(7) L. Vancea, M. J. Bennett, C. E. Jones, R. A. Smith, and W. A. G. Graham, *Inorg. Chem.*, **16**, 897 (1977).

(8) The reported structures are *cis*-Fe[PPh(OEt)₂]₄H₂,⁹ tris(tropolonato)aluminum(III),¹⁰ Fe(S₂CNEt₂)₂S₂C₂(CF₃)₂,¹¹ and *cis*-Fe(CO)₄-(SiMe₃)₂.⁷

(9) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 3482 (1970); L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *ibid.*, **94**, 1135 (1972).

(10) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **94**, 8046 (1972).

(11) D. L. Johnston, W. L. Rohrbaugh, and W. D. Horrocks, Jr., *Inorg. Chem.*, **10**, 1474 (1971).

(12) As is conventional in this field, the equatorial carbonyl groups are defined as those which are trans to the ER₃ ligands.

(13) This program, ISOC, was originally written by R. S. Gay and E. H. Brooks of this department and has been in routine use for over 8 years.

(14) J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 264 (1967).

(15) O. Kahn and M. Bigorgne, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 2483 (1965).

(16) F. Hein and W. Jehn, *Justus Liebigs Ann. Chem.*, **684**, 4 (1965).

(17) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 7, 1208 (1968).

(18) K. Noack and M. Ruch, *J. Organomet. Chem.*, **17**, 309 (1969).

(19) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(20) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(22) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(23) R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Am. Chem. Soc.*, **98**, 2484 (1976).

(24) Using the crude estimates of σ-donor properties based on force constants,²⁵ one calculates the σ parameter for SiMe₃ groups as −0.84²⁶ compared with −0.59 for SnPh₃.²⁵

(25) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(26) The force constant calculation is based on band positions of Me₃SiMn(CO)₅ at 2094 (A₁), 2001 (A₁), and 1992 (E) cm⁻¹, as reported by W. Jetz, Ph.D. Thesis, University of Alberta, Edmonton, 1970.

(27) The van der Waals half-thickness of an aromatic ring is 1.85 Å, whereas the van der Waals radius for a methyl group is 2.0 Å: F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., p 120.

(28) A compilation is given by P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 2097 (1975).

(29) H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967).

(30) F. Hein and E. Heuser, *Z. Anorg. Allg. Chem.*, **254**, 139 (1947); **255**, 125 (1947).

(31) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(32) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(33) The values of Table IX were estimated from the coalescence temperature and the low-temperature limiting axial–equatorial chemical shift difference.¹ In ref 1 it was noted that in these simple spectra, the values estimated in this way are in excellent agreement with the results of more elaborate simulation methods.

(34) D. L. Lichtenberger, D. R. Kidd, P. A. Loeffler, and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 629 (1976).

(35) L. Kruczynski and J. Takats, *Inorg. Chem.*, **15**, 3140 (1976), have correlated chemical shifts with free energies of activation for carbonyl permutation in a series of (1–4-η-diene)tricarbonyliron complexes. The trend is qualitatively the same as in the iron–tin complexes, which may be coincidental in view of the wide difference in the systems.

(36) R. Ball and M. J. Bennett, *Inorg. Chem.*, **11**, 1086 (1972).

Dinuclear-Bridged d⁸ Metal Complexes. 6. Crystal and Molecular Structure and Infrared Study of [Rh(SC₆H₅)(CO)(P(CH₃)₃)]₂¹

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The crystal and molecular structure of *cis*-di(μ-phenylthiolato)-dicarbonylbis(trimethylphosphine)dirhodium (I) has been determined from a single crystal by use of x-ray crystallographic methods. The space group is $P2_1/c$ with a = 13.843 (6), b = 16.912 (8), c = 11.235 (5) Å, β = 96.66 (7)°, Z = 4. Parameters of 28 nonhydrogen atoms in the asymmetric unit were refined by full-matrix least-squares techniques to a conventional R factor of 0.045. In a dinuclear unit, each rhodium atom is in a square-planar environment being bonded to a carbon atom of a carbonyl group, a phosphorus atom of a trimethylphosphine ligand, and two bridging sulfur atoms of two phenylthiolato groups. The dihedral angle of 113° between such two square planes leads to a "bent" geometry with an intramolecular rhodium–rhodium distance of 3.061 (1) Å. The compound is in the anti conformation with respect to the Rh₂(SC₆H₅)₂ core and the phenyl group in the exo position lies between the phosphine ligands. On the basis of the x-ray structure the infrared spectra in the solid state are interpreted by using the factor group approach. In addition an isomerization phenomenon in solution is discussed.

