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PYRAZOLATE THIOCARBONYLRHODIUM COMPLEXES. X-RAY STRUCTURE OF $[Rh(\mu\text{-}3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$

R. USÓN, L.A. ORO, M.A. CIRIANO, D. CARMONA,

Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza (Spain)

A. TIRIPICCHIO and M. TIRIPICCHIO CAMELLINI

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, Parma (Italy)

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Summary

The preparation and properties of complexes of general formulae $[Rh(CS)(HL)(PR_3)_2]ClO_4$ (HL = pyrazole (HPz), 3-methylpyrazole (H3-MePz), 3,5-dimethylpyrazole (H3,5-Me_2Pz), PR_3 = triphenylphosphine, tricyclohexylphosphine) and $[(PR_3)_2(CS)Rh(\mu\text{-}Pz)AuPPh_3]ClO_4$ are reported. Complexes of the first set react with potassium hydroxide to give $[Rh(\mu\text{-}L)(CS)(PPh_3)]_2$ or $RhPz(CS)(PR_3)_2$ complexes. The structure of the complex $[Rh(3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$ has been determined by X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12.700(11)$, $b = 17.217(16)$, $c = 23.041(18)$ Å, $\beta = 116.55(8)°$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.059$ for 1978 independent reflections. The structure consists of dimeric complexes, in which each rhodium atom is in a square-planar environment being bonded to a carbon atom of a thiocarbonyl ligand, a phosphorus atom of a triphenylphosphine molecule and to two nitrogen atoms of pyrazolate ligands bridging the metal atoms. The dihedral angle of 71.1° between such two square planes leads to a bent configuration with an intramolecular rhodium—rhodium distance of 3.220 Å. The thiocarbonyl and triphenylphosphine ligands are in a *trans* disposition.

Introduction

Although the first thiocarbonyl rhodium complex, $RhCl(CS)(PPh_3)_2$, was reported in 1966 [1], some ten years elapsed before additional types of thiocarbonyl rhodium complexes were described [2—7]. In particular, we have

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reported that cationic species of the type $[Rh(CS)(PR_3)_2(Me_2CO)_x]^+$ (PR_3 = PPh_3 or PCy_3) react with pyridine or nitrile-type ligands, to give $[Rh(CS)(N\text{-donor})(PR_3)_2]ClO_4$ complexes [4,7]. In the present paper we describe some related complexes with pyrazole- and pyrazolate-type ligands. There is an increasing interest in pyrazolato derivatives due to their ability to act as either exobidentate or monodentate ligands [8,9].

Part of this paper has been the subject of a preliminary communication [10].

Results and discussion

Addition of pyrazole-type ligands to species of the type $[Rh(CS)(PR_3)_2(Me_2CO)_x]^+$ [4,7] (prepared by treatment of $RhCl(CS)(PR_3)_2$ in dichloromethane/acetone with silver perchlorate) gives cationic rhodium complexes (eq. 1):

$$[Rh(CS)(PR_3)_2(Me_2CO)_x]ClO_4 + HL \rightarrow [Rh(CS)(HL)(PR_3)_2]ClO_4 + x\ Me_2CO \quad (1)$$

(PR_3 = PPh_3, L = Pz, 3-MePz, 3,5-Me_2Pz; PR_3 = PCy_3, L = Pz, 3,5-Me_2Pz)

The elemental analyses (carbon, hydrogen and nitrogen), molar conductivities (1 : 1 electrolytes), colours and yields of isolated $[Rh(CS)(HL)(PR_3)_2]ClO_4$ complexes are listed in Table 1. The IR spectra of the complexes show the characteristic bands of the uncoordinated perchlorate anion [11], absorptions due to ν(N—H) in the 3240—3160 cm^{-1} region, along with strong bands due to ν(CS) in the 1325—1315 cm^{-1} region for the triphenylphosphine derivatives and at 1285 cm^{-1} for the tricyclohexylphosphine derivatives. (The difference can be explained by assuming that the more basic tricyclohexylphosphine increases the extent of Rh—C back-bonding.)

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, IR DATA, COLOUR AND YIELDS FOR THE CATIONIC COMPLEXES

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(CS) (cm^{-1})	Colour	Yield (%)
	C	H	N				
$[Rh(CS)(HPz)(PPh_3)_2]ClO_4$	56.4 (57.2)	4.1 (4.1)	3.7 (3.3)	130	1325 ^{a}	orange	89
$[Rh(CS)(H3\text{-}MePz)(PPh_3)_2]ClO_4$	56.8 (57.7)	4.4 (4.25)	3.6 (3.3)	135	1317 ^{a}	orange	88
$[Rh(CS)(H3,5\text{-}Me_2Pz)(PPh_3)_2]ClO_4$	57.6 (58.2)	4.5 (4.4)	3.3 (3.2)	124	1315 ^{a}	orange	96
$[Rh(CS)(HPz)(PCy_3)_2]ClO_4$	55.3 (54.9)	8.5 (8.1)	3.1 (3.2)	129	1285 ^{b}	orange	60
$[Rh(CS)(H3,5\text{-}Me_2Pz)(PCy_3)_2]ClO_4$	54.2 (55.8)	8.5 (8.2)	3.3 (3.1)	105	1285 ^{b}	pink	37
$[(PPh_3)_2(CS)Rh(\mu\text{-}Pz)Au(PPh_3)]ClO_4$	52.9 (53.7)	3.8 (3.7)	2.1 (2.2)	133	1310 ^{b}	orange	88
$[(PCy_3)_2(CS)Rh(\mu\text{-}Pz)Au(PPh_3)]ClO_4$	51.2 (52.2)	6.5 (6.35)	2.1 (2.1)	129	1285 ^{a}	pink	70

^{a} Nujol mulls. ^{b} KBr disks.

