(3)	1.504(5)
S(4)–C(5)	1.807(6)	C(5)–C(6)	1.459(6)

[a] Parameters involving the phenyl groups and the THF solvent molecule are available as Supplementary Material (Table S-5). [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

minimize contacts between ligands on the adjacent metals. In addition, the phenyl substituents on the PPh_3 groups are staggered with respect to the carbonyl on the adjacent metal, again minimizing contacts.

The *cis*-arrangement of the bridging anionic ligands allows the complex to be folded such that the metal coordination planes are non-parallel, being tilted to each other by 38.5°. This tilt is substantially closer to parallel than that observed (54.3° [1]) in the COD precursor, **1**, and this more nearly parallel alignment is accompanied by a dramatic decrease in Rh–Rh separation from 3.7154(5) Å in **1** to 3.2435(3) Å in **3** (see Table 5), presumably reflecting the decrease in steric interactions upon substituting a COD ligand for CO and PPh_3.

The bonding of the rhodium atoms to the ligands appears to be unexceptional, with all Rh–ligand bonds agreeing well with those in closely related species [14–18], and all angles (see Table 6) being as expected for the square planar geometry. Within the mercaptothiazolinate ligands the parameters are essentially as expected. The N(1)–C(1) and N(2)–C(4) distances (1.278(4), 1.287(4) Å) are typical for N=C double bonds [19] and are significantly shorter than the N(1)–C(3) and N(2)–C(6) singly bonded distances of 1.466(4) and 1.476(4) Å, respectively. Both exocyclic C–S distances (1.696(4), 1.720(4) Å) are somewhat shorter than the endocyclic ones (range, 1.753(3) to 1.807(6) Å), suggesting somewhat greater multiple bond character in the former [19]. All angles within the rings also are as expected with those at S(2) and S(4) being more acute, giving rise to strain at these atoms owing to the larger covalent radius of sulfur.

(ii) [Rh(μ-S₂NC₃H₄)(CO)(PMe₃)]₂ (4). As shown in Fig. 2, compound **4** very closely resembles **3**, and the parameters given in Tables 7 and 8 clearly show that most bond lengths and angles within the complex are essentially indistinguishable from those of **3**; these parameters will therefore not be discussed further. The few differences that occur appear to result from the rather large difference in size of the two phosphine groups. Although the Rh–P distances in these PPh_3 and PMe_3 analogues do not differ appreciably, the Rh–S distances opposite these phosphines

Table 6

Selected angles (deg) for compound **3** [a]

