Synthesis and Hydroformylation Reaction of Dinuclear Rhodium(I) Complexes with Mixed Bridging Ligands. *X*-Ray Structure of $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$†

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The preparation and properties of dinuclear complexes containing one azolate (az) and one t-butylthio group as bridging ligands are described. Bubbling of carbon monoxide through dichloromethane solutions of $[Rh_2(\mu\text{-}az)(\mu\text{-}SBu^t)(\eta^4\text{-}cod)_2]$ (cod = cyclo-octa-1,5-diene), followed by addition of phosphorus donor ligands (L) affords the complexes $[Rh_2(\mu\text{-}az)(\mu\text{-}SBu^t)(CO)_2L_2]$. The crystal and molecular structure of *cis*-$[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (pz = pyrazolate) was determined from a single crystal by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1$, with a = 10.789 7(2), b = 12.226 0(3), c = 10.431 4(2) Å, β = 110.515(1)°, and Z = 2. The final agreement factors were R = 0.036 and R' = 0.044. In the dinuclear complex each rhodium atom is in a distorted square arrangement. The dihedral angle of 63.1(2)° between the two co-ordination planes leads to a bent geometry with a rhodium–rhodium distance of 3.477 0(9) Å. The $[Rh_2(\mu\text{-}az)(\mu\text{-}SBu^t)(CO)_2L_2]$ complexes are good precursors for the hydroformylation reaction of olefins under mild conditions.

Since the good catalytic activity, under mild conditions, of the precursor $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ was recognised,[1] a series of studies[2–5] have explored this dinuclear system. It was shown that various phosphite or phosphine ligands and substituents on the sulphur atoms can modulate the activity.[4] The thiolate bridges can be replaced by pyrazolate ligands, although the catalytic activity is lowered.[3] In any case the catalytic cycles presumably involve dinuclear species[3–5] but, so far we have not obtained direct evidence.

X-Ray studies on some selected thiolate[6] or pyrazolate[7] complexes have shown the presence of 'bent' double square-planar structures. A representative formulation for active dinuclear catalyst precursors is $[Rh_2(\mu\text{-}X)_2(CO)_2L_2]$; however, whilst the carbonyl and phosphorus donor ligands (L) are in a *trans* arrangement for X = pyrazolate,[7] a *cis* arrangement, in the solid state, is present for X = SPh.[6] In order to gain more insight into these very complicated systems and particularly to observe if disproportionation takes place in solutions, we decided to introduce two different bridges between the two rhodium atoms and to follow the chemistry of these hetero-bridged species.

The present study deals with the synthesis of various complexes having the $Rh(\mu\text{-}az)(\mu\text{-}SBu^t)Rh$ core [az = pyrazolate (pz) or benzotriazolate (btz)], the *X*-ray structure of one of the series, and the catalytic activity of the phosphite-substituted complexes which could be correlated with the presence of a dinuclear intermediate species in the catalytic cycle.

Experimental

All solvents were dried, distilled, and stored under a nitrogen atmosphere. The reactants were of commercial origin and used without further purification provided they did not contain peroxides; all the reagents were saturated with nitrogen prior to use. All the preparations were carried out under nitrogen on a vacuum line using Schlenk techniques.

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded on Bruker WM 250 or Varian XL 200 spectrometers; ^{31}P chemical shifts are positive downfield from external 85% H_3PO_4 in D_2O. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

The complexes $[Rh_2(\mu\text{-}pz)_2(CO)_4]$ (**1**),[7] $[Rh_2(\mu\text{-}btz)_2(CO)_4]$ (**2**),[8] $[Rh_2(\mu\text{-}SBu^t)_2(CO)_4]$ (**3**),[9] $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ (**4**),[10] $[Rh(acac)(\eta^4\text{-}cod)]$ (**5**) (cod = cyclo-octa-1,5-diene, acac = acetylacetonate), [11]$[RhCl(Hpz)(\eta^4\text{-}cod)]$ (**6**),[12] and $[RhCl(Hbtz)(\eta^4\text{-}cod)]$ (**7**)[8] were prepared according to literature methods.

Synthesis of $[Rh_2(\mu\text{-}pz)(\mu\text{-}Cl)(\eta^4\text{-}cod)_2]$ (**9**).—Complex (**9**) was prepared by adding a solution of (**6**) (0.150 g, 0.47 mmol) in acetone (10 cm³) to a solution of (**5**) (0.148 g, 0.47 mmol) in dichloromethane (10 cm³). The resulting mixture was stirred for 15 min. The resulting complex (**9**) was not isolated and the solution directly used for preparation of (**8**).

Complex (**9**) can be isolated in the solid state by adding methanol to the above solution (yield 50%) (Found: C, 43.8; H, 4.90; N, 5.25. Calc. for $C_{19}H_{27}ClN_2Rh_2$: C, 43.5; H, 5.20; N, 5.35%).