Introduction

From a previous infrared and NMR study¹ the [Rh-(SR)(CO) (PA₃)]₂ coordination compounds have been shown to have a "bent" double square planar structure. When SR are the *tert*-butylthiolato bridging groups, the compounds were suggested to exist in the cis configuration either in solution or in the solid state. Nevertheless for the parent phenylthiolato complexes, various isomers were detected in solution and thus unambiguous conclusions about their geometry were not easy to set up, especially for the compound where PA₃ = P(CH₃)₃; indeed this dicarbonyl complex exhibits three CO stretching bands in the solid state.

For these reasons, it was of interest to undertake an x-ray structural determination of [Rh(SC₆H₅)(CO)(P(CH₃)₃)]₂ and thus to compare its geometry with that of [RhCl(C-O)(P(CH₃)₂C₆H₅)]₂ previously described.² Moreover, by analysis of the observed differences in the M₂X₂ core an attempt was made to evaluate the factors governing the geometry of dinuclear-bridged d⁸ metal complexes of these and closely related compounds.

Experimental Section

[Rh(SC₆H₅)(CO)(P(CH₃)₃)]₂ was prepared as previously described.¹ The crystallization was performed in toluene to which hexane was added without mixing. Suitable crystals were obtained when the mutual diffusion of both solvents is carried out at −20 °C.

Infrared Studies. The infrared spectra were recorded with a Perkin-Elmer 225 grating apparatus equipped with a scale expander in optical density. Cyclohexane solutions or cesium bromide dispersions were used. In the ν_{CO} region of interest, the spectra were calibrated by water vapor lines. Line shape analyses were performed with a Du Pont 310 curve resolver. The part due to diffusion was very small and therefore neglected without any consequence on the Lorentz shape analysis (Chart I).

Data Collection. Diffraction data were collected at room temperature (22 °C) with an Enraf-Nonius CAD 4 computer-controlled four-circle diffractometer. Graphite-monochromatized Mo Kα radiation and a take-off angle of 4.5° were used. Intensities were collected using the $\omega-2\theta$ scan technique. The scan width was 1° + 0.35 tan θ; the counter aperture was 3.0 mm in width. Background measurements were obtained during a scan, at each end of the scan interval, with a total duration equal to half of the scan time. A total of 4114 intensities (±h, k > 0, l > 0) of independant reflections were

Table II. Atomic Parameters for Rh$_2$(SC$_6$H$_5$)$_2$(CO)$_2$(P(CH$_3$)$_3$)$_2$

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh(1)	0.1336 (1)	0.0149 (1)	−0.2409 (1)	0.0046 (1)	0.0031 (1)	0.0086 (1)	−0.0001 (1)	−0.0001 (1)	−0.0001 (1)
Rh(2)	0.3091 (1)	−0.0343 (1)	−0.3662 (1)	0.0059 (1)	0.0029 (1)	0.0064 (1)	0.0004 (1)	−0.0001 (1)	−0.0001 (1)
S(1)	0.2863 (1)	0.0780 (1)	−0.2451 (1)	0.0051 (1)	0.0027 (1)	0.0071 (1)	−0.0003 (1)	−0.0005 (1)	−0.0001 (1)
S(2)	0.2376 (1)	−0.0986 (1)	−0.2076 (2)	0.0058 (1)	0.0027 (1)	0.0074 (2)	−0.0002 (1)	−0.0004 (1)	0.0001 (1)
P(1)	0.0038 (2)	−0.0655 (2)	−0.2387 (3)	0.0051 (1)	0.0052 (1)	0.0150 (3)	−0.0012 (1)	0.0001 (1)	0.0001 (1)
P(2)	0.3284 (2)	−0.1513 (1)	−0.4571 (2)	0.0093 (2)	0.0034 (1)	0.0080 (2)	0.0012 (1)	0.0006 (1)	−0.0005 (1)
C(1)	0.0568 (6)	0.1017 (6)	−0.2682 (9)	0.0061 (5)	0.0048 (4)	0.0175 (12)	0.0001 (4)	0.0015 (7)	−0.0001 (6)
O(1)	0.0087 (6)	0.1566 (5)	−0.2848 (10)	0.0107 (6)	0.0054 (4)	0.0378 (18)	0.0035 (4)	0.0023 (8)	0.0015 (6)
C(2)	0.3520 (7)	0.0173 (5)	−0.4917 (8)	0.0088 (6)	0.0039 (3)	0.0107 (9)	0.0004 (4)	0.0007 (6)	0.0001 (5)
O(2)	0.3781 (6)	0.0489 (5)	−0.5731 (6)	0.0163 (8)	0.0070 (4)	0.0112 (7)	−0.0007 (4)	0.0050 (6)	0.0021 (4)
C(3)	−0.0074 (9)	−0.1154 (9)	−0.0945 (12)	0.0120 (10)	0.0108 (9)	0.0210 (17)	−0.0042 (7)	0.0027 (11)	0.0061 (10)
C(4)	−0.1176 (7)	−0.0230 (8)	−0.2825 (13)	0.0047 (6)	0.0088 (7)	0.0304 (21)	−0.0003 (5)	−0.0004 (8)	−0.0006 (10)
C(5)	0.0041 (8)	−0.1502 (7)	−0.3411 (12)	0.0094 (8)	0.0056 (5)	0.0276 (20)	−0.0019 (5)	−0.0024 (10)	−0.0047 (8)