S(1)–Rh(1)–P(1)	166.34(3)	Rh(2)–N(1)–C(3)	118.8(2)
S(1)–Rh(1)–N(2)	87.61(8)	C(1)–N(1)–C(3)	114.1(3)
S(1)–Rh(1)–C(7)	89.2(1)	Rh(1)–N(2)–C(4)	126.3(2)
P(1)–Rh(1)–N(2)	93.77(7)	Rh(1)–N(2)–C(6)	120.2(2)
P(1)–Rh(1)–C(7)	88.7(1)	C(4)–N(2)–C(6)	113.4(3)
N(2)–Rh(1)–C(7)	175.7(1)	S(1)–C(1)–S(2)	117.6(2)
S(3)–Rh(2)–P(2)	164.39(3)	S(1)–C(1)–N(1)	128.3(3)
S(3)–Rh(2)–N(1)	88.82(7)	S(2)–C(1)–N(1)	114.1(3)
S(3)–Rh(2)–C(8)	89.7(1)	S(2)–C(2)–C(3)	104.8(3)
P(2)–Rh(2)–N(1)	91.73(7)	N(1)–C(3)–C(2)	107.9(3)
P(2)–Rh(2)–C(8)	88.3(1)	S(3)–C(4)–S(4)	117.7(2)
N(1)–Rh(2)–C(8)	174.6(1)	S(3)–C(4)–N(2)	126.5(3)
Rh(1)–S(1)–C(1)	106.1(1)	S(4)–C(4)–N(2)	115.7(3)
C(1)–S(2)–C(2)	89.6(2)	S(4)–C(5)–C(6)	107.7(3)
Rh(2)–S(3)–C(4)	106.3(1)	N(2)–C(6)–C(5)	110.0(4)
C(4)–S(4)–C(5)	90.0(2)	Rh(1)–C(7)–O(1)	179.1(3)
Rh(1)–P(1)–C(11)	117.6(1)	Rh(2)–C(8)–O(2)	177.5(3)
Rh(1)–P(1)–C(21)	117.0(1)	P(1)–C(11)–C(12)	118.9(3)
Rh(1)–P(1)–C(31)	111.9(1)	P(1)–C(11)–C(16)	122.8(3)
C(11)–P(1)–C(21)	103.3(1)	P(1)–C(21)–C(22)	118.8(3)
C(11)–P(1)–C(31)	102.7(1)	P(1)–C(21)–C(26)	123.0(3)
C(21)–P(1)–C(31)	102.2(1)	P(1)–C(31)–C(32)	117.8(3)
Rh(2)–P(2)–C(41)	119.0(1)	P(1)–C(31)–C(36)	123.1(3)
Rh(2)–P(2)–C(51)	110.0(1)	P(2)–C(41)–C(42)	118.9(3)
Rh(2)–P(2)–C(61)	115.8(1)	P(2)–C(41)–C(46)	120.5(3)
C(41)–P(2)–C(51)	104.4(1)	P(2)–C(51)–C(52)	124.2(3)
C(41)–P(2)–C(61)	102.2(2)	P(2)–C(51)–C(56)	117.5(3)
C(51)–P(2)–C(61)	103.8(1)	P(2)–C(61)–C(62)	119.0(3)
Rh(2)–N(1)–C(1)	127.0(2)	P(2)–C(61)–C(66)	122.7(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

do differ, with those opposite PMe$_3$ in **4** (av. 2.395(1) Å) being somewhat longer than those opposite PPh$_3$ in **3** (av. 2.378(1) Å). This appears not to result from steric influences, since the larger PPh$_3$ group gives rise to shorter Rh–S distances, but rather may result from a weakening of the Rh–S bonds *trans* to the more basic

Table 7

Selected distances (Å) for compound **4** [a]

Rh(1)–S(1)	2.394(1)	S(2)–C(2)	1.805(5)	O(1)–C(7)	1.147(5)
Rh(1)–P(1)	2.268(1)	S(3)–C(4)	1.718(4)	O(2)–C(8)	1.153(5)
Rh(1)–N(2)	2.097(3)	S(4)–C(4)	1.767(4)	N(1)–C(1)	1.286(5)
Rh(1)–C(7)	1.801(5)	S(4)–C(5)	1.812(5)	N(1)–C(3)	1.476(5)
Rh(2)–S(3)	2.396(1)	P(1)–C(9)	1.808(5)	N(2)–C(4)	1.286(5)
Rh(2)–P(2)	2.257(1)	P(1)–C(10)	1.812(5)	N(2)–C(6)	1.481(5)
Rh(2)–N(1)	2.105(3)	P(1)–C(11)	1.832(5)	C(2)–C(3)	1.520(6)
Rh(2)–C(8)	1.789(4)	P(2)–C(12)	1.798(5)	C(5)–C(6)	1.527(7)
S(1)–C(1)	1.709(4)	P(2)–C(13)	1.806(6)		
S(2)–C(1)	1.772(4)	P(2)–C(14)	1.829(5)		

