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Contribution from the Groupe d'Etude et d'Application des complexes métalliques,
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Dinuclear Bridged d^8 Metal Complexes. V. Preparation and Structure of $[Rh(SR)(CO)_2L]_2$ and $[Rh(SR)(CO)L]_2$ Complexes (L = Tertiary Phosphine; R = C_6H_5, *t*-C_4H_9)[1,2]

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Addition of a tertiary phosphine ligand PA_3 to di-μ-phenyl-(or di-μ-*tert*-butyl-)thiolatotetracarbonyldirhodium(I) affords the pentacoordinated dinuclear rhodium complexes $[Rh(SR)(CO)_2L]_2$. NMR and infrared data are consistent with a double tetragonal-pyramidal structure, both phosphines being in the apical positions. These complexes are of low stability and lose more or less easily 2 equiv of CO giving $[Rh(SR)(CO)L]_2$. These thiolato-bridged complexes $[Rh(SR)(CO)L]_2$ have been prepared by substitution of the chloro bridges in $[RhCl(CO)L]_2$ with LiSR. Infrared and NMR data are consistent with rhodium atoms being in a square-planar environment and the structure is bent along the S–S axis. With R = *t*-Bu and with PA_3 = PMe_3, PMe_2Ph, or $P(NMe_2)_3$, a single cis isomer was found either in solution or in the solid state. However, for other prepared compounds a mixture of isomers in equilibrium was detected. The geometry of various isomers is discussed.

Introduction

Chatt and Hart[3] have shown that substitution of the chloro bridges in the complexes $Pt_2Cl_4(PA_3)_2$ by thiolato groups gives more inert derivatives toward bridge-splitting reagents. These thiolato-bridged complexes $Pt_2Cl_2(SR)_2(PA_3)_2$ exist as cis and trans isomers;[3] the more stable isomer is cis when R is aliphatic and trans when R is aromatic.

On the other hand, with dinuclear complexes of Pt(II), it is interesting to note that removing the Cl bridges by thiolato bridges modifies the structure from a planar to a bent one. Indeed in $[PtCl_2(PPr_3)]_2$[4] all atoms are coplanar while in $[PtCl(SEt)(PPr_3)]_2$[5] a dihedral angle of 130° is observed. For the dinuclear $[RhCl(CO)(PMe_2Ph)]_2$ complex a recent X-ray structural determination[1] shows a bent configuration. From the related influence of the thiolato bridges it is thus reasonable to think that for dinuclear thiolato-bridged complexes of Rh(I) the structure is still a bent one.

Previous thiolato-bridged rhodium complexes have been reported, namely, $[Rh(SR)(CO)_2]_2$[6-11] $Rh(SR)(CO)(PA_3)_2$,[8,12] $[C_8H_{12}Rh(SR)]_2$,[13] and $[Rh(SR)(P(OPh)_3)_2]_2$.[13]

In the present paper we wish to report the results of our investigations of the reactivity of $[Rh(SR)(CO)_2]_2$ complexes toward nucleophiles. The structure of the $[Rh(SR)(CO)_2PA_3]_2$ pentacoordinated complexes is described. The preparation and structure of $[Rh(SR)(CO)(PA_3)]_2$ compounds in their isomeric forms are reported.

Experimental Section

The $[RhCl(CO)_2]_2$,[14] $[Rh(SPh)(CO)_2]_2$ (**1**),[9] and $[RhCl(CO)PA_3]_2$[15] compounds were prepared as previously described.

All solvents were distilled and used under nitrogen atmosphere. Thiophenol, *tert*-butyl mercaptan, butyllithium, trimethyl phosphite, and triphenyl- and tricyclohexylphosphines were obtained from Fluka Co.; the tris(dimethylamino)phosphine was a gift from the Pierrefitte Co. The ligands $P(CH_3)_3$[16] and $P(CH_3)_2C_6H_5$[17] were prepared by published methods. Rhodium trichloride trihydrate was obtained from the "Compagnie des Métaux Précieux". Microanalyses were carried out by the "Service Central de Microanalyses du CNRS".

Infrared spectra were recorded with a Perkin-Elmer 225 grating spectrometer in hexadecane solutions or in cesium bromide pellets; in the carbonyl stretching region the spectra were calibrated by water vapor lines. Lorentz line shape analysis of the optical density of infrared curves was performed with a Du Pont 310 curve resolver. The Raman spectra were obtained in the solid state with a T 800 spectrometer equipped with an ionized argon laser (4880 Å, 1 W) from the Spectra Physics Co.