Group	$x_c{}^b$	y_c	z_c	δ	ϵ	η
Ring 1	0.3362 (9)	−0.1945 (8)	−0.4974 (12)	−2.268 (17)	−2.224 (11)	0.665 (18)
Ring 2	0.3383 (10)	−0.1947 (9)	−0.4812 (14)	−1.560 (14)	−2.802 (10)	1.136 (19)
Ring 3	0.2799 (2)	0.2432 (2)	−0.3813 (3)	2.106 (4)	2.375 (3)	2.444 (4)
Ring 4	0.3787 (2)	−0.0678 (2)	0.0324 (3)	2.709 (3)	1.924 (3)	0.156 (8)

^{a} The form of the anisotropic thermal ellipsoid is exp$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} The various group parameters have been defined previously (ref 7 and 8). Rings 1 and 2 contain the carbon atoms disordered around atom P(2); see text. Rings 3 and 4 are the phenyl rings.

Chart I. Crystal Data

Formula: C$_{20}$H$_{28}$O$_2$S$_2$P$_2$Rh$_2$
Formula wt: 632.3
Unit cell: monoclinic
  $a = 13.843$ (6) Å
  $b = 16.912$ (8)
  $c = 11.235$ (5)
  $\beta = 96.66$ (7)°
  $V = 2612.5$ Å^3
Space group: $P2_1/c$ from systematic absences
  $0k0, k = 2n + 1$ and $h0l, l = 2n + 1$
$d_x = 1.607$ g cm^{-3}, $z = 4$
$d_o = 1.60$ g cm^{-3} (by flotation in aqueous solution of ZnCl$_2$ at 22° C)
$F(000) = 1264$ e
Radiation: Mo Kα and pyrolytic graphite monochromator
  (λMo K$\alpha = 0.710$ 69 Å)
μ(Mo Kα) = 15.04 cm^{-1}
Crystal shape: parallelepiped with bounding faces of the forms {100}, {010}, and {001}; the distances between the faces of these forms are 0.30, 0.25, and 0.35 mm; The crystal was mounted with 100 approximately along the spindle axis

measured within the interval $2 \leq \theta \leq 25°$. Three check reflections were monitored every 100 reflections and showed no significant changes in intensity.

Data processing was carried out with the MAXE program.[3] Peak counts were corrected for background to yield the net integrated intensity I. The standard deviations of the intensities were calculated according to the formula $\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ where CT is the total integrated peak count obtained during a scan time t_c, B_1 and B_2 are background counts obtained during a time t_b, and $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$. The value of p was selected as 0.02. The values of I and $\sigma(I)$ were next corrected for Lorentz and polarization effects.

No absorption corrections were made because of the relatively low absorption coefficient value: $\mu = 15.04$ cm^{-1} for Mo Kα and $\mu r = 0.45$ for the selected crystal.

Structure Solution and Refinement. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques.[4] The quantity minimized is $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure amplitudes put on the same scale where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = (\sum_w(|F_o| - |F_c|)^2/\sum_w F_o^2)^{1/2}$. Relativistic Hartree–Fock scattering factors were used along with the appropriate anomalous dispersion values.[5]

From the Patterson function, both rhodium and both sulfur atoms as well as one phosphorus atom were located, $R = 0.24$. On subsequent difference Fourier maps, all other atoms but hydrogen and the three carbon atoms of the methyl groups around one phosphorus atom were