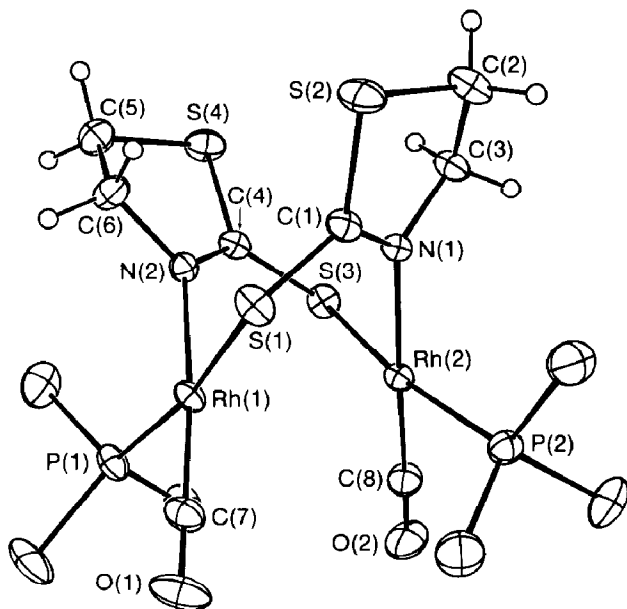[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Fig. 2. A perspective view of $[Rh(\mu\text{-}S_2NC_3H_4)(CO)(PMe_3)]_2$ (4) showing the numbering scheme. 20% thermal ellipsoids are shown except for mercaptothiazolinate hydrogens which are shown artificially small. Hydrogens on the PMe_3 ligands are omitted.

[20,21] PMe_3 groups. It should be pointed out however that in a somewhat analogous compound, $[Rh(\mu\text{-}SPh)(CO)(PMe_3)]_2$ the Rh–S distances opposite the PMe_3 groups (av. 2.376(2) Å) were found to be shorter than those opposite the CO groups (2.400(2) Å) [16]. The major influence in the smaller PMe_3 group in 4 is manifest in a much smaller Rh(1)–Rh(2) separation of only 3.0524(4) Å and in a more acute angle between the two rhodium coordination planes; in 4 these planes

Table 8

Selected angles (deg) for compound 4 [a]

S(1)–Rh(1)–P(1)	170.52(4)	Rh(1)–P(1)–C(9)	117.7(2)	Rh(1)–N(2)–C(6)	119.1(3)
S(1)–Rh(1)–N(2)	88.49(9)	Rh(1)–P(1)–C(10)	113.9(2)	C(4)–N(2)–C(6)	112.8(3)
S(1)–Rh(1)–C(7)	90.4(2)	Rh(1)–P(1)–C(11)	116.3(2)	S(1)–C(1)–S(2)	118.0(2)
P(1)–Rh(1)–N(2)	89.28(9)	C(9)–P(1)–C(10)	102.8(3)	S(1)–C(1)–N(1)	127.1(3)
P(1)–Rh(1)–C(7)	90.9(2)	C(9)–P(1)–C(11)	101.9(3)	S(2)–C(1)–N(1)	114.9(3)
N(2)–Rh(1)–C(7)	174.8(2)	C(10)–P(1)–C(11)	102.1(3)	S(2)–C(2)–C(3)	105.2(3)
S(3)–Rh(2)–P(2)	169.72(4)	Rh(2)–P(2)–C(12)	116.1(2)	N(1)–C(3)–C(2)	108.3(4)
S(3)–Rh(2)–N(1)	87.71(9)	Rh(2)–P(2)–C(13)	117.7(2)	S(3)–C(4)–S(4)	117.8(2)
S(3)–Rh(2)–C(8)	92.6(2)	Rh(2)–P(2)–C(14)	113.8(2)	S(3)–C(4)–N(2)	126.6(3)
P(2)–Rh(2)–N(1)	90.87(9)	C(12)–P(2)–C(13)	103.2(3)	S(4)–C(4)–N(2)	115.6(3)
P(2)–Rh(2)–C(8)	88.4(1)	C(12)–P(2)–C(14)	102.0(3)	S(4)–C(5)–C(6)	104.1(3)
N(1)–Rh(2)–C(8)	177.8(2)	C(13)–P(2)–C(14)	101.8(3)	N(2)–C(6)–C(5)	108.5(4)
Rh(1)–S(1)–C(1)	104.4(1)	Rh(2)–N(1)–C(1)	125.6(3)	Rh(1)–C(7)–O(1)	177.3(5)
C(1)–S(2)–C(2)	90.5(2)	Rh(2)–N(1)–C(3)	120.3(3)	Rh(2)–C(8)–O(2)	178.4(4)
Rh(2)–S(3)–C(4)	103.8(1)	C(1)–N(1)–C(3)	114.0(3)		
C(4)–S(4)–C(5)	90.2(2)	Rh(1)–N(2)–C(4)	128.1(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