New heterometallic complexes of rhodium(I) with gold(I) have been prepared according to eq. 2 by using the coordination ability of $Au(Pz)(PPh_3)$ [12]:

$$[Rh(CS)(PR_3)_2(Me_2CO)_x]ClO_4 + Au(Pz)(PPh_3) \rightarrow [(PR_3)_2(CS)Rh(\mu\text{-}Pz)Au(PPh_3)]ClO_4 + x\ Me_2CO \quad (2)$$

($PR_3 = PPh_3, PCy_3$)

These are the first complexes in which two different metallic centers are bridged by one pyrazolate anion. The analytical data and properties for these heterometallic complexes are shown in Table 1. Recently the synthesis and the crystal structure of the heterometallic complex $(PEt_3)_2Pt(\mu\text{-}Pz)_2Cr(CO)_4$, with a double pyrazolate bridge was reported [13].

The reaction of cationic complexes of the type $[Rh(CS)(HL)(PPh_3)_2]ClO_4$ with potassium hydroxide in diethylether/methanol leads to displacement of one mole of triphenylphosphine from the coordination sphere of the rhodium ion, with formation of binuclear complexes according to eq. 3.

$$[Rh(CS)(HL)(PPh_3)_2]ClO_4 + KOH \rightarrow 1/2[Rh(\mu\text{-}L)(CS)(PPh_3)]_2 + PPh_3 + KClO_4 + H_2O \quad (3)$$

(L = Pz, 3-MePz, 3,5-Me_2Pz, indazolate (Idz))

Other methods used for forming the binuclear complexes involved the following reactions:

$$RhCl(CS)(PPh_3)_2 + NaOH + HL \rightarrow 1/2[Rh(\mu\text{-}L)(CS)(PPh_3)]_2 + PPh_3 + NaCl + H_2O \quad (4)$$

$$[Rh(CS)(PPh_3)_2(Me_2CO)_x]ClO_4 + KOH + HL \rightarrow 1/2[Rh(\mu\text{-}L)(CS)(PPh_3)]_2 + PPh_3 + KClO_4 + x\ Me_2CO + H_2O \quad (5)$$

The complexes were isolated as red crystalline solids and were characterized by elemental analyses, IR spectra, and molecular weight measurements (Table 2).

The complex $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ reacts with perchloric acid in the presence of triphenylphosphine to give $[Rh(CS)(HPz)(PPh_3)_2]ClO_4$. No reaction was observed when a benzene/methanol solution of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ was refluxed in the presence of lithium chloride and triphenylphosphine, but *trans*-$RhCl(CS)(PPh_3)_2$ [1] was isolated when a chloroform solution of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ and triphenylphosphine was refluxed.

All attempts to isolate the related tricyclohexylphosphine derivative, $[Rh(\mu\text{-}Pz)(CS)(PCy_3)]_2$, were unsuccessful. Thus, treatment of *trans*-$RhCl(CS)(PCy_3)_2$ with sodium hydroxide and pyrazole or of $[Rh(CS)(HPz)(PCy_3)_2]ClO_4$ with potassium hydroxide gave the pink complex $Rh(Pz)(CS)(PCy_3)_2$. The related $Rh(Pz)(CS)(PPh_3)_2$ complex was isolated at −50°C after treating an ethereal suspension of $[Rh(CS)(HPz)(PPh_3)_2]ClO_4$ with potassium hydroxide in methanol. When a solution of $Rh(Pz)(CS)(PPh_3)_2$ is allowed to reach room temperature it loses very readily one mole of triphenylphosphine to give $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ as the final product. The following reaction scheme can be proposed

$$\begin{tikzcd}
{[Rh(CS)(HPz)(PPh_3)_2]ClO_4} \arrow[dr, "KOH"] & \\
& Rh(Pz)(CS)(PPh_3)_2 \arrow[d, "-PPh_3"] \\
RhCl(CS)(PPh_3)_2 \arrow[ur, "NaOH{,}HPz"'] & 1/2[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2
\end{tikzcd}$$

Elimination of coordinated triphenylphosphine leading to the formation of binuclear rhodium pyrazolate complexes, was recently observed during the preparation of $[Rh(\mu\text{-}Pz)(COD)]_2$ from $[Rh(COD)(PPh_3)_2]^+$ and RhCl(COD)-(PPh_3) [14]. These results show that the "Rh(μ-Pz)Rh" bridge is fairly stable.