The proton magnetic studies were performed on a Varian Associates A-60A spectrometer. Dichloromethane, deuteriochloroform, benzene, and deuteriotoluene were used as solvents and tetramethylsilane as internal standard. Nuclear Overhauser experiments were carried out on a Varian Associates HA 100 spectrometer. Deuteriotoluene was used as solvent, a small quantity of benzene as lock signal, and TMS as reference for integration measurements.

The mass spectra were recorded with a Varian MAT 311 spectrometer.

Molecular weights were determined by tonometry in benzene using a Mechrolab apparatus.

Melting points were determined in air.

Preparation and Detection of Complexes

Our main observations concerning the $[RhSR(CO)_2]_2$, $[Rh(SR)(CO)_2L]_2$, and $[Rh(SR)(CO)L]_2$ complexes are summarized as follows.

$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2]_2$ (2). A 0.414-g amount of $[RhCl(CO)_2]_2$ (1.06 mmol) was dissolved in 20 ml of hexane and 0.242 ml (2.12 mmol) of $t\text{-}C_4H_9SH$ was added at 68°C. The solution was concentrated under reduced pressure. By crystallization at −78°C orange crystals were obtained and dried in vacuo. A 0.470-g amount of product was obtained (yield ≃90%).; mp 103°C. Anal. Calcd: C, 29.04; H, 3.65; S, 12.92. Found: C, 29.00; H, 3.68; S, 12.99.

$[Rh(SC_6H_5)(CO)_2P(CH_3)_3]_2$ (3). A 0.177-g sample of **1** (0.33 mmol) was dissolved in 15 ml of benzene and 0.067 ml (0.66 mmol) of trimethylphosphine was added in two steps. At half-stoichiometry the infrared spectra showed clearly equal quantities of **1** and **3** (2063 (vs), 2003 (vs), 1985 (vs) cm^{-1}). After complete addition of phosphine the infrared and NMR spectra showed the presence of a single product. Benzene was removed rapidly under reduced pressure to give a brown-yellow oil. Hexane was added and crystallization at −20°C gave a yellow powder of **17** whereas the supernatant solution contained a mixture of **3** and **17**.

A 0.100-g amount of **17** was dissolved in 15 ml of CH_2Cl_2. CO was bubbled into the solution. After 1 hr the infrared and NMR spectra showed the formation of **3** to be complete. The mass spectrum of the CH_2Cl_2 solution revealed the existence of only **17**. The following complexes were similarly prepared: **$[Rh(SC_6H_5)(CO)_2P(C_6H_{11})_3]_2$ (4)**, **$[Rh(SC_6H_5)(CO)_2P(C_6H_5)_3]_2$ (5)**, **$[Rh(SC_6H_5)(CO)_2P(N(CH_3)_2)_3]_2$ (6)**. The mass spectral study of the CH_2Cl_2 solution of **5** failed to show the molecular ions of **5** due to extensive decomposition above 130°C.

$[Rh(SC_6H_5)(CO)_2P(OCH_3)_3]_2$ (7). A 0.328-g amount of **1** (0.612 mmol) was dissolved in benzene and progressive quantities of trimethyl phosphite were added at room temperature (1.224 mmol, 0.174 ml). When 0.074 ml (0.46 mmol) was added, a slight gas loss was observed; the infrared spectra in benzene–hexadecane solution showed the presence of **1** and **7** (2064 (vs), 2015 (vs), and 2006 (vs) cm^{-1}) and a small quantity of **19** (2008 and 1994 cm^{-1}). When the stoichiometry of ligand was reached, the infrared spectra exhibit only the bands due to **19**.

$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_{11})_3]_2$ (8). A 0.258-g quantity of **2** (0.52 mmol) was dissolved in 10 ml of CH_2Cl_2 and the addition of 0.292 g of tricyclohexylphosphine (1.04 mmol) dissolved in 10 ml of CH_2Cl_2 was monitored by infrared spectroscopy. The progressive formation of **8** was observed. When the stoichiometric quantity was added, the ir spectra showed only the presence of **8**. The solvent was removed under reduced pressure. Addition of hexane gave a small quantity of insoluble yellow compound and a yellow solution. Attempts to obtain crystals of **8** failed. The following complexes were similarly prepared: **$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_5)_3]_2$ (9)**, **$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(CH_3)_2C_6H_5]_2$ (10)**, **$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(N(CH_3)_2)_3]_2$ (11)**, **$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(OCH_3)_3]_2$ (12)**—this complex was observed in the same conditions as 7.