are inclined by only 30.0°. It appears that the smaller PMe$_3$ groups allow the close approach of the two metals and a more parallel alignment of the metal planes. Possibly to offset any increased steric interaction brought about by the compression of the two metal centers, the two rhodium planes are staggered (32.4°) somewhat more in 4 than in 3.

(b) Discussion of chemistry. The reaction of [Rh(μ-S$_2$NC$_3$H$_4$)(COD)]$_2$ (1) with CO results in facile replacement of the two diolefin ligands by four carbonyl groups yielding the wine-red compound, [Rh(μ-S$_2$NC$_3$H$_4$)(CO)$_2$]$_2$ (2). Although this species was not isolated, but instead was always generated in situ, its IR spectrum, its subsequent chemistry (vide infra) and its similarity to known compounds make its formulation, as shown, quite reasonable. The IR spectrum, having bands at 2094(s), 2058(m), 2045 (w,sh), and 2018(s) cm^{-1}, is consistent with the C_2 structure shown and agrees well with that of the closely related mercaptopyridinate-bridged species,
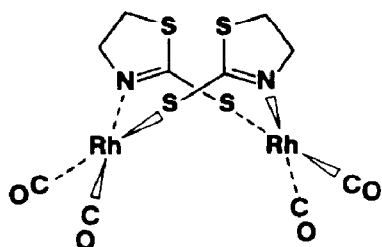
[Ir(μ-SC$_5$H$_4$N)(CO)$_2$]$_2$ [3]. The IR spectrum of 2 also resembles that of the much studied, chloro-bridged analogue, [Rh(μ-Cl)(CO)$_2$]$_2$ [22], except that the lower symmetry of 2 gives rise to the additional weak shoulder at 2045 cm^{-1}.

Reaction of 2 with monodentate phosphine or phosphite ligands results in replacement of one carbonyl group on each metal to give the species in which the

L = PPh$_3$ (3)

= PMe$_3$ (4)

= P(OPh)$_3$ (5)

= P(OMe)$_3$ (6)
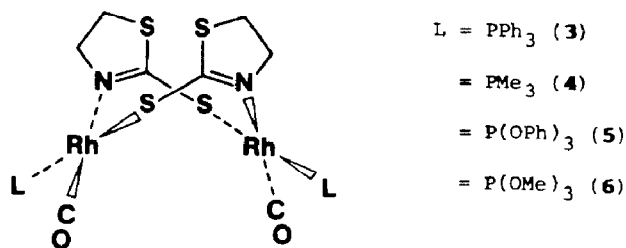
two remaining carbonyls and the two phosphines are mutually *trans* on adjacent metals. This trans arrangement has been inferred from the structural determinations of 3 and 4 (vide supra). In solution no evidence of the other (*cis*) isomer was observed in any of these products. For the bulky PPh$_3$ or P(OPh)$_3$ groups the *trans* geometry is expected, however with the smaller phosphines (particularly PMe$_3$) the *cis* geometry is not expected to be particularly unfavorable. Certainly in the related thiolato-bridged species [Rh(μ-SPh)(CO)(PMe$_3$)]$_2$ [16] both isomers were observed in solution, with the *cis* isomer being favored in the solid state. The spectroscopic parameters are in complete agreement with the structural formulations. All show the expected two carbonyl stretches in the IR spectra (except for CH$_2$Cl$_2$ solutions of 3 for which there is only one band), in a region typical of rhodium(I) species. Furthermore, for the series of ligands PMe$_3$, PPh$_3$, P(OMe)$_3$, and P(OPh)$_3$ an