Crystal structure of the complex $[Rh(\mu\text{-}3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$

The crystal structure consists of discrete dimeric *trans*-di-μ(3,5-dimethylpyrazolato)dithiocarbonylbis(triphenylphosphine)dirhodium(I) complexes, separated by normal Van der Waals distances. Figure 1 shows a view of the complex, which has two pyrazolate ligands nearly symmetrically bridging the two Rh atoms. The coordination around each Rh atom is almost square planar and involves a carbon atom of a thiocarbonyl group, a phosphorus atom of a triphenylphosphine, and two nitrogen atoms of the two bridging Pz ligands. Both square-planar arrangements are imperfect, especially that about the Rh(1) atom; the displacements of Rh(1), P(1), C(1), N(1), N(3) and of Rh(2), P(2), C(2), N(2), N(4) atoms from the mean planes passing through them are 0.03, 0.03, −0.22, −0.01, 0.18 and −0.02, −0.01, 0.09, −0.04, −0.02 Å, respectively. The dihedral angle between the two square planes of 71.1° gives a bent configuration to the complex, in which the CS and PPh_3 ligands are in a *trans* arrangement. The intramolecular Rh(1)—Rh(2) distance of 3.220 Å is too long to suggest a metal—metal interaction. Selected bond distances and angles in the complex are given in Table 3.

TABLE 2

ANALYTICAL RESULTS, MOLECULAR WEIGHTS, IR DATA AND YIELDS FOR THE NEUTRAL COMPLEXES

Complex	Found (calcd.) (%)			Mol. wt. ($CHCl_3$) (found (calcd.))	ν(CS) (cm^{-1})	Yield (%)
	C	H	N			
$[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$	55.6 (55.5)	4.0 (3.8)	5.7 (5.9)	883 (953)	1924vs, 1305(sh) [a]	75
$[Rh(\mu\text{-}3\text{-}MePz)(CS)(PPh_3)]_2$	56.8 (56.3)	4.6 (4.1)	5.3 (5.7)	940 (981)	1290vs, 1300(sh) [a]	66
$[Rh(\mu\text{-}3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$	57.5 (57.15)	4.6 (4.4)	5.4 (5.55)	1036 (1009)	1288vs, 1302(vs) [a]	50
$[Rh(\mu\text{-}Idz)(CS)(PPh_3)]_2$	58.5 (59.3)	3.9 (3.8)	5.1 (5.3)	—	1290vs, 1300(sh) [a]	50
$Rh(pz)(CS)(PPh_3)_2$	63.5 (65.0)	4.6 (4.5)	4.1 (3.8)	—	—	—
$Rh(Pz)(CS)(PCy_3)_2$	60.5 (62.0)	8.9 (9.0)	3.4 (3.6)	—	1285vs [a]	57

[a] Nujol mull.

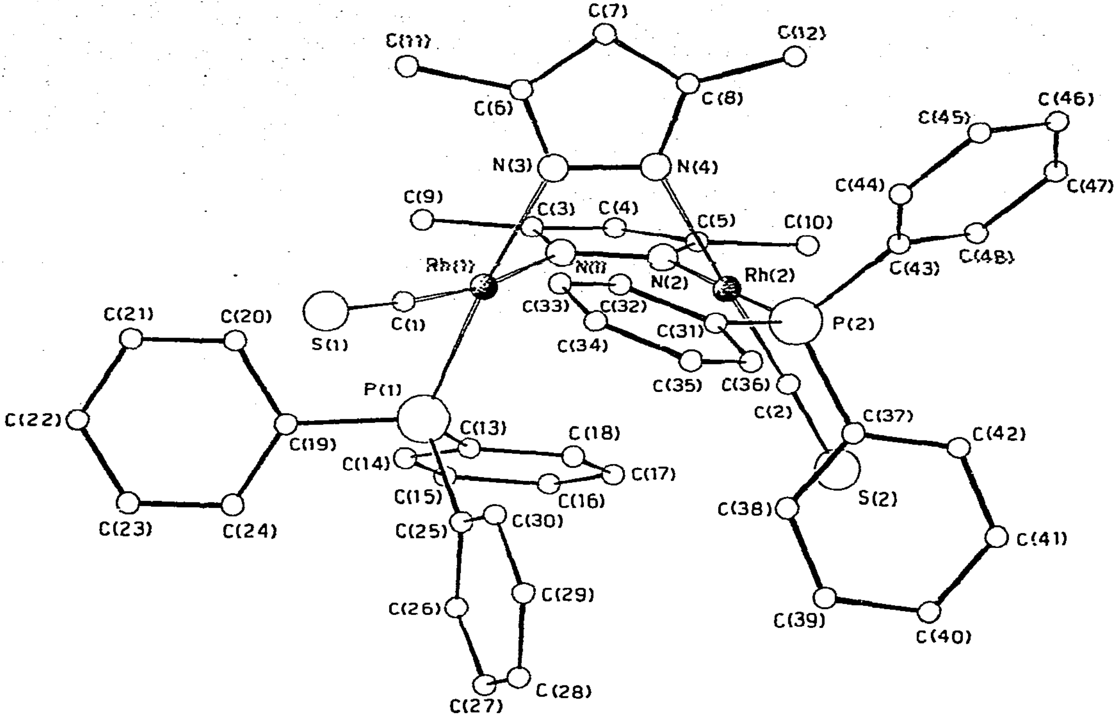

Fig. 1. View of the molecular shape of the complex $[Rh(3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$ with the atomic numbering scheme.