Table III. Derived Parameters for the Group Atoms

	x	y	z	β, Å^2
		Group 1		
C(6)	0.3318 (13)	−0.2406 (13)	−0.3721 (14)	8.2 (5)
C(7)	0.4398 (11)	−0.1670 (13)	−0.5366 (18)	6.9 (5)
C(8)	0.2370 (11)	−0.1760 (13)	−0.5836 (16)	8.6 (5)
		Group 2		
C(6)′	0.4167 (14)	−0.2141 (15)	−0.3669 (17)	7.3 (6)
C(7)′	0.3733 (16)	−0.1542 (14)	−0.5993 (17)	10.7 (6)
C(8)′	0.2248 (12)	−0.2159 (15)	−0.4775 (20)	9.8 (6)
		Group 3		
C(11)	0.2806 (4)	0.1702 (2)	−0.3239 (4)	3.6 (1)
C(12)	0.2259 (4)	0.1805 (3)	−0.4348 (4)	4.9 (2)
C(13)	0.2252 (4)	0.2535 (3)	−0.4922 (4)	5.5 (2)
C(14)	0.2791 (4)	0.3161 (3)	−0.4388 (4)	5.6 (2)
C(15)	0.3338 (4)	0.3058 (3)	−0.3279 (4)	5.9 (2)
C(16)	0.3345 (4)	0.2329 (3)	−0.2704 (4)	4.8 (2)
		Group 4		
C(21)	0.3175 (3)	−0.0786 (3)	−0.0737 (3)	3.6 (1)
C(22)	0.4145 (3)	−0.1018 (3)	−0.0665 (4)	4.3 (1)
C(23)	0.4757 (3)	−0.0910 (3)	0.0396 (4)	5.1 (2)
C(24)	0.4399 (3)	−0.0570 (3)	0.1384 (3)	5.0 (2)
C(25)	0.3429 (3)	−0.0338 (3)	0.1312 (4)	5.3 (2)
C(26)	0.2817 (3)	−0.0446 (3)	0.0252 (4)	4.7 (2)

found. A least-squares refinement with all atoms in the structure but the six carbon atoms of the methyl groups bounded to the phosphorus atoms and variable isotropic thermal parameters led to $R = 0.095$. The subsequent difference Fourier sections on two planes, one perpendicular to the Rh(1)–P(1) direction and the other one perpendicular to the Rh(2)–P(2) direction, both 1.56 Å away from the phosphorus atoms,[6] were performed in order to locate the C atoms of the two PMe$_3$ groups. The methyl groups around P(1) are perfectly ordered while those around P(2) are disordered. On the next least-squares refinement, the three carbon atoms of the first group were refined as independant atoms while the carbon atoms of the other group were refined as two independant rigid groups of three idealized atoms (C–C = 2.80 Å)[6] with variable occupancy factors: x and 1 − x. This refinement showed x to be equal to 50% within the related standard deviation. In the last step of refinement, variable anisotropic thermal parameters were used for the nongroup atoms, while both phenyl rings and both sets of methyl groups on P(2) were treated as rigid groups[7,8] with individual isotropic thermal parameters. The values of R and R_w were respectively 0.045 and 0.053.

At this point, 156 variable parameters were refined using 3749 observed reflections (i.e., those having $I > 2\sigma(I)$). A final difference electron density map was qualitatively featureless.

In Table I we present the values of $|F_o|$ and $|F_c|$ for those reflections used in the refinement. In Table II are listed the atomic and group

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min.	Inter	Max.
Rh(1)	0.202 (1)	0.214 (1)	0.241 (1)
Rh(2)	0.198 (2)	0.202 (1)	0.246 (1)
S(1)	0.190 (3)	0.204 (2)	0.241 (2)
S(2)	0.197 (3)	0.205 (3)	0.250 (2)
P(1)	0.207 (3)	0.283 (3)	0.313 (3)
P(2)	0.205 (3)	0.231 (3)	0.308 (3)
C(1)	0.240 (10)	0.265 (11)	0.333 (12)
O(1)	0.218 (10)	0.363 (10)	0.490 (12)
C(2)	0.235 (11)	0.260 (10)	0.293 (11)
O(2)	0.223 (9)	0.334 (9)	0.401 (9)
C(3)	0.229 (14)	0.358 (15)	0.470 (17)
C(4)	0.211 (13)	0.356 (14)	0.444 (15)
C(5)	0.209 (13)	0.329 (13)	0.449 (15)

parameters, together with their standard deviations as derived from the inverse matrix. In Table III we present the positions of the C atoms of the methyl groups and phenyl rings which may be derived from the data of Table II. Table IV lists the root-mean-square amplitudes of vibration for those atoms refined anisotropically.

Description and Discussion of the Structure

The present crystal structure consists of discrete dinuclear units of the formula $[Rh(SC_6H_5)(CO)(P(CH_3)_3)]_2$. The geometry of the asymmetric unit of one molecule, along with the numbering system used elsewhere, is presented in Figure 1. Table V lists most intramolecular bond distances and bond angles of interest. The coordination around each rhodium atom is almost square-planar as predicted[1] by IR and NMR spectroscopy. The dihedral angle between the two square planes of 113.0 (3)° gives a bent configuration to the molecule in which the CO and phosphine ligands are in a cis arrangement. The intramolecular Rh(1)–Rh(2) distance of 3.061 (1) Å suggests a metal–metal interaction while the S(1)–S(2) distance of 3.100 (3) Å may be considered as a nonbonding one for sulfur atoms. The three P–(CH₃) bonds and the Rh–P bond form a distorted tetrahedral geometry about the phosphorus atoms. The phenylthiolato bridging groups are in an anti configuration: the exo position being occupied by the phenyl group which lies between the bulky phosphine ligands while the phenyl group of the second thiolato unit is in the endo position and is perpendicular to the first one. For a cis isomer, such a geometry is that one which would be expected so as to minimize the steric hindrance effects.