The general procedure of synthesis for the $[Rh(SR)(CO)L]_2$ complexes (Table I) is exemplified in the case of **$[Rh(S\text{-}t\text{-}C_4H_9(CO)P(CH_3)_3]_2$ (13)**. A 0.925-g amount of $[RhCl(CO)P(CH_3)_3]_2$ (1.907 mmol) was dissolved in 30 ml of toluene and 3.814 mmol of $t\text{-}C_4H_9SLi$ (obtained by mixing of 2.125 ml of butyllithium at 1.795 *M* and 0.433 ml of *tert*-butyl mercaptan) in 20 ml of toluene–ether mixture was added at room temperature. The solution was stirred for 4 hr. The solvent was evaporated under reduced pressure, the product was extracted from the solid residue with toluene, and hexane was added. Crystallization at −20°C gave 0.92 g of brown crystals.

See Table I for analytical and physical data.

Results and Discussion

(1) Structure of the $[Rh(SR)(CO)_2(PA_3)]_2$ Complexes. The addition of a tertiary phosphine ligand PA_3 to the carbonyl compounds $[Rh(SR)(CO)_2]_2$ (**1**, **2**) was monitored by infrared

Table I. Analytical and Physical Data

No.	L	Solvent of recrystn	Yield, %	% calcd						% found						Mol wt		Color	Mp, °C
				C	H	S	N	Cl	P	C	H	S	N	Cl	P	Calcd	Found		
									$[Rh(S\text{-}t\text{-}C_4H_9)(CO)L]_2$ Complexes										
13	$P(CH_3)_3$	Toluene–hexane	85	32.44	6.13	10.82		0	10.46	32.67	6.08	10.79		0	10.65	592	568	Brown	152–154 dec
14	$P(CH_3)_2C_6H_5$	Hexane	90	43.58	5.63	8.95		0	8.64	43.76	5.63	8.97		0	8.80	716	698	Yellow	112
15	$P(N(CH_3)_2)_3$	Hexane	90	34.47	7.10	8.36	10.96	0	8.08	35.04	7.31	8.32	10.86	0	8.16	767	784	Brown-yellow	145 dec
16	$P(OCH_3)_3$	Hexane	85	27.92	5.27	9.31		0	9.00	28.22	5.53	9.17		0	9.35	688	709	Yellow	99
									$[Rh(SC_6H_5)(CO)L]_2$ Complexes										
17	$P(CH_3)_3$	Toluene–hexane	75	37.99	4.46	10.14		0	9.79	38.11	4.53	9.87		0	9.74	632	603	Brown	145–150 dec
18	$P(N(CH_3)_2)_3$	Toluene–hexane	75	38.72	5.75	7.95	10.42	0	7.68	39.01	5.80	7.75	9.71	0	7.39	807	772	Brown	132–135 dec
19	$P(OCH_3)_3$	Toluene–hexane	85	32.98	3.87			0	8.50	33.50	4.01			0	8.85		[a]	Brown	106 dec

[a] Decomposition of the product has prevented good measurement.

Table II. Infrared and Some NMR Data for $[Rh(SR)(CO)_2(PA_3)]_2$ Complexes[a]