The central six-membered ring Rh_2N_4 adopts a boat conformation, the most common arrangement in complexes with a double pyrazolate bridge (for example in $Pd_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(CH_2CHCH_2)_2$ [15] and $(PEt_3)_2Pt(\mu\text{-}Pz)_2Cr(CO)_4$ [13]), although a chair in $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Pz)]_2$ [16] and a planar conformation in $[Ni(NO)(\mu\text{-}3,5\text{-}Me_2Pz)]_2$ [17] have been also reported. The Rh(1) and Rh(2) atoms are out of the mean plane passing through the four nitrogen atoms of 1.25 and 1.26 Å respectively. The torsion angles in the ring denote the nearly perfect boat conformation:

Rh(1)N(1)N(2)Rh(2)	—4.9°
N(1)N(2)Rh(2)N(4)	—60.2°
N(2)Rh(2)N(4)N(3)	65.7°
Rh(2)N(4)N(3)Rh(1)	—2.7°
N(4)N(3)Rh(1)N(1)	—60.7°
N(3)Rh(1)N(1)N(2)	67.9°

The thiocarbonyls are terminal with Rh(1)—C(1)—S(1) and Rh(2)—C(2)—S(2) angles of 175 and 176°. The Rh—C (1.77 Å) and C—S (1.56 Å) bond distances are comparable with those (1.79 and 1.54 Å, respectively) in $RhCl(CS)(PPh_3)_2$, which was until now the only thiocarbonyl-rhodium complex, of which the crystal structure had been determined [18].

The structure of the present complex is very similar to that of the complex $[Rh(\mu\text{-}Pz)(CO)P(OPh)_3]_2$ [14], in which the carbonyl and the triphenylphos-

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

a) In the Rh coordination sphere			
Rh(1)—P(1)	2.28(1)	Rh(2)—P(2)	2.26(3)
Rh(1)—N(1)	2.08(2)	Rh(2)—N(2)	2.07(3)
Rh(1)—N(3)	2.10(2)	Rh(2)—N(4)	2.14(2)
Rh(1)—C(1)	1.77(3)	Rh(2)—C(2)	1.77(2)
P(1)—Rh(1)—N(1)	93.5(6)	P(2)—Rh(2)—N(2)	179.3(6)
P(1)—Rh(1)—N(3)	174.5(5)	P(2)—Rh(2)—N(4)	95.2(5)
P(1)—Rh(1)—C(1)	88.6(9)	P(2)—Rh(2)—C(2)	89.1(9)
N(1)—Rh(1)—N(3)	82.9(8)	N(2)—Rh(2)—N(4)	84.1(7)
N(1)—Rh(1)—C(1)	170.6(1.1)	N(2)—Rh(2)—C(2)	91.5(1.0)
N(3)—Rh(1)—C(1)	95.5(1.0)	N(4)—Rh(2)—C(2)	174.5(1.0)
b) In the thiocarbonyls			
C(1)—S(1)	1.56(3)	C(2)—S(2)	1.56(3)
Rh(1)—C(1)—S(1)	175(2)	Rh(2)—C(2)—S(2)	176(2)
c) In the pyrazolate ligands			
N(1)—N(2)	1.35(3)	N(3)—N(4)	1.36(3)
N(1)—C(3)	1.39(4)	N(3)—C(6)	1.31(3)
N(2)—C(5)	1.31(3)	N(4)—C(8)	1.36(3)
C(3)—C(4)	1.36(3)	C(6)—C(7)	1.39(4)
C(3)—C(9)	1.50(4)	C(6)—C(11)	1.55(4)
C(4)—C(5)	1.40(4)	C(7)—C(8)	1.34(4)
C(5)—C(10)	1.51(4)	C(8)—C(12)	1.46(4)
N(2)—N(1)—C(3)	107(2)	N(4)—N(3)—C(6)	109(2)
N(2)—N(1)—Rh(1)	118(2)	N(4)—N(3)—Rh(1)	116(1)
C(3)—N(1)—Rh(1)	135(2)	C(6)—N(3)—Rh(1)	135(2)
C(5)—N(2)—Rh(2)	135(2)	C(8)—N(4)—Rh(2)	136(1)
C(5)—N(2)—N(1)	110(2)	C(8)—N(4)—N(3)	109(2)
Rh(2)—N(2)—N(1)	115(1)	Rh(2)—N(4)—N(3)	116(1)
C(4)—C(3)—N(1)	109(2)	C(7)—C(6)—C(11)	129(2)
C(9)—C(3)—N(1)	119(2)	C(7)—C(6)—N(3)	108(2)
C(4)—C(3)—C(9)	131(3)	C(11)—C(6)—N(3)	122(2)
C(5)—C(4)—C(3)	105(2)	C(8)—C(7)—C(6)	108(2)
C(10)—C(5)—N(2)	124(3)	C(12)—C(8)—N(4)	122(2)
C(10)—C(5)—C(4)	127(3)	C(12)—C(8)—C(7)	131(3)
N(2)—C(5)—C(4)	109(2)	N(4)—C(8)—C(7)	107(2)
d) In the triphenylphosphine ligands			
P(1)—C(13)	1.80(2)	P(2)—C(31)	1.82(1)
P(1)—C(19)	1.83(2)	P(2)—C(37)	1.82(2)
P(1)—C(25)	1.82(2)	P(2)—C(43)	1.83(2)
C(13)—P(1)—C(19)	104.5(9)	C(31)—P(2)—C(37)	101.1(8)
C(13)—P(1)—C(25)	98.8(9)	C(31)—P(2)—C(43)	103.7(8)
C(13)—P(1)—Rh(1)	115.2(6)	C(31)—P(2)—Rh(2)	119.6(6)
C(19)—P(1)—C(25)	106.6(8)	C(37)—P(2)—C(43)	104.1(8)
C(19)—P(1)—Rh(1)	114.5(6)	C(37)—P(2)—Rh(2)	114.1(6)
C(25)—P(1)—Rh(1)	115.5(7)	C(43)—P(2)—Rh(2)	112.5(6)