Synthesis of $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\eta^4\text{-}cod)_2]$ (**8**).—To the previous mixture, a solution of methanol (5 cm³) containing $KSBu^t$ (0.47 mmol, prepared by treating $HSBu^t$ with potassium

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† μ-(Pyrazolato-N^1N^2)-μ-t-butylthio-bis[carbonyl(trimethyl phosphite) rhodium(I)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

hydroxide in methanol) was added at 20 °C. After stirring for 15 min, the solvent was evaporated under reduced pressure and an orange residue was obtained. It was dissolved in dichloromethane and the KCl was filtered off. The filtrate was reduced to 5 cm^3; n-hexane was added to precipitate an orange powder which was washed with n-hexane and dried under vacuum (yield 80%). Recrystallization at -20 °C from a saturated diethyl ether solution gave orange crystals (Found: C, 47.8; H, 6.15; N, 4.85. Calc. for $C_{23}H_{36}N_2Rh_2S$: C, 47.75; H, 6.25; N, 4.85%). ^{1}H N.m.r. ($CDCl_3$): δ 1.11 (s, Bu^t), two broad peaks centred at 2 and 4 (cod), 6.1 (t, J_{H-H} = 2, pz), and 7.2 (d, J_{H-H} = 2 Hz, pz).

Preparation of [Rh$_2$(μ-btz)(μ-SBu^t)(η^4-cod)$_2$] (**10**).—Following the same procedure as for complex (**8**), complex (**10**) was obtained as an orange powder (yield 70%) by addition at room temperature of KSBu^t (0.32 mmol) to an acetone solution of (**7**) (0.120 g, 0.32 mmol) and (**5**) (0.100 g, 0.32 mmol) (Found: C, 48.9; H, 6.10; N, 6.75. Calc. for $C_{26}H_{37}N_3Rh_2S$: C, 49.6; H, 5.90; N, 6.70%).

Preparation of the Complexes [Rh$_2$(μ-az)(μ-SBu^t)(CO)$_4$] [az = pz (**11**) *or* btz (**12**)].—Complex (**8**) (0.020 g) was dissolved in dichloromethane (10 cm^3); CO was allowed to bubble gently in the solution for 5 min. The orange solution turned light yellow. Evaporation of the solvent gave a yellow oily residue of (**11**). I.r. (CH_2Cl_2): 2 078m, 2 068s, and 2 010s cm^{-1} [ν(CO)]. For the synthesis of (**13**), complex (**11**) was prepared directly in solution just after the carbonylation. The same procedure as above was used to prepare (**12**) from (**10**). I.r. (CH_2Cl_2): 2 087m, 2 074s, and 2 019s cm^{-1} [ν(CO)].

Preparation of the Complexes [Rh$_2$(μ-az)(μ-SBu^t)(CO)$_2$L$_2$], (**13**)—(**17**).—The general method used is illustrated by the case of [Rh$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (**13**); the others were prepared similarly.

To the carbonyl complex (**11**), prepared from (**8**) (0.010 g), was added trimethyl phosphite (0.0044 cm^3) at room temperature. The solution turned yellow and was stirred for 10 min. Evaporation of the solvent gave a yellow microcrystalline residue (yield 85%). Recrystallization from a saturated ether solution at -20 °C gave crystals of a suitable size for *X*-ray analysis (Found: C, 26.9; H, 4.40; N, 4.40. Calc. for $C_{15}H_{30}N_2O_8P_2Rh_2S$: C, 27.05; H, 4.55; N, 4.20%). ^{1}H N.m.r. ($CDCl_3$): δ 1.58 (s, Bu^t), 3.67 (d, J_{P-H} = 12.5, POMe), 6.04 (t, J_{H-H} = 2, pz), 7.41 (d, J_{H-H} = 2 Hz, pz); ^{31}P-{^{1}H} n.m.r. ($CDCl_3$): δ 133.79 (d, J_{Rh-P} = 245 Hz). I.r. (CH_2Cl_2): 1 995s and 1 990s cm^{-1} [ν(CO)].