Compd	ν_{CO}, cm^{-1} (hexadecane)	δ, ppm (TMS); J, Hz
$[Rh(SC_6H_5)(CO)_2(P(OCH_3)_3)]_2$, **3**	2064 vs 2015 vs 2006 vs	
$[Rh(SC_6H_5)(CO)_2(P(N(CH_3)_2)_3]_2$, **4**	2061 vs 2001 vs 1987 vs	$\delta^b{}_{CH_3}$ −2.75 d; $J_{PH} = 10.3$
$[Rh(SC_6H_5)(CO)_2(P(C_6H_5)_3)]_2$, **5**	2062 vs 2003 vs 1995 vs	
$[Rh(SC_6H_5)(CO)_2(P(C_6H_{11})_3)]_2$, **6**	2061 vs 2000 vs 1976 vs	
$[Rh(SC_6H_5)(CO)_2(P(CH_3)_3)]_2$, **7**	2063 vs 2003 vs 1985 vs	$\delta^b{}_{CH_3}$ −1.37 dd; $J_{PH} = 9.9$, $J_{RhH} = 1.5$; $\delta^b{}_{C_6H_5}$ −7.13 m, −7.72 m
$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2(P(OCH_3)_3)]_2$, **8**	2057 vs 1996 vs 1986 vs	
$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2(P(N(CH_3)_2)_3)]_2$, **9**	2051 vs 1988 vs 1966 vs	$\delta^b{}_{CH_3}$ −2.79 d, $\delta^b{}_{t\text{-}C_4H_9}$ −1.53 s; $J_{PH} = 10.5$
$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2(P(CH_3)_2C_6H_5)]_2$, **10**	2053 vs 1990 vs 1968 vs	$\delta^c{}_{CH_3}$ −1.48, $\delta^c{}_{t\text{-}C_4H_9}$ −1.60 s; $J_{PH} = 9$
$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2(P(C_6H_5)_3)]_2$, **11**	2052 vs 1990 vs 1972 vs	
$[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2(P(C_6H_{11})_3)]_2$, **12**	2051 vs 1988 vs 1961 vs	$\delta^b{}_{t\text{-}C_4H_9}$ 1.49 s

[a] Abbreviations: s, singlet; d, doublet; dd, double doublet; m, multiplet. [b] CH_2Cl_2 solution. [c] Benzene solution.

spectroscopy and it was shown that disappearance of the CO stretchings for **1** or **2** was complete when 2 equiv of phosphine was added. When the ratio PA_3:Rh = 1 was reached, only three CO bands remained in the infrared spectra. Therefore, these observations are consistent with the formation of a complex formulated as $[Rh(SR)(CO)_2PA_3]_2$. Any attempt to crystallize the obtained compounds failed, decarbonylation occurring to give more or less quickly the $[Rh(SR)(CO)(PA_3)]_2$ complexes. We determined that this decarbonylation is a reversible process.

Attempts to obtain well-resolved Raman spectra were unsuccessful because of extensive decomposition of the solutions. In addition, the parent ions of the compounds in solution were undetected in mass spectrometry because of low thermal stability. In these conditions both infrared and NMR data were obtained only for freshly prepared compounds (Table II).

The three CO stretching bands give strong evidence of a dinuclear structure in which rhodium atoms are pentacoordinated. Moreover, the equivalence of the *tert*-butyl proton signals and the presence of a single ligand PA_3 proton signal suggest a C_{2v} symmetry. It would be very useful to obtain $[Rh(SR)(CO)_3]_2$ for an ir argumentation of the structure. Unfortunately attempts to add CO under 1 atm failed to give the expected product. All possible basic conformations have been examined in Table III. This table lists the ir CO stretching active modes determined for each geometry. As unambiguously shown for $Rh_2Cl(SR)(CO)_4$,[11] the configuration in the bridging atoms does not perturb the local symmetry of the CO groups. The syn–anti isomerism has been neglected in Table III. Thus only structures IIg and IIj are possible. NMR data are consistent with both geometries and moreover suggest that both *tert*-butyl groups are in syn positions.

We tried to reach the θ value, which is the dihedral angle between the planes of the CO groups of the two $Rh(CO)_2$ moieties from observed intensities of CO stretching bands.[20] Indeed, the calculated ratio between the intensities of the various active modes is easily obtained using eq 1–4. (See

$$I_{A_1}/I_{B_1} = \cot^2 (\theta/2) \quad (1)$$

$$I_{A_1}/I_{B_2} = \cot^2 (\zeta/2) \cos^2 (\theta/2) \quad (2)$$

$$I_{B_1}/I_{B_2} = \cot^2 (\zeta/2) \sin^2 (\theta/2) \quad (3)$$

$$(I_{A_1} + I_{B_1})/I_{B_2} = \cot^2 (\zeta/2) \quad (4)$$

Figure 1 for the identification of angles.)

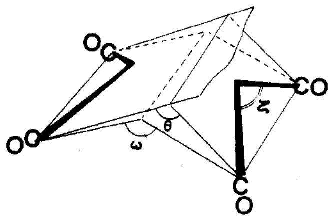


Figure 1.