phite replace the thiocarbonyl and triphenylphosphine ligands. The more relevant differences concern the dihedral angle between the two square planes (86.2° against 71.1°) and the intramolecular Rh(1)—Rh(2) distance (3.568 Å against 3.220 Å). The Rh—C bonds (1.84 and 1.82 Å) with the carbonyls are longer than those (1.77 Å) with the thiocarbonyls, confirming that metal to ligand π backbonding decreases passing from CS to CO. Although very few structures of complexes with the thiocarbonyl ligand have been reported, some of which have the thiocarbonyls disordered, the shortening of the metal—C bonds involving thiocarbonyl ligands compared with those involving carbonyl ligands was observed also in the structures of the complexes $W(CO)_4(CS)(CNC_6H_{11})$ [19] (W—CS = 1.994, mean W—CO = 2.064 Å) and $[Ir(CO)_2(CS)(PPh_3)_2][PF_6] \cdot Me_2CO$ [20] (mean Ir—CS = 1.867, mean Ir—CO = 1.937 Å). The Rh-P bonds to triphenylphosphine (2.28 and 2.28 Å) are longer than those to triphenylphosphite (2.188 and 2.191 Å) ligands in the carbonylrhodium complex, but comparable with those found in $[Rh(SPh)(CO)(PMe_3)]_2$ (2.256 and 2.257 Å) [21] and in $[RhCl(CO)(PMe_2Ph)]_2$ (2.220 and 2.230 Å) [22], these results can be explained in terms of the better π acceptor character of the phosphite compared with the phosphine ligand.

The two pyrazolate rings in the present complex are planar and nearly perpendicular to each other (the angle formed by the two rings is 82.3°). The N(1), N(2), C(3), C(4), C(5), Rh(1), Rh(2) atoms are displaced from the mean plane passing through the first five atoms by 0.02, —0.01, —0.04, 0.05, —0.02, 0.21, and —0.02 Å, and the N(3), N(4), C(6), C(7), C(8), Rh(1), Rh(2) from the mean plane passing through the other pyrazolate ring by 0.01, —0.01, —0.02, 0.01, 0.01, 0.10 and —0.04 Å.

Experimental

Reactions were carried out at room temperature under air unless otherwise specified. Solvents were distilled before use. C, H, N analysis were carried out with a Perkin-Elmer 240 microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls or KBr disks. Molecular weights were measured with a Perkin-Elmer 115 osmometer. Conductivities were generally measured in ca. 5×10^{-4} M acetone solutions with a Phillips 9501/01 conductimeter.

Preparation of the complexes of the $[Rh(CS)(HL)(PR_3)_2]ClO_4$ type

The general method for the synthesis of these complexes is illustrated by the case of $[Rh(CS)(HPz)(PCy_3)_2]ClO_4$. The others (Table 1) were prepared similarly.

To a solution of $RhCl(CS)(PCy_3)_2$ (0.184 g, 0.247 mmol) in dichloromethane was added silver perchlorate (0.051 g, 0.247 mmol) in acetone. The suspension was stirred for 45 min and then filtered. The filtrate was mixed with pyrazole (0.017 g, 0.25 mmol) in dichloromethane. The orange solution was evaporated under vacuum and ether was added. The solid which separated was filtered off, washed with ether, and air dried.

A solution of $[Rh(CS)(HIdz)(PPh_3)_2]ClO_4$ was prepared similarly and was used as such in further reactions.