In the $[RhCl(CO)_2]_2$ studied by Dahl et al.[9] a bent geometry has been found and, because of intermolecular metal–metal distances of 3.31 Å, these authors claimed that the dihedral angle gave evidence of an octahedral hybridization for the Rh(I) atoms. However, in the di-μ-chloro-bridged rhodium(I) complexes, η-$C_8H_{12}Rh_2Cl_2[P(OPh)_3]_2$[10] and $Rh_2Cl_2(CO)_2$-$(PMe_2Ph)_2$,[2] values of 122.6 (2) and 123.0 (1)° have been found for the dihedral angle, whereas the closest distances of two rhodium atoms belonging to neighboring molecules are equal to 6.4 and 5.3 Å. The present structural determination
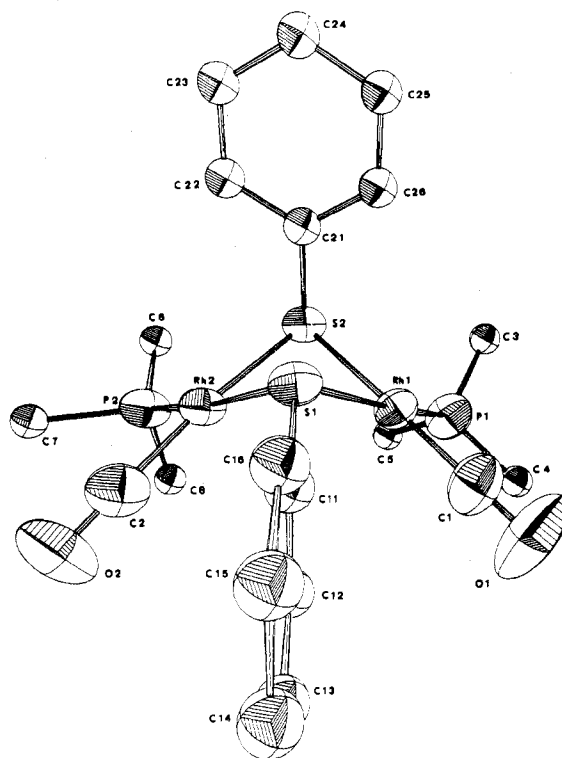

Figure 1. A drawing of the $[Rh(SC_6H_5)(CO)P(CH_3)_3]_2$ molecule with omission of the three other carbon atoms which form a disordered environment around P(2) (see text). The atoms are drawn at their 50% probability ellipsoids except for the carbon atoms of the trimethylphosphine groups which are on an arbitrary scale.

(113.0 (3)° and 6.9 Å) is the third in the field of dinuclear, bridged, rhodium(I) phosphorus ligand-containing complexes and gives thus new evidence that the bent geometry is an intrinsic salient feature for this type of dinuclear molecule.

Table VI shows the values of the dihedral angle CO and the metal–metal distance d_{M-M} in the presently known such complexes. Although few structural data about comparable complexes are now available, it can be concluded that for dinuclear $Rh_2Cl_2L_2L'_2$ derivatives (where L, L' = CO, monodentate olefin or diolefin, tertiary phosphine, or phosphite and L_2 = bidentate diolefin) the double square-planar arrangement is characterized by a hinged geometry with $\omega \simeq 120°$ and $d_{Rh-Rh} \simeq 3.1$ Å (Table VI).

It is of interest also to compare structures **6** and **7**. Indeed these two compounds are identical but for the nature of the bridges. In compound **6** the bridges are chlorine atoms, while in complex **7** they are phenylthiolato groups. Values in Table VI show that the Rh_2S_2 core is significantly more compact than the Rh_2Cl_2 one.