Attempted Synthesis of [(η^4-cod)Rh(μ-pz)(μ-SBu^t)Pd(η^3-C$_3$H$_5$)].—A dichloromethane solution (20 cm^3) of [Pd(Hpz)Cl(η^3-C$_3$H$_5$)] {0.40 mmol; prepared *in situ* by reacting [Pd$_2$(μ-Cl)$_2$(η^3-C$_3$H$_5$)$_2$] (0.073 g, 0.20 mmol) with Hpz (0.027 g, 0.040 mmol)} was added to a solution of [Rh(acac)(η^4-cod)] (0.124 g, 0.40 mmol) in dichloromethane (5 cm^3). After evaporation of the solvent under reduced pressure, the residue was dissolved in acetone (10 cm^3) and treated with a methanol solution (10 cm^3) of KSBu^t (0.40 mmol; prepared by treating HSBu^t with potassium hydroxide). The solution was vigorously stirred for 15 min. The solvent was removed under reduced pressure, the residue dissolved in dichloromethane, and KCl was eliminated by filtration through Celite. The resulting solution was concentrated to 5 cm^3 and stored overnight at -10 °C; a yellow-orange precipitate was obtained, which was isolated, washed with hexane and dried *in vacuo*. Hydrogen-1 n.m.r. analysis indicated a symmetrical pyrazolato ligand, therefore we suspected a mixture of two complexes. This powder was treated with diethyl ether (20 cm^3) so that a yellow solution was obtained and an orange powder collected. The orange material was identified as [Rh$_2$(μ-pz)$_2$(η^4-cod)$_2$] (yield 80%). The related [Pd$_2$(μ-SBu^t)$_2$(η^3-C$_3$H$_5$)$_2$] was isolated from the yellow solution (yield 60%). Both complexes were identified by comparison with pure samples obtained by reaction of [M$_2$(μ-Cl)$_2$L$_2$] (M = Rh, L = η^4-cod; M = Pd, L = η^3-C$_3$H$_5$) with the corresponding ligand Kpz (M = Rh) and KSBu^t (M = Pd).

Crystal Structure Determination.—*Crystal data*. $C_{15}H_{30}N_2O_8P_2Rh_2S$, monoclinic, space group $P2_1$, $Z = 2$, M = 666.2, a = 10.789 7(2), b = 12.226 0(3), c = 10.431 4(2) Å, β = 110.515(1)°, U = 1 288.79(5) Å^3. A prismatic crystal with distorted hexagonal base (0.27 × 0.27 × 0.17 × 0.10 mm) was used for the analysis on a Philips PW 1100 diffractometer, with Cu-K_α radiation, graphite oriented monochromator, ω–2θ scans, bisecting geometry, 1 × 1 detector apertures, and a scan width of 1.5°. Data were collected up to θ = 65°. The cell parameters were obtained from a least-squares fit of the angular positions of 96 reflections up to θ = 45°. The stability and orientation of the crystal were checked by measuring two standard reflections which did not show significant variation during collection. An empirical absorption correction was applied[13] after isotropic refinement which gave maximum and minimum absorption corrections of 1.587 and 0.727.

The structure was solved by standard Patterson and direct methods.[14–16] Harker sections and refinement by least-squares methods on F_o defined the space group $P2_1$. The H atoms were obtained from a difference synthesis and included isotropically in the final cycles of refinement. Of the 2 305 independent

Table 1. Final atomic co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.230 80(7)	0.000 0(0)	0.199 05(6)
Rh(2)	0.227 44(6)	0.270 12(7)	0.302 06(6)
S	0.093 0(2)	0.114 3(2)	0.276 0(2)
P(1)	0.342 6(2)	−0.096 5(2)	0.099 4(2)
P(2)	0.334 3(3)	0.426 3(2)	0.298 6(3)
N(1)	0.213 7(8)	0.132 7(7)	0.063 8(8)
N(2)	0.197 9(7)	0.240 7(6)	0.097 5(8)
C(3)	0.176 8(12)	0.299 0(11)	−0.015 3(11)
C(4)	0.176 7(11)	0.236 8(10)	−0.121 9(11)
C(5)	0.199 6(11)	0.134 2(10)	−0.071 6(10)
C(6)	0.244 4(14)	−0.109 5(10)	0.315 1(12)
O(6)	0.250 7(15)	−0.182 4(9)	0.383 2(12)
C(7)	0.264 3(10)	0.293 4(7)	0.484 3(10)
O(7)	0.288 6(10)	0.309 1(9)	0.597 4(8)
C(8)	0.047 7(11)	0.070 3(9)	0.423 3(11)
C(9)	0.166 8(15)	0.044 2(11)	0.549 0(12)
C(10)	−0.037 9(14)	−0.031 5(10)	0.376 5(16)
C(11)	−0.030 6(16)	0.162 5(13)	0.455 4(17)
O(12)	0.462 5(7)	−0.041 2(7)	0.065 4(9)
C(12)	0.561 7(13)	0.016 5(16)	0.174 1(15)
O(13)	0.398 9(8)	−0.206 1(6)	0.175 7(8)
C(13)	0.468 5(19)	−0.284 2(13)	0.122 7(22)
O(14)	0.266 3(8)	−0.130 1(8)	−0.055 6(8)
C(14)	0.142 9(15)	−0.185 1(16)	−0.087 8(18)
O(15)	0.381 2(9)	0.488 7(7)	0.438 6(8)
C(15)	0.456 0(19)	0.590 7(11)	0.461 6(18)
O(16)	0.260 2(9)	0.514 7(8)	0.186 5(9)
C(16)	0.130 5(16)	0.558 9(16)	0.180 6(22)
O(17)	0.459 7(13)	0.426 9(9)	0.255 0(18)
C(17)	0.533 4(15)	0.337 2(14)	0.248 8(18)