Preparation of $[(PR_3)_2(CS)Rh(\mu\text{-}Pz)Au(PPh_3)]ClO_4$

To a dichloromethane/acetone solution of $[Rh(CS)(PR_3)_2(Me_2CO)_x]ClO_4$ ($PR_3 = PPh_3$ [4], PCy_3 [7]), prepared as above, was added a stoichiometric amount of $Au(Pz)(PPh_3)$, in dichloromethane. The resulting orange solution was evaporated under vacuum and the product crystallised by addition of ether. The solid was filtered off, washed with ether, and air dried.

Preparation of the complexes of the $[Rh(\mu\text{-}L)(CS)(PPh_3)]_2$ type

The compounds were prepared by three general routes described below; route (i) gives the highest yields.

i) Preparation of $[Rh(\mu\text{-}3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$. A suspension of $[Rh(CS)(H3,5\text{-}Me_2Pz)(PPh_3)_2]ClO_4$ (0.073 g, 0.084 mmol) in ether (25 ml) was allowed to react for 2 h with potassium hydroxide (0.084 mmol) in methanol (1 ml). The resulting red-purple solution was filtered and the filtrate evaporated to dryness to give a dark-red solid. This was recrystallised from ether/methanol and then filtered off, washed with methanol, and air dried. The compound can be additionally recrystallised from dichloromethane/methanol.

$[Rh(\mu\text{-}Idz)(CS)(PPh_3)]_2$, $[Rh(\mu\text{-}3\text{-}MePz)(CS)(PPh_3)]_2$ and $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ were made in a similar way. The latter was purified by washing with small fractions of acetone and then with methanol.

ii) Preparation of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$. To a solution of $RhCl(CS)(PPh_3)_2$ (0.530 g, 0.75 mmol) in dichloromethane (25 ml) was added a mixture of pyrazole (0.051 g, 0.75 mmol) and sodium hydroxide (0.30 g, 7.5 mmol) in methanol (25 ml) and water (7 ml). The resulting orange solution was left overnight and then evaporated to give a red oily residue, which was repeatedly washed with water, methanol/water and methanol. The oil was dissolved in dichloromethane and the product precipitated by addition of methanol as a red solid, which was filtered off and washed with methanol. The crude product was dissolved in dichloromethane/ether (1/2) and recrystallised by addition of methanol to give a dark-red solid, which was filtered off, washed with methanol, and air dried.

$[Rh(\mu\text{-}3\text{-}MePz)(CS)(PPh_3)]_2$ and $[Rh(\mu\text{-}3,5\text{-}Me_2Pz)(CS)(PPh_3)]_2$ were prepared in a similar way and recrystallised from dichloromethane/methanol.

iii) Preparation of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$. A solution of $[Rh(CS)(PPh_3)_2(Me_2CO)_x]ClO_4$, prepared as above described from $RhCl(CS)(PPh_3)_2$ (0.209 g, 0.296 mmol) and silver perchlorate (0.061 g, 0.297 mmol), was treated for 1 h with a solution of pyrazole (0.020 g, 0.297 mmol) and potassium hydroxide (0.30 mmol) in methanol. The resulting red solution was evaporated to dryness and the residue was extracted with dichloromethane and the product precipitated from the extract by addition of methanol.

Reaction of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ with perchloric acid and triphenylphosphine

Perchloric acid (1.55 g/ml) (10 μl, 0.1 mmol) was added to a suspension of $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ (0.047 g, 0.05 mmol) and triphenylphosphine (0.026 g, 0.1 mmol) in acetone (10 ml), to give a brown solution which turned orange after 30 min. The solvent was pumped off and the residue was recrystallised from dichloromethane/ether to give $[Ph(CS)(HPz)(PPh_3)_2]ClO_4$ as an orange solid, which was filtered off, washed with ether, and air dried.

Preparation of $Rh(Pz)(CS)(PCy_3)_2$

i) From $RhCl(CS)(PCy_3)_2$. A solution of $RhCl(CS)(PCy_3)_2$ (0.103 g, 0.14 mmol) in dichloromethane (20 ml) was treated for 30 min with a mixture of pyrazole (0.010 g, 0.15 mmol) and sodium hydroxide (1.5 mmol) in methanol (10 ml) and water (1.5 ml). The solution was evaporated to dryness to leave an oily residue which crystallised as a pink solid upon washing with water and then with methanol. The product was filtered off, washed with methanol, and air dried.

ii) From [Rh(CS)(HPz)(PCy$_3$)$_2$]ClO$_4$. A suspension of [Rh(CS)(HPz)(PCy$_3$)$_2$]ClO$_4$ (0.046 g, 0.052 mmol) in ether was treated with potassium hydroxide (0.053 mmol) in 0.5 ml of methanol. The resulting orange solution was filtered and the filtrate evaporated to dryness. The residue was recrystallised from dichloromethane/hexane to give a pink solid, which was filtered off, washed with hexane, and air dried.