Table V. Selected Bond Distances (Å) and Angles (deg) in $Rh_2(SC_6H_5)_2(CO)_2(P(CH_3)_3)_2$

Rh(1)–C(1)	1.817 (9)	P(1)–C(3)	1.850 (12)	Rh(2)–S(1)	2.379 (2)
Rh(1)–P(1)	2.256 (2)	P(1)–C(5)	1.837 (11)	Rh(2)–S(2)	2.398 (2)
Rh(1)–S(1)	2.372 (2)	S(1)–S(2)	3.100 (3)	C(2)–O(2)	1.152 (10)
Rh(1)–S(2)	2.403 (2)	Rh(2)–C(2)	1.815 (9)	P(1)–C(4)	1.843 (11)
C(1)–O(1)	1.145 (11)	Rh(2)–P(2)	2.257 (2)	Rh(1)–Rh(2)	3.06 (1)
C(1)–Rh(1)–P(1)	92.1 (3)	C(3)–P(1)–Rh(1)	115.7 (4)	Rh(1)–S(2)–Rh(2)	79.2 (1)
C(1)–Rh(1)–S(1)	98.0 (3)	Rh(1)–C(1)–O(1)	179.6 (1.6)	C(5)–P(1)–C(3)	101.5 (7)
C(1)–Rh(1)–S(2)	178.8 (4)	Rh(1)–S(1)–C(11)	114.4 (4)	C(5)–P(1)–C(1)	131.2 (5)
P(1)–Rh(1)–S(1)	169.6 (1)	Rh(1)–S(2)–C(21)	105.7 (4)	C(4)–P(1)–C(1)	117.7 (4)
P(1)–Rh(1)–S(2)	88.8 (1)	C(2)–Rh(2)–P(2)	90.2 (3)	C(3)–P(1)–C(1)	125.7 (5)
S(1)–Rh(1)–S(2)	81.0 (1)	C(2)–Rh(2)–S(1)	97.9 (3)	Rh(2)–C(2)–O(2)	178.5 (9)
Rh(1)–S(1)–Rh(2)	80.2 (1)	C(2)–Rh(2)–S(2)	174.7 (3)	Rh(2)–S(1)–C(11)	114.4 (5)
C(5)–P(1)–C(4)	101.8 (6)	P(2)–Rh(2)–S(1)	171.7 (1)	Rh(2)–S(2)–C(21)	106.3 (4)
C(5)–P(1)–Rh(1)	113.8 (4)	P(2)–Rh(2)–S(2)	91.1 (1)		
C(4)–P(1)–C(3)	104.2 (6)	S(1)–Rh(2)–S(2)	80.9 (1)		

Table VI

Compd	ω, deg	d_{M-M}, Å	Ref
(1) $(RhCl(CO)_2)_2$	124	3.12	9
(2) $(\eta\text{-}1,5\text{-}C_8H_{12}RhCl)_2$	180	3.50	11
(3) $(RhCl(C_2H_4)_2)_2$	115.8	3.02	12
(4) $(RhCl(C_6H_{10})_2)_2$	115.8	3.090	13
(5) $(\eta\text{-}1,5\text{-}C_8H_{12})Rh_2Cl_2(P(OPh)_3)_2$	122.6	3.138	10
(6) $(RhCl(CO)(PMe_2Ph))_2$	123.0	3.167	2
(7) $(Rh(SPh)(CO)(PMe_3))_2$	113.0	3.061	This work
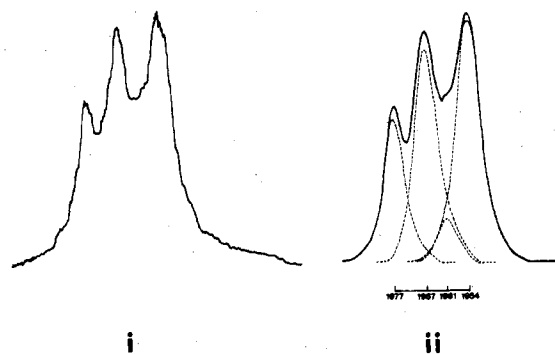
Figure 2. Infrared spectrum of $[Rh(SC_6H_5)(CO)(P(CH_3)_3)]_2$ in the solid state (i); lorentzian components of infrared bands and their envelope (ii).

The two Rh–S bond distances trans to the phosphorus atoms of 2.372 (2) and 2.378 Å compare well with the Pt–S distances trans to the phosphorus atoms of 2.378 (6) and 2.368 (6) Å in $[PtCl(SEt)(PPr_3)]_2$.[14] Similarly the Rh–P bond distances of 2.256 (3) and 2.258 (3) Å are almost the same as the Pt–P bond distances of 2.267 (7) and 2.257 (7) Å in [PtCl(SEt)(PPr_3)]_2 but are longer than those observed of 2.230 (3) and 2.220 (2) Å in compound **5** with bridging chlorine atoms. This lengthening agrees well with the trans influences expected for the various ligands.[15,16] The two Rh–S bond distances trans to the carbonyl groups of 2.403 (2) and 2.398 (2) Å are much longer than those trans to phosphine groups. If we regard S(1) and S(2) as approximately tetrahedrally coordinated with the lone pair as the fourth virtual ligand, then the lone pair S(1) is localized outside the dihedral angle in an exo position while that one of S(2) is localized inside in an endo position. Such a localization for the S(2) lone pair is likely to be involved in the lengthening of the two Rh–S bond distances.