Table 2. ^{31}P-{^1H} N.m.r.[a] and i.r. data for the complexes [$Rh_2(\mu$-az)(μ-$SBu^t)(CO)_2L_2$] [az = pyrazolate (pz) or benzotriazolate (btz); L = CO, $P(OMe)_3$, $P(OPh)_3$, or PPh_3]

	Complex	ν(CO)/cm^{-1}	δ(^{31}P-{^1H})/p.p.m.	$^1J_{Rh-P}$/Hz
(11)	[$Rh_2(\mu$-pz)(μ-$SBu^t)(CO)_4$]	[b]2 078m, 2 068s, 2 010s		
(13)	[$Rh_2(\mu$-pz)(μ-$SBu^t)(CO)_2\{P(OMe)_3\}_2$]	[c]1 995s, 1 990s	133.78	245
(14)	[$Rh_2(\mu$-pz)(μ-$SBu^t)(CO)_2\{P(OPh)_3\}_2$]	[d]2 012s, 2 004s	115.4	265
(15)	[$Rh_2(\mu$-pz)(μ-$SBu^t)(CO)_2(PPh_3)_2$]	[d]1 988s, 1 978s	145.6	235
(12)	[$Rh_2(\mu$-btz)(μ-$SBu^t)(CO)_4$]	[b]2 087m, 2 074s, 2 019s		
(16)	[$Rh_2(\mu$-btz)(μ-$SBu^t)(CO)_2\{P(OMe)_3\}_2$]	[c]2 001s, 1 985s	142.7	260
(17)	[$Rh_2(\mu$-btz)(μ-$SBu^t)(CO)_2\{P(OPh)_3\}_2$]	[c]2 007s, br	125.8	264

[a] In $CDCl_3$ solution, δ values downfield from external H_3PO_4. [b] In CH_2Cl_2 solution. [c] In toluene solution. [d] Nujol mull.

Table 3. Selected geometrical parameters with estimated standard deviations in parentheses

(*a*) Interatomic distances (Å)

Rh(1)–Rh(2)	3.477 0(9)	Rh(2)–C(7)	1.823(10)	C(8)–C(9)	1.513(15)	P(2)–O(17)	1.571(18)
Rh(1)–S	2.376(3)	N(1)–N(2)	1.392(12)	C(8)–C(10)	1.524(17)	C(12)–O(12)	1.442(16)
Rh(1)–P(1)	2.192(3)	N(2)–C(3)	1.325(14)	C(8)–C(11)	1.515(22)	C(13)–O(13)	1.439(24)
Rh(1)–N(1)	2.116(9)	C(3)–C(4)	1.347(17)	P(1)–O(12)	1.605(9)	C(14)–O(14)	1.423(19)
Rh(1)–C(6)	1.776(13)	C(4)–C(5)	1.349(16)	P(1)–O(13)	1.569(8)	C(15)–O(15)	1.459(18)
Rh(2)–S	2.352(2)	C(6)–O(6)	1.127(17)	P(1)–O(14)	1.590(8)	C(16)–O(16)	1.482(21)
Rh(2)–P(2)	2.237(3)	C(7)–O(7)	1.132(13)	P(2)–O(15)	1.567(9)	C(17)–O(17)	1.369(22)
Rh(2)–N(2)	2.075(8)	C(8)–S	1.848(14)	P(2)–O(16)	1.587(9)		

(*b*) Bond angles (°)