Preparation of Rh(Pz)(CS)(PPh$_3$)$_2$

To a suspension of [Rh(CS)(HPz)(PPh$_3$)$_2$]ClO$_4$ (0.061 g, 0.073 mmol) in ether (10 ml) at room temperature was added potassium hydroxide (0.1 mmol) in methanol (1 ml). The resulting orange solution was immediately cooled to —70°C and filtered. The filtrate was evaporated at —50°C to give an orange oil which was crystallised by addition of cold hexane to give an orange solid, which was washed with cold hexane and dried under vacuum at —50°C.

X-Ray data collection

A flat red-orange crystal of [Rh(3,5-Me$_2$Pz)(CS)(PPh$_3$)]$_2$, having dimensions of ca. 0.05 × 0.19 × 0.22 mm, was mounted and aligned on an on-line single-crystal automated Siemens AED diffractometer, using the Nb-filtered Mo-K_α radiation ($\bar{\lambda}$ = 0.710688 Å). The setting of 18 reflections with θ in the range 10.50—12.70 Å were determined and used to calculate the refined cell constants. Crystal data are as follows: $C_{48}H_{44}N_4P_2Rh_2S_2$, M = 1008.78, monoclinic, a 12.700(11), b 17.217(16), c 23.041(18) Å, β 116.55(8)°, V = 4507(7) Å^3, Z = 4, $d_{calc.}$ 1.487 g/cm^3, μ(Mo-K_α) 78.88 cm^{-1}; space group $P2_1/c$ (from systematic absences). A complete set of intensity data was collected within the angular range $3 \leqslant \theta \leqslant 22°$. The θ—2θ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. A total of 5526 independent reflections were measured, of which 1978 were employed in the analysis having $I \geqslant 2\sigma(I)$; the remaining 3548 were considered unobserved. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied. The first absolute scale and the mean temperature factor were determined by Wilson's method.

Structure determination and refinement

Initial positional parameters of the rhodium atoms were determined from a Patterson map. A Fourier synthesis, calculated with phases of these atoms, revealed the positions of all other non-hydrogen atoms. Refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [23] with initially isotropic and then anisotropic thermal parameters only for the Rh, S and P atoms. The carbon atoms of the phenyl groups were treated as rigid groups of D_{6h} symmetry with C—C distances of 1.395 Å. The hydrogen atoms were placed at their geometrically calculated positions and

TABLE 4

FRACTIONAL ATOMIC COORDINATES (×10^4) FOR THE NON-HYDROGEN ATOMS WITH e.s.d.'s IN PARENTHESES

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Rh(1)	3082(2)	2390(1)	2365(1)	C(20)	5862(10)	3262(9)	3270(7)
Rh(2)	637(2)	1946(1)	1138(1)	C(21)	6989(10)	3431(9)	3752(7)
S(1)	3458(8)	3067(6)	3796(4)	C(22)	7443(10)	4180(9)	3805(7)
S(2)	—246(7)	3131(6)	—131(4)	C(23)	6771(10)	4759(9)	3376(7)
P(1)	3770(6)	3543(4)	2190(3)	C(24)	5644(10)	4589(9)	2894(7)
P(2)	—1005(5)	2217(4)	1252(3)	C(25)	2783(15)	4365(10)	2030(9)
N(1)	3164(16)	1851(12)	1576(9)	C(26)	2919(15)	5030(10)	1725(9)
N(2)	2149(16)	1697(11)	1047(9)	C(27)	2154(15)	5657(10)	1608(9)
N(3)	2333(15)	1328(11)	2432(8)	C(28)	1254(15)	5618(10)	1797(9)
N(4)	1320(14)	1121(10)	1912(8)	C(29)	1119(15)	4952(10)	2103(9)
C(1)	3226(21)	2762(15)	3113(12)	C(30)	1883(15)	4326(10)	2219(9)
C(2)	125(19)	2569(15)	458(11)	C(31)	—874(12)	2483(10)	2048(5)
C(3)	4071(21)	1612(14)	1437(11)	C(32)	173(12)	2342(10)	2604(5)
C(4)	3605(22)	1403(16)	803(13)	C(33)	259(12)	2525(10)	3214(5)
C(5)	2380(21)	1418(15)	585(12)	C(34)	—701(12)	2849(10)	3267(5)
C(6)	2619(20)	782(14)	2873(11)	C(35)	—1747(12)	2990(10)	2711(5)
C(7)	1798(23)	184(15)	2618(13)	C(36)	—1834(12)	2807(10)	2101(5)
C(8)	998(19)	402(13)	2023(11)	C(37)	—1856(13)	3032(8)	762(7)
C(9)	5321(23)	1737(15)	1928(13)	C(38)	—1362(13)	3768(8)	955(7)
C(10)	1451(25)	1213(17)	—86(14)	C(39)	—1901(13)	4415(8)	573(7)
C(11)	3768(24)	812(16)	3517(13)	C(40)	—2934(13)	4326(8)	—2(7)
C(12)	17(23)	—21(15)	1519(13)	C(41)	—3428(13)	3591(8)	—195(7)
C(13)	3974(15)	3586(10)	1468(7)	C(42)	—2889(13)	2944(8)	187(7)
C(14)	5073(15)	3719(10)	1489(7)	C(43)	—2050(12)	1409(8)	1001(7)
C(15)	5199(15)	3706(10)	917(7)	C(44)	—2483(12)	1072(8)	1402(7)
C(16)	4224(15)	3559(10)	325(7)	C(45)	—3240(12)	435(8)	1184(7)
C(17)	3125(15)	3426(10)	305(7)	C(46)	—3564(12)	136(8)	565(7)
C(18)	2999(15)	3439(10)	876(7)	C(47)	—3132(12)	473(8)	164(7)
C(19)	5190(10)	3841(9)	2841(7)	C(48)	—2375(12)	1109(8)	382(7)