Discussion of the Infrared Spectra.
Isomerization in Solution

Infrared spectra of a single crystal of the present compound exhibit three CO stretching bands as shown in Figure 2. The presence of more CO bands than expected for an isolated molecule necessarily leads to consideration of the contents of the unit cell. The group factor approach has been used. The group factor of the four molecules of the primitive cell is C_{2h}. There is no atom in a special position. The symmetry elements are $2C_2 i$ and $2\sigma_h$ perpendicular to the two C_2 axes. By considering only the internal coordinates of the CO groups, the correlation diagram for the eight CO vectors is the following:

Isolated molecules C_s	Site group C_1	Group factor C_{2h}
$4\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$	8A	2 Ag 2 Bg 2 Au 2 Bu
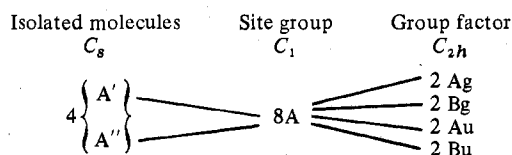
The four Ag and Bg modes are Raman active while the four Au and Bu modes are infrared active. The curve analysis reveals the presence of a fourth weak stretching band (Figure
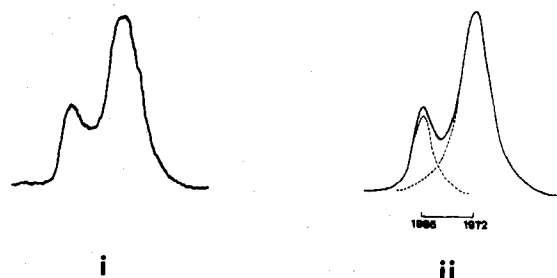

Figure 3. Infrared spectrum of $[Rh(SC_6H_5)(CO)(P(CH_3)_3)]_2$ in cyclohexane solution (i) and the curve analysis (ii).

2). Although the determination of its position is relatively precise, its measured intensity can vary to a slight extent according to the heights taken into account for the most intense peaks. Resolution giving 1977 cm^{-1} (21% of the total intensity), 1967 (33%) 1961 (6%), and 1954 (40%) was retained (Figure 2). Moreover a qualitative prediction of various intensities was attempted. Of the two modes derived from the symetric mode in the isolated molecule (A'), the Au(sym) mode should be of strong intensity whereas the Bu(sym) mode should be of medium intensity. For the two modes derived from the antisymmetric mode (A''), we can expect Au(a) of strong intensity while Bu(a) should be weak. On this basis, the following assignment is proposed: 1967 Au(sym) s; 1977 Bu(sym) s or m; 1954 Au(a) s; 1961 Bu(a) w. The splitting of 13 cm^{-1} between Au modes or 16 cm^{-1} between Bu modes well agrees with the 15 cm^{-1} splitting generally observed in the cis compounds of the *tert*-butylthiolato series analyzed elsewhere and therefore is related with the intramolecular CO–CO interaction constant. However, the 10 and 8 cm^{-1} deviations between Au(sym) and Bu(sym) modes (respectively (sym) and (a)) are related with the interaction constants between the various molecules inside the unit cell. When crystals of the present compound are dissolved in cyclohexane, the infrared spectra exhibit two CO stretching bands at 1985 (22%) and 1972 cm^{-1} (78%) (Figure 3). From the relative intensities of these two modes, it seems quite reasonable to assign, assuming the retention of the dihedral angle ω,[2] a trans geometry to the complex. The presence of the cis isomer has not been detected. When the spectra were recorded in cyclohexane–dichloromethane mixtures as solvents an evolution was observed. However, due to the widening of the bands, the curve analysis was fruitless. Nevertheless, by ^{1}H NMR experiments[1] in dichloromethane solutions, two PMe$_3$ signals were detected (δ –1.58 and –1.29 ppm) in the relative intensities 40/60. All these observations can be rationalized in terms of a solvent-dependent equilibrium between the cis and a trans isomer for the complex $[RhSC_6H_5(CO)(P(CH_3)_3]_2$. This leads, by crystallization at low temperature, to crystals of the cis form.