P(1)-Rh(1)–C(6)	89.4(4)	C(8)–S–Rh(1)	119.3(4)	Rh(2)–P(2)–O(17)	120.6(4)	N(1)–N(2)–Rh(2)	115.8(6)
P(1)–Rh(1)–S	172.0(1)	C(8)–S–Rh(2)	118.2(4)	P(1)–O(12)–C(12)	117.8(8)	C(5)–N(1)–Rh(1)	130.6(7)
N(1)–Rh(1)–C(6)	178.8(5)	Rh(1)–S–Rh(2)	94.7(1)	P(1)–O(13)–C(13)	122.3(10)	C(3)–N(2)–Rh(2)	137.4(8)
N(1)–Rh(1)–S	81.7(3)	Rh(1)–P(1)–O(12)	119.9(3)	P(1)–O(14)–C(14)	118.0(9)	N(1)–N(2)–C(3)	106.5(8)
P(2)–Rh(2)–C(7)	87.6(3)	Rh(1)–P(1)–O(13)	113.5(3)	P(2)–O(15)–C(15)	123.3(9)	N(2)–C(3)–C(4)	112.3(10)
P(2)–Rh(2)–S	171.9(1)	Rh(1)–P(1)–O(14)	116.5(3)	P(2)–O(16)–C(16)	120.2(10)	C(3)–C(4)–C(5)	104.9(10)
N(2)–Rh(2)–C(7)	176.4(4)	Rh(2)–P(2)–O(15)	113.6(3)	P(2)–O(17)–C(17)	125.7(10)	C(4)–C(5)–N(1)	110.7(9)
N(2)–Rh(2)–S	82.8(2)	Rh(2)–P(2)–O(16)	117.6(4)	N(2)–N(1)–Rh(1)	123.3(6)	C(5)–N(1)–N(2)	105.6(6)

(*c*) Torsion angles (°)

Rh(1)–N(1)–N(2)–Rh(2)	11.2(9)	Rh(1)–P(1)–O(12)–C(12)	50.5(10)	Rh(1)–S–C(8)–C(9)	54.8(10)
N(1)–N(2)–Rh(2)–S	−46.2(6)	Rh(1)–P(1)–O(13)–C(13)	176.3(10)	Rh(1)–S–C(8)–C(10)	−65.8(9)
N(2)–Rh(2)–S–Rh(1)	56.2(2)	Rh(1)–P(1)–O(14)–C(14)	−53.6(11)	Rh(1)–S–C(8)–C(11)	175.7(8)
Rh(2)–S–Rh(1)–N(1)	−50.6(2)	Rh(2)–P(2)–O(15)–C(15)	178.2(10)	Rh(2)–S–C(8)–C(9)	−59.2(10)
S–Rh(1)–N(1)–N(2)	30.8(6)	Rh(2)–P(2)–O(16)–C(16)	58.0(12)	Rh(2)–S–C(8)–C(10)	−179.8(7)
C(6)–Rh(1)–Rh(2)–C(7)	8.7(7)	Rh(2)–P(2)–O(17)–C(17)	−16.9(18)	Rh(2)–S–C(8)–C(11)	61.7(10)
P(1)–Rh(1)–Rh(2)–P(2)	0.3(1)				

(*d*) Least-square planes; deviations (Å) of some atoms in square brackets

Plane 1: N(1), P(1), C(6), S [Rh(1), −0.041 9(6); Rh(2), −1.766 3(7)]
Plane 2: N(2), P(2), C(7), S [Rh(2), −0.026 7(7); Rh(1), −1.917 3(6)]
Plane 3: N(1), N(2), C(3), C(4), C(5) Plane 4: N(1), N(2), S Plane 5: N(1), S, Rh(1)
Plane 6: C(6), P(1), Rh(1) Plane 7: N(2), S, Rh(2) Plane 8: C(7), P(2), Rh(2)

Planes	Angles (°)	Planes	Angles (°)	Planes	Angles (°)	Planes	Angles (°)
1—2	63.1(2)	3—4	31.6(4)	4—6	24.0(6)	5—6	175.4(3)
1—4	25.1(5)	4—5	153.8(5)	4—7	41.9(4)	7—8	173.2(2)
2—4	41.6(4)			4—8	138.4(5)		

reflections, 2 266 were considered observed [$I > 3\sigma(I)$]. Refinement converged to $R = 0.036$ and $R' = 0.044$. Weights were applied so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$ using the functions $w = K/[f(F_o)]\cdot[g(\sin\theta/\lambda)]$, K being a scale factor to ensure that $\langle w\Delta^2F\rangle = 1$.

The final average shift/error was 0.96 for the 317 variables with a maximum thermal parameter of 0.17(1) $Å^2$ for U_{11}[O(6)]. The highest final residual electron density was 0.91 e $Å^{-3}$. Final positional parameters for the non-hydrogen atoms are given in Table 1.

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

Catalytic Experiments.—All catalytic experiments were performed in a 150-cm^3 stainless steel autoclave (SOTELEM Co.), fitted with a stirring head. The temperature was maintained at 80 °C by circulation of water in a double jacket. The mixture of synthesis gas ($CO:H_2 = 1:1$) was prepared in a gas tank, then introduced at a constant pressure of 5 bar. The drop of pressure in the tank was followed with a pressure gauge connected to an electronic recorder.