TABLE 5

CALCULATED FRACTIONAL COORDINATES (×10^4) FOR THE HYDROGEN ATOMS

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
H(4)	4074	1257	526	H(23)	7123	5339	3417
H(7)	1804	—358	2856	H(24)	5123	5037	2562
H(91)	5905	1518	1740	H(26)	3617	5060	1579
H(92)	5483	1433	2370	H(27)	2259	6172	1371
H(93)	5477	2350	2028	H(28)	662	6103	1707
H(101)	1869	997	—372	H(29)	423	4922	2250
H(102)	941	1724	—315	H(30)	1778	3811	2455
H(103)	878	771	—51	H(32)	916	2092	2563
H(111)	3820	305	3804	H(33)	1069	2416	3645
H(112)	3769	1328	3783	H(34)	—634	2991	3739
H(113)	4516	824	3413	H(35)	—2490	3241	2752
H(121)	—87	—574	1708	H(36)	—2644	2916	1670
H(122)	195	—115	1108	H(38)	—562	3837	1400
H(123)	—781	314	1369	H(39)	—1519	4985	722
H(14)	5827	3832	1947	H(40)	—3351	4827	—298
H(15)	6050	3810	933	H(41)	—4228	3523	—640
H(16)	4321	3548	—117	H(42)	—3272	2375	37
H(17)	2371	3313	—153	H(44)	—2232	1304	1881
H(18)	2148	3335	860	H(45)	—3575	174	1495
H(20)	5510	2683	3229	H(46)	—4150	—357	396
H(21)	7510	2983	4084	H(47)	—3384	241	—316
H(22)	8315	4311	4178	H(48)	—2040	1369	71

TABLE 6

THERMAL PARAMETERS ($\times 10^4$) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	256(11)	289(14)	284(11)	−63(11)	115(9)	−56(11)
Rh(2)	204(10)	303(13)	248(11)	−9(11)	80(8)	21(11)
S(1)	1109(70)	840(65)	573(51)	−335(53)	504(51)	−271(63)
S(2)	679(56)	1011(72)	582(53)	417(54)	291(45)	249(56)
P(1)	339(38)	277(42)	258(37)	−48(32)	101(32)	−18(33)
P(2)	267(33)	292(43)	206(33)	−6(29)	86(28)	13(29)

	U		U		U		U
N(1)	347(50)	C(10)	575(83)	C(23)	463(74)	C(36)	432(72)
N(2)	339(53)	C(11)	523(80)	C(24)	462(73)	C(37)	270(55)
N(3)	255(48)	C(12)	438(72)	C(25)	530(78)	C(38)	463(75)
N(4)	208(45)	C(13)	356(68)	C(26)	498(78)	C(39)	738(98)
C(1)	391(70)	C(14)	409(69)	C(27)	827(107)	C(40)	610(85)
C(2)	358(61)	C(15)	543(81)	C(28)	796(103)	C(41)	692(96)
C(3)	344(65)	C(16)	696(94)	C(29)	611(92)	C(42)	488(76)
C(4)	470(74)	C(17)	649(89)	C(30)	598(86)	C(43)	232(56)
C(5)	408(70)	C(18)	482(74)	C(31)	296(57)	C(44)	368(67)
C(6)	320(62)	C(19)	287(61)	C(32)	350(61)	C(45)	557(81)
C(7)	464(71)	C(20)	365(68)	C(33)	486(74)	C(46)	556(83)
C(8)	248(58)	C(21)	399(69)	C(34)	427(71)	C(47)	409(68)
C(9)	468(73)	C(22)	438(74)	C(35)	454(68)	C(48)	413(70)

The anisotropic parameters are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + hka^*b^*U_{12})]$

included in the final structure factor calculations with isotropic thermal parameters. The final R value was 0.059 for the observed reflections only. The function minimized in the least-squares calculations was $\Sigma |w \Delta F|^2$; unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to F_0. The atomic scattering factors (corrected for the anomalous dispersion of Rh, S, and P) were taken from the international Tables [24]. Final atomic coordinates for non-hydrogen atoms and for hydrogen atoms (in the calculated positions) are given in Tables 4 and 5, respectively. The anisotropic and isotropic thermal parameters for the non-hydrogen atoms are given in Table 6. A list of observed and calculated structure factors is available from the authors on request.

All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

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