With the reasonable assumption of $\zeta \simeq 90°$, it follows from (4) that the B_2 mode possesses the strongest intensity. Therefore, the two bands at higher frequencies are attributed to A_1 and B_1 modes, and from their almost equal intensities, the dihedral angle could be closed to 90° (from (1)).

Such values are consistent with a metal atom drawn up from the square-plane environment and lead to the distorted structure IIj which can be described as a double tetragonal pyramid.

Concerning the *tert*-butyl groups, examination of molecular models shows that the steric hindrance probably compels them into syn-endo positions (Figure 2).

(2) Structure of the $[Rh(SR)(CO)PA_3]_2$ Complexes. The decarbonylation of the pentacoordinated complexes **3–12** which affords the dinuclear compounds $[Rh(SR)(CO)(PA_3)]_2$ (III) is sometimes a slow and incomplete process. More conveniently, these complexes have been prepared by treatment of $[RhCl(CO)PA_3]_2$[15] with the lithium compound LiSR in

Table III. Possible Conformations for $[Rh(SR)(CO)_2PA_3]_2$ Complexes and Prediction of Ir ν_{CO} Active Modes

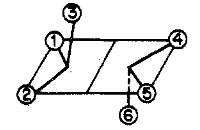
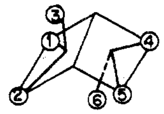
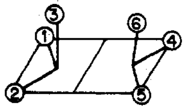
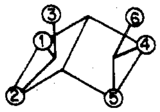
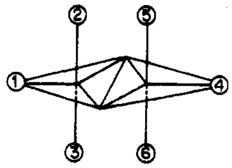
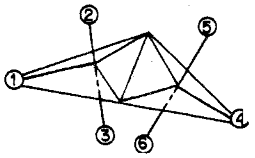
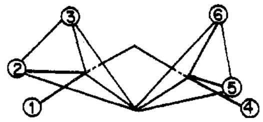
	No.	Positions of PA_3	Point group symmetry	Ir-active modes
	IIa	3, 6	C_{2h}	$2(A_u + B_u)$
	IIb	1, 5	C_i	$2(2\ A_u)$
	IIc	1, 4	C_2	$4(2\ A + 2\ B)$
	IId	3, 6	C_s	$4(2\ A' + 2\ A'')$
	IIe	1, 5	C_1	$4(4\ A)$
	IIf	1, 4	C_1	$4(4\ A)$
	IIg	3, 6	C_{2v}	$3(A_1 + B_1 + B_2)$
	IIh	1, 5	C_2	$4(2\ A + 2\ B)$
	IIi	1, 4	C_s	$4(2\ A' + 2\ A'')$
	IIj	3, 6	C_{2v}	$3(A_1 + B_1 + B_2)$
	IIk	1, 5	C_2	$4(2\ A + 2\ B)$
	IIl	1, 4	C_s	$4(2\ A' + 2\ A'')$
	IIm	1, 4	D_{2h}	$2(B_{1u} + B_{2u}$
	IIn	2, 6	C_{2h}	$2(2\ B_u)$
	IIo	2, 5	C_{2v}	$4(2\ A_1 + 2\ B_2)$
	IIp	1, 4	C_{2v}	$4(2\ A_1 + 2\ B_2)$
	IIq	2, 6	C_s	$4(2\ A' + 2\ A'')$
	IIr	2, 5	C_{2v}	$4(2\ A_1 + 2\ B_2)$
	IIs	1, 4; 2, 5; 3, 6	C_s	$4(2\ A' + 2\ A'')$
	IIt	1, 5; 1, 6; 2, 4; 3, 4 2,6; 3,5	C_1	$4(4\ A)$