increase in carbonyl stretching frequencies is observed which parallels those observed for the same ligands (L) in $Ni(CO)_3L$ [20], reflecting the expected decrease in ligand basicities through this series. All complexes display the expected doublet in the $^{31}P\{^1H\}$ NMR spectra owing to coupling to rhodium, and all chemical shifts for these resonances are in keeping with the values observed for other compounds of the same ligands [23].

Compound **3** could also be prepared by the reaction of $RhCl(CO)(PPh_3)_2$ with the mercaptothiazolinate anion as shown in eq. 1. Although this preparation worked

$$2RhCl(CO)(PPh_3)_2 + 2S_2NC_3H_4^- \rightarrow \left[Rh(\mu\text{-}S_2NC_3H_4)(CO)(PPh_3)\right]_2 + 2Cl^-$$
$$+ 2PPh_3 \qquad (1)$$

well, the route through the COD dimer **1** proved to be more convenient, particularly for the preparation of the other phosphine and phosphite products (**4–6**).

The 2-mercaptothiazolinate anion is structurally not unlike the 2-(diphenylphosphino)pyridine ligand (Ph_2Ppy), which has previously been studied as a bridging group in binuclear rhodium complexes [24]; both ligands display analogous bites, binding to metals via nitrogen and either sulfur or phosphorus. The major differences in the two groups are in their steric bulk, with the (diphenylphosphino)pyridine being significantly larger by virtue of the phenyl substituents, and in their charge, with the phosphine being neutral and the thiazolinate being an anion. Both ligands have been used to bridged two square planar rhodium(I) centers, giving rise to rather analogous binuclear species. In spite of the similarities however, the structure obtained with the two bridging groups are substantially different. With the phosphinopyridine ligand a *trans* arrangement of the two groups, to give A-frame-type species such as $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2]$ [24], is observed, whereas all known complexes involving the mercaptothiazolinate [1] and related bridging groups [2,3,13] have a *cis*-bridging arrangement with a folded structure which now seems typical of these anion-bridged complexes [14–18,22,25]. Clearly the small bite of the bidentate anionic ligands should favor the *cis* over the *trans* arrangement of bridging groups in complexes which are not metal–metal bonded. However the *trans* arrangement of the mercaptothiazolinate ligand should be possible in metal–metal bonded species, in which the metal–metal separation and the ligand bite are comparable, as was observed with the phosphinopyridine ligand [24]. We therefore suggest that the species, $[Rh_2(\mu\text{-}S_2NC_3H_4)_2(\mu\text{-}CO)(L)_2]$ ($L = PR_3$ or $P(OR)_3$), analogous to the Ph_2Ppy complex above, are promising candidates for having an A-frame structure with a *trans* alignment of mercaptothiazolinate groups. Attempts to synthesize these species by carbonyl removal from **3–6** have thus far been unsuccessful, although efforts are continuing to obtain A-frame species with mercaptothiazolinate bridges in order to effect transformations between these two major classes of binuclear complexes of rhodium(I) and iridium(I).

Whether or not the *trans* arrangement of mercaptothiazolinate groups is favored, it is clear, based on the already short Rh–Rh separation in **4** and on the Ir–Ir bond confirmed in the related species, $[Ir_2(\mu\text{-}SNC_5H_4)_2(CO)_4(I)(CH_2I)]$ [3], that Rh–Rh bond formation will be possible in our series of compounds. This is an important aspect of the chemistry of such species since the making and breaking of metal–metal bonds is of fundamental importance, accompanying oxidative addition and reductive elimination reactions in multinuclear complexes [26]. Such reactions are currently being studied.

Acknowledgements

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