A solution containing the complex (0.1 mmol Rh), hex-1-ene (5 cm^3, 40 mmol), and toluene (25 cm^3) was introduced (by suction) into the autoclave. It was heated at 80 °C under stirring for 5 min, during which time the system reached equilibrium; then the autoclave was pressurized with synthesis gas at 5 bar. After the run the solution was transferred into a Schlenk tube. The composition of the solution was determined by gas-phase chromatography on a Intersmat IGC 131 apparatus equipped with a column (6 m × 0.125 in) of OV 17 on chromosorb W.H.P.

After five runs a blank experiment was performed and no catalytic activity was noted. No decomposition of the rhodium complexes on the walls of the autoclave was observed. Almost all the experiments were repeated twice.

Results and Discussion

We have recently reported a variety of heterobridged dirhodium complexes containing, along with azolate type (az) ligands, simple anions such as Cl, OH, N_3, or SCN, in which single atoms are the bridging groups.[8,17,18] Because of the pseudo-halide attributes of the organothiolato anions,[19] the formation of mixed-bridged complexes containing the $Rh_2(\mu\text{-az})(\mu\text{-SR})$ core is expected. Thus, the reaction of the complexes $[Rh_2(\mu\text{-az})(\mu\text{-Cl})(\eta^4\text{-cod})_2]$, prepared *in situ* by linkage of two rhodium-containing fragments, $[Rh(acac)(\eta^4\text{-cod})]$ (**5**) and $[RhCl(Haz)(\eta^4\text{-cod})]$ [az = pz (**6**) or btz (**7**)], with $KSBu^t$ affords the mixed-bridged dirhodium complexes $[Rh_2(\mu\text{-az})(\mu\text{-SBu}^t)(\eta^4\text{-cod})_2]$ [az = pz (**8**) or btz (**10**)].

Bubbling of carbon monoxide through dichloromethane solutions of complexes (**8**) and (**10**) leads to the displacement of the cyclo-octa-1,5-diene ligands and to the formation of carbonyl derivatives of formula $[Rh_2(\mu\text{-az})(\mu\text{-SBu}^t)(CO)_4]$ [az = pz (**11**) or btz (**12**)], but these were not isolated as solids due to their tendency to form oils. They show three representative ν(CO) bands in the 2 100—2 000 cm^{-1} region.

As expected, addition of phosphites $[P(OMe)_3$ or $P(OPh)_3]$ or triphenylphosphine to dichloromethane solutions of $[Rh_2(\mu\text{-az})(\mu\text{-SBu}^t)(CO)_4]$ complexes led to evolution of carbon monoxide and formation of derivatives of the type *cis*-$[Rh_2(\mu\text{-az})(\mu\text{-SBu}^t)(CO)_2L_2]$ [az = pz, L = $P(OMe)_3$ (**13**), $P(OPh)_3$ (**14**), or PPh_3 (**15**); az = btz, L = $P(OMe)_3$ (**16**) or $P(OPh)_3$ (**17**)]. The proposed *cis* arrangement has been confirmed for complex (**13**) by *X*-ray methods (see below). Representative spectroscopic data for complexes (**11**)—(**17**) are collected in Table 2.

It is of interest that the heterobridged complexes $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ and $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_4]$ were slowly formed by mixing the homobridged complexes $[Rh_2(\mu\text{-pz})_2(CO)_2L_2]$ and $[Rh_2(\mu\text{-SBu}^t)_2(CO)_2L_2]$ [L = $P(OMe)_3$ or CO], according to i.r. and ^{31}P n.m.r. evidence. No dismutation of the heterobridged complexes was observed.

Finally, attempts to prepare the mixed-bridged heteronuclear complex $[(\eta^4\text{-cod})Rh(\mu\text{-pz})(\mu\text{-SBu}^t)Pd(\eta^3\text{-C}_3H_5)]$, by reacting $[Rh(acac)(\eta^4\text{-cod})]$ with $[Pd(Hpz)Cl(\eta^3\text{-C}_3H_5)]$ [18] and $KSBu^t$, were unsuccessful due to the operation of the redistribution reaction (1).

$$2[Rh(acac)(\eta^4\text{-cod})] + 2[Pd(Hpz)Cl(\eta^3\text{-C}_3H_5)] + 2\ KSBu^t \longrightarrow [Rh_2(\mu\text{-pz})_2(\eta^4\text{-cod})_2] + [Pd_2(\mu\text{-SBu}^t)_2(\eta^3\text{-C}_3H_5)_2] + 2\ Hacac + 2\ KCl \qquad (1)$$

This behaviour is probably favoured by the expected stability of the $Pd_2(\mu\text{-SBu}^t)_2$ framework containing palladium–sulphur bonds. In this context it is interesting to mention that a related heteronuclear rhodium–palladium complex, with heterobridging nitrogen donor ligands, of formula $[(CO)_2Rh(\mu\text{-pz})(\mu\text{-N}_3)Pd(\eta^3\text{-C}_3H_5)]$ has been prepared recently and structurally characterized.[18] Heterobimetallic d^8 complexes are generally difficult to isolate due to their tendency to undergo redistribution reactions.[20]