Table IV. Infrared, Raman, and NMR Data of $[Rh(SR)(CO)(PA_3)]_2$ Complexes

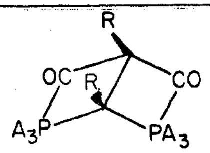
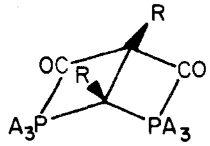
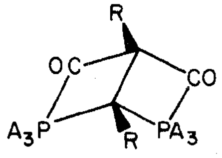
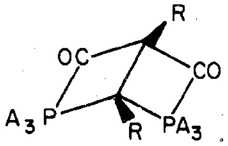
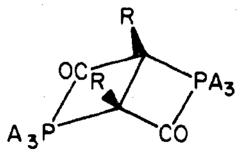
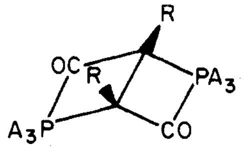
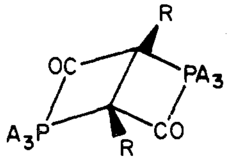
Compd	ν_{CO}, cm^{-1} Hexadecane	CsBr	Raman	δ_R, ppm	δ_{PA_3}, ppm	J_{PH}, Hz	J_{RhH}, Hz
$[Rh(S\text{-}t\text{-}Bu)(CO)(PMe_3)]_2$, **13a**	1965 vs			-1.89^{a}	-1.22^{a}	9	1.2
	1951 vs			-1.61			
$[Rh(S\text{-}t\text{-}Bu)(CO)(PMe_2Ph)]_2$, **14a**	1966 vs		1961 vs	-1.90^{a}	-1.48^{a}	9	1^{e}
	1952 vs		1942 vs	-1.37			
$[Rh(S\text{-}t\text{-}Bu)(CO)(P(NMe_2)_3)]_2$, **15a**	1967 vs		1955 vs	-1.64^{b}	-2.78^{b}	9.4	
	1953 vs		1943 vs	-1.50			
$[Rh(S\text{-}t\text{-}Bu)(CO)(P(OMe)_3)]_2$, **16a + 16b**	1996 vs	1987 vs		$-1.87^{a,c}$	-3.50^{a}	11.5	
	1986 vs	1972 vs		-1.68			
	1976 vs						
$[Rh(SPh)(CO)(PMe_3)]_2$, 17	1985 m	1977 s		-7.82^{d}	-1.58^{d}	9.6	1.2
	1972 vs	1967 vs		-7.18	-1.29	9.6	1.2
		1954 vs					
$[Rh(SPh)(CO)(P(NMe_2)_3)]_2$, 18	1987 vs	1975 vs		-7.79^{b}	-2.76^{b}	9.9	
	1974 s	1960 vs		-7.08			
	1968 vs						
$[Rh(SPh)(CO)(P(OMe)_3)]_2$, 19	2008 s, b				-3.59^{b}	12.3	
	1994 vs, b				-3.68	12.3	
					-3.75	11.0	
					-3.77	12.3	

[a] Benzene solutions. [b] $CDCl_3$ solutions. [c] Triplet; $J = 0.4$ Hz. [d] CH_2Cl_2 solutions. [e] At −10°C.

toluene–ether solutions. The substitution of the bridges is fast, as shown by monitoring the reaction by infrared spectroscopy.

Elemental analysis, relative intensities of ligands, and *tert*-butyl (or phenyl) proton NMR signals (Table IV) and molecular weights are consistent with the $[Rh(SR)(CO)(PA_3)]_2$ formula. As no fine structure due to the cis phosphorus–phosphorus coupling of a $X_9AA'X'_9$ system[22] but rather doublets were observed in the NMR spectra and a splitting of ~15 cm^{-1} [15] was measured in the infrared spectra, it appears that one phosphine ligand and one CO group are coordinated to each rhodium atom. If we assume these complexes to have a "bent" double square-planar structure similar to $[RhCl(CO)(PMe_2Ph)]_2$ determined by an X-ray study,[1] seven isomers can be, a priori, expected, according to whether the CO groups are cis or trans with regard to the core $Rh_2(SR)_2$ or whether the R groups are mutually syn or anti.

Table V[a]

No.	Isomer	Symmetry	Ir ν_{CO} modes	No. of PA_3 signals	No. of R signals
IIIa		*Cs*	A′ + A″[b]	1	2
IIIb		*Cs*	A′ + A″[b]	1	2
IIIc		*Cs*	A′ + A″[b]	1	2
IIId		*Cs*	A′ + A″[b]	1	2
IIIe		C_2	A + B[c]	1	1
IIIf		C_1	2 A[c]	2	2
IIIg		C_2	A + B[c]	1	1

[a] NMR and infrared data expected for each isomer of $[RhSR(CO)L]_2$ (the S and Rh atoms have been omitted for clarity). [b] Closed intensities expected. [c] Quite different intensities expected.