Molecular Structure of *cis*-$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$.—A view of the molecular structure is shown in Figure 1, together with the numbering scheme used in the crystallographic work. Thus, the complex is dinuclear, with a pseudo-mirror plane passing through the S atom and bisecting the pyrazolate ring, with the carbonyl ligands, related by this mirror plane, in a *cis* configuration, and the sulphur atom *trans* to the trimethyl phosphite ligands. A similar configuration has been previously found for the related complex *cis*-$[Rh_2(\mu\text{-Cl})(\mu\text{-SBu}^t)(CO)_2(PBu^t_3)_2]$.[21]

The two metal atoms present a square-planar environment that is distorted, as the four atom sets, co-ordinating to each metal atom, are not planar [N(1), P(1), C(6), S and N(2), P(2), C(7), S respectively for Rh(1) and Rh(2)]. The dihedral angle between the least-squares planes through these co-ordinating

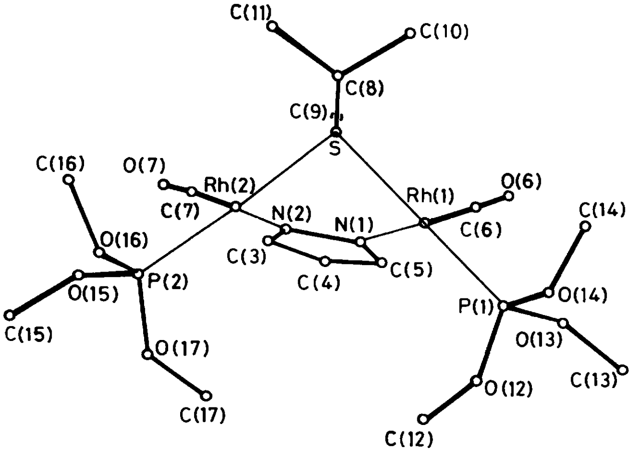

Figure 1. Molecular structure of the complex $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (**13**), with the atomic numbering scheme

Table 4. Selected catalytic data for $[Rh_2(\mu\text{-az})(\mu\text{-SBu}^t)(CO)_2L_2]$ complexes used in the hydroformylation of hex-1-ene*

	Catalyst precursor	Reaction time (min)	Yield (%)	Selectivity in aldehyde (%)	n-Heptanal / 2-Methylhexanal Ratio
(**13**)	$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$	104	98	100	1.56
(**14**)	$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OPh)_3\}_2]$	110	98	100	1.27
(**15**)	$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2(PPh_3)_2]$	125	80	100	1.38
(**16**)	$[Rh_2(\mu\text{-btz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$	184	99	100	1.5
(**17**)	$[Rh_2(\mu\text{-btz})(\mu\text{-SBu}^t)(CO)_2\{P(OPh)_3\}_2]$	200	96	100	1.08

* Reaction conditions: 0.1 mmol Rh, 40 mmol hex-1-ene; CO:H_2 = 1:1, total pressure 5 bar at 80 °C; solvent toluene (25 cm^3).

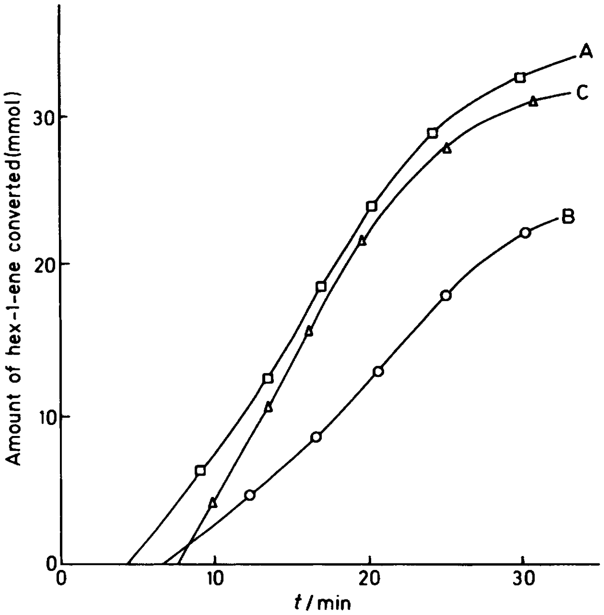

Figure 2. Hydroformylation of hex-1-ene by dinuclear rhodium complexes: A, $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ (**4**); B, $[Rh_2(\mu\text{-}pz)_2(CO)_2\{P(OMe)_3\}_2]$ (**18**); C, $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (**13**)