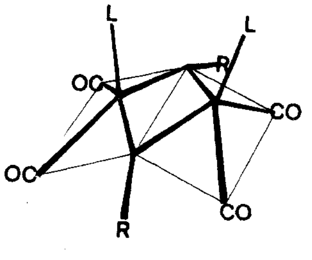


Figure 2. Proposed structure for $[Rh(SR)(CO)_2L]_2$ complexes.

Table V summarizes the number of NMR signals and the intensities of the C–O stretching modes expected for each isomer.

In the case of *tert*-butylthiolato-bridged complexes **13–15**, a single isomer was obtained. The infrared spectra show two CO stretching bands with the same intensity in solution and in the solid state. Extensive decomposition of the products in solution has precluded Raman spectroscopy determinations; however, in the solid state two CO stretching bands of the same intensity were observed (Table IV). Such results are in favor of a cis structure for which both CO vectors form an angle of ~90°. Similarly, as expected for such a geometry, two *tert*-butyl signals and only one ligand signal were observed in the NMR spectrum (Table IV). Moreover, molecular models (SASM scale models) show clearly that the *tert*-butyl groups cannot lie in the endo position (IIIc and IIId) between the two phosphine ligands because of steric hindrance considerations. Thus two possible isomers IIIa and IIIb are now to be considered. The proximity of *tert*-butyl groups in the IIIa isomer and not in IIIb prompted us to perform a nuclear Overhauser effect[23] experiment in the case of the $[Rh(S\text{-}t\text{-}Bu)(CO)(PMe_3)]_2$ complex. A slight decrease in the intensity of one *tert*-butyl signal was observed when the other was irradiated. Similarly irradiation of the methyl ligand proton or the *tert*-butyl groups induced a small decrease in intensity of the observed signals. These results are not significant enough to be able to choose unambiguously between the syn-exo isomer (IIIa) and the anti one (IIIb), and even less so to be able to assign both *tert*-butyl signals.

For the $[Rh(S\text{-}t\text{-}Bu)(CO)P(OMe)_3]_2$ complex two CO stretching bands appear in the solid state with almost the same intensity. With the splitting of 15 cm^{-1} being the same as those in compounds **13–15**, this compound is presumed to have the form IIIa or IIIb. However the infrared spectra of hexadecane solutions exhibit three CO stretching bands at 1997, 1986, and 1976 cm^{-1}, and the NMR spectra at room temperature show the resonance due apparently to a single isomer. A variable-temperature experiment revealed that an exchange phenomenon occurs but the slow-exchange limits were not reached. It is possible therefore to consider that an exchange between the two IIIa and IIIb isomers occurs in solution, only one isomer being present in the solid state.

For the phenylthiolato-bridged complexes the constraint occurring in the *tert*-butyl group no longer exists and the seven isomers can be expected. In Table IV, the infrared and NMR data show that in the solid state the compound can exist as a cis isomer (**18**) whereas in solution the trans isomer (**17**) can be observed.

Finally, it is of interest to compare the reactivity of thiolato-bridged carbonyl complexes to that of their chloro-bridged analog $[RhCl(CO)_2]_2$. Indeed it has been shown[21] that addition of a phosphine ligand to $[RhCl(CO)_2]_2$ gives rise to a series of equilibria between monomeric and dimeric species. On the contrary, in the present study, no monomeric species have been detected, but pentacoordinated dinuclear complexes are obtained. Both observations are in favor of more stable thiolato-bridged complexes toward bridge splitting by nucleophilic ligands.