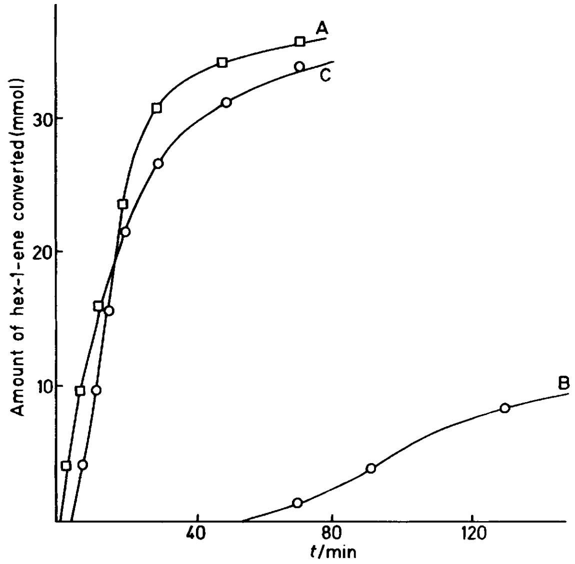

Figure 3. Hydroformylation of hex-1-ene by dinuclear rhodium complexes: A, $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ (**4**); B, $[Rh_2(\mu\text{-}btz)_2(CO)_2\{P(OMe)_3\}_2]$ (**19**); C, $[Rh_2(\mu\text{-}btz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (**16**)

sets is 63.1(2)°, so the complex presents a bent conformation. The two Rh atoms deviate from these planes towards the convex part of that angular region, but deviations are within those of the four atoms comprising each plane [0.05(1) Å and 0.08(1) Å, around Rh(1) and Rh(2) respectively]. The Rh(1)–Rh(2) distance of 3.477 0(9) Å excludes any metal–metal interaction. An intramolecular distance of 3.568 Å has been found for the pyrazolate complex *trans*-$[Rh_2(\mu\text{-}pz)_2(CO)_2\{P(OPh)_3\}_2]$;[7] however, the related complex *cis*-$[Rh_2(\mu\text{-}SPh)_2(CO)_2(PMe_3)_2]$ shows a Rh–Rh distance of 3.061 Å indicative of a metal–metal interaction.[6]

The angular geometry around the P atoms is distorted, from the ideal tetrahedral one, in a similar way for the pseudo-mirror related parts [*i.e.*, Rh(1)–P(1)–O(12) 119.9(3) *versus* Rh(2)–P(2)–O(17) 120.6(4)°, *etc.*; see Table 3]. The two Rh–S distances [2.376(3) and 2.352(2) Å] are similar to those found in the structure of $[Rh_2(\mu\text{-}SPh)_2(CO)_2(PMe_3)_2]$, 2.372(2) and 2.379(2) Å.[6] The angles around the S atom add up to 332.2(2)°. The Rh–N distances are comparable to those found in other dinuclear pyrazolate complexes.[7,22–24] The ring formed by the Rh(1), N(1), N(2), Rh(2), and S atoms adopts a distorted envelope conformation (see torsion angles in Table 3), flapping at the S atom.

Catalytic Experiments.—It was of interest to explore carefully the catalytic activity of the $[Rh_2(\mu\text{-}az)(\mu\text{-}SBu^t)(CO)_2L_2]$ complexes under the same conditions as those observed for the symmetrical complexes $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2L_2]$ and $[Rh_2(\mu\text{-}az)_2(CO)_2L_2]$ previously studied. Very mild conditions were chosen, 5 bar and 80 °C (Table 4). Figures 2 and 3 show the kinetic curves for the various systems under consideration, the former relating to the pyrazolate bridging ligand, the latter to benzotriazolate; $L = P(OMe)_3$ in every case.

Curve A in both Figures 2 and 3 relates to complex (**4**) and demonstrates the high activity of this precursor. Under our conditions the linear: branched aldehyde ratio is in the range 0.6—1.5 : 1. The two complexes (**13**) (Figure 2, curve C) and (**16**) (Figure 3, curve C) show lower activity, particularly for the latter compound; however the selectivities are about the same as for (**4**). As shown by our i.r. studies the heterobridged complexes (**13**) and (**16**) do not give rise to a detectable dismutation and were found to be unchanged after reaction, except for a small amount of the species $[Rh_2(\mu\text{-}az)(\mu\text{-}SBu^t)(CO)_4]$. The corresponding curves C of Figures 2 and 3 are very close to the kinetic curve of complex (**4**). Presumably the electron densities on the two rhodium atoms throughout the catalytic cycle are comparable so that the rate-determining step(s) could be the same. A catalytic cycle was recently proposed[4] in which all the intermediate species remain dinuclear; species (**13**) and (**16**) perhaps could follow such a cycle.

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