Registry No. $[Rh(SPh)(CO)_2]_2$, 24818-80-2; $[RhCl(CO)_2]_2$, 14523-22-9; $[RhCl(CO)P(CH_3)_3]_2$, 49634-24-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2]_2$, 54032-58-5; $[Rh(SC_6H_5)(CO)_2P(CH_3)_3]_2$, 56348-51-7; $[Rh(SC_6H_5)(CO)_2P(C_6H_{11})_3]_2$, 56348-52-8; $[Rh(SC_6H_5)(CO)_2P(C_6H_5)_3]_2$, 56348-53-9; $[Rh(SC_6H_5)(CO)_2P(N(CH_3)_2)_3]_2$, 56348-54-0; $[Rh(SC_6H_5)(CO)_2P(OCH_3)_3]_2$, 56348-55-1; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_{11})_3]_2$, 56348-56-2; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_5)_3]_2$, 56348-57-3; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(CH_3)_2C_6H_5]_2$, 56390-02-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(N(CH_3)_2)_3]_2$, 56348-58-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(OCH_3)_3]_2$, 56348-59-5; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(CH_3)_3]_2$, 54032-62-1; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(CH_3)_2C_6H_5]_2$, 54032-64-3; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(N(CH_3)_2)_3]_2$, 54032-66-5; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(OCH_3)_3]_2$, 54032-68-7; $[Rh(SC_6H_5)(CO)P(CH_3)_3]_2$, 54032-61-0; $[Rh(SC_6H_5)(CO)P(N(CH_3)_2)_3]_2$, 54032-65-4; $[Rh(SC_6H_5)(CO)P(OCH_3)_3]_2$, 54032-67-6; $P(CH_3)_3$, 594-09-2; $P(OCH_3)_3$, 121-45-9.

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Aryldiazo Complexes. Syntheses and Reactions of New Complexes of Osmium and Ruthenium

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Aryldiazo complexes, $[M(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (M = Os, Ru; Ph = C_6H_5), have been prepared by allowing diazonium salts to react with $M(CO)_3(PPh_3)_2$. Infrared spectra of the Ru complex suggest the presence of two isomers both in solution and in the solid state. These complexes react with a variety of coordinating anions (X^-), to form $MX(CO)_2(NNPh)(PPh_3)_2$. The osmium derivatives have $\nu(NN)$ near 1455 cm^{-1}, which is the lowest value yet reported for a nonbridging aryldiazo ligand. The first aryldiazo–hydrido complexes, $MH(CO)_2(NNPh)(PPh_3)_2$ and $MH(CO)(NNPh)(PPh_3)_2$, were prepared by deprotonation of the respective phenyldiazene complexes, $MH(CO)_2(HNNPh)(PPh_3)_2^+$ and $MH(CO)(HNNPh)(PPh_3)_3^+$. The compound $OsCl_3(NNPh)(PPh_3)_2$ has also been prepared. A large number of the foregoing complexes have been synthesized with selective ^2H and ^{15}N labels. Infrared and NMR spectra show $MX(CO)_2(NNPh)(PPh_3)_2$ and the analogous hydrido complex to be pseudooctahedral with trans phosphine ligands, cis carbonyl ligands, and a doubly bent phenyldiazenido ($NNPh^-$) ligand. Similarly, $MH(CO)(NNPh)(PPh_3)_2$ possesses a trigonal-bipyramidal geometry with trans phosphine ligands and an equatorial, singly bent phenyldiazoniumato ($NNPh^+$) ligand. Isotopic substitution of the diazo ligand shows that $\nu(NN)$ is often vibrationally coupled with phenyl vibrational modes and that two or three bands sometimes shift upon ^{15}N substitution. Vibrational coupling is also observed in the higher energy region (1850–1900 cm^{-1}) in the compound $RuCl_3(NNC_6D_5)(PPh_3)_2$. The wide range in the values of $\nu(NN)$, $RuCl_3(NNPh)(PPh_3)_2$ (1882 cm^{-1}), vs. $RuCl(CO)_2(NNPh)(PPh_3)_2$ (1462 cm^{-1}), indicates that the N–N stretching frequencies are sensitive to the electronic and steric environment of the diazo ligand. The aryldiazo complexes are compared with analogous, isoelectronic nitrosyl complexes of Os and Ru.

Introduction

Although the first molybdenum–[2] and platinum–aryldiazo[3] complexes were reported over 10 years ago, it has been only in the last several years that appreciable numbers of aryldiazo complexes have been prepared. Even so, there are relatively few such complexes known when compared with the number of analogous nitrosyl complexes. Aryldiazo complexes have been reported for all members of the Cr, Mn, Fe, Co, and Ni triads with the exception of Ni, Pd, and Tc.[4,5] Part of the interest in aryldiazo and other diazo ligands has been generated by the close relationship of these ligands to dinitrogen and nitrosyl ligands. Recent work has shown that diazo ligands can be prepared from coordinated dinitrogen in Re, Mo, and W complexes.[6] Furthermore, aryldiazo ligands resemble