References and Notes

(1) Part 5: P. Kalck and R. Poilblanc, *Inorg. Chem.*, **14**, 2779 (1975).
(2) J.-J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilblanc, *Inorg. Chem.*, **14**, 743 (1975).
(3) J. Y. Le Marouille, Thèse 3ème Cycle, Rennes, 1972.
(4) In addition to local programs for the CII-IRIS 80, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Johnson's ORTEP II thermal plotting program, Busing and Levy's

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ORFLS program, and Ibers' NUCLS least-squares program.
(5) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. 4, Kynock Press, Birmingham, England, 1973, Table 2.2A.
(6) Geometry deduced from R. L. Kuczkowski and P. S. Bryan, *J. Chem. Phys.*, **55**, 3049 (1971).
(7) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(8) R. Eisenberg and J. A Ibers, *Inorg. Chem.*, **4**, 773 (1965).
(9) L. F. Dahl, C. Martell, and D. J. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
(10) J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).

(11) J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).
(12) K. Klanderman and L. F. Dahl, unpublished results quoted by L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 7292 (1969).
(13) M. G. B. Drew, S. H. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1484 (1973).
(14) M. C. Hall, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc., Dalton Trans.*, 1544 (1972).
(15) F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973).
(16) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

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Synthesis, Properties, and X-Ray Characterization of 3d Metal–Mercapto and –Methylthio Complexes with the Poly(tertiary phosphines) Tris(2-diphenylphosphinoethyl)amine and Tris(2-diphenylphosphinoethyl)phosphine

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By reaction of hydrogen sulfide or methyl mercaptan with iron(II), cobalt(II), and nickel(II) aquo ions in the presence of the poly(tertiary phospine) ligands tris(2-diphenylphosphinoethyl)amine, np_3, and tris(2-diphenylphosphinoethyl)phosphine, pp_3, mercapto and methylthio complexes of the formula $[M(SR)L]BPh_4$ (R = H, CH_3) are formed. They are low spin with a five-coordinate trigonal-bipyramidal stereochemistry. The x-ray structures of the three isomorphous complexes $[Fe(SH)(pp_3)]BPh_4$ (I), $[Co(SCH_3)(np_3)]BPh_4 \cdot (CH_3)_2CO$ (II), and $[Ni(SH)(pp_3)]BPh_4$ (III) are reported. The compounds crystallize in the triclinic $P\bar{1}$ space group, with two molecules per unit cell and with the following lattice constants: (I) a = 18.854 (25) Å, b = 16.467 (17) Å, c = 10.222 (9) Å, α = 94.13 (8)°, β = 95.66 (10)°, γ = 97.67 (11)°; (II) a = 18.626 (13) Å, b = 16.659 (10) Å, c = 10.096 (6) Å, α = 93.53 (5)°, β = 94.68 (6)°, γ = 98.15 (6)°; (III) a = 18.854 (8) Å, b = 16.440 (8) Å, c = 10.204 (4) Å, α = 94.36 (4)°, β = 95.83 (5)°, γ = 98.17 (6)°.

Introduction

As has been recently pointed out,[1] soluble metal complexes containing H_2S, SH^-, and S^{2-} as ligands are very rare, since they tend to revert to binary sulfides, which are the most stable and insoluble compounds.

Only two metal complexes with coordinated H_2S, having formulas $[Ru(NH_3)_5(H_2S)](BF_4)_2$[2] and $W(CO)_5(H_2S)$,[3] have been isolated until now. Few mercapto complexes have been reported, among which are the following 3d metal derivatives: $Mn_2(SH)_2(CO)_8$, $Ni(SH)(C_5H_5)(P(C_4H_9)_3)$, and $[Cr(S-H)(H_2O)_5]SO_4$.[4] The numerous compounds containing the S^{2-} ligand are generally polymeric. Only few examples of thio complexes of the types L_nM—S—ML_n and L_nM=S are known in transition metal chemistry[1] among which the nickel(II) complex with formula $[(p_3)Ni$—S—$Ni(p_3)](BPh_4)_2$,[5] where p_3 is the ligand 1,1,1-tris(diphenylphosphinomethyl)-ethane, constitutes the first example of a diamagnetic nickel(II) compound with a tetrahedral coordination.

The stability of these sulfur–metal complexes is certainly strongly influenced by the steric requirements of the ligands and by the nature of the donor atoms. They should be able to engage all of the metal orbitals in covalent σ and π bonds, thus preventing the formation of extra metal–sulfur and metal–metal bonds which in turn would lead to the formation of polymeric insoluble metal sulfides.

We have found that salts of divalent 3d metals like iron, cobalt, and nickel react with hydrogen sulfide in the presence of the potentially tetradentate tripod ligands tris(2-di-phenylphosphinoethyl)phosphine, pp_3, or tris(2-diphenyl-phosphinoethyl)amine, np_3, forming stable monomeric mer-capto complexes with the general formula $[M(SH)L]BPh_4$ (L = pp_3, M = Fe, Co, Ni; L = np_3, M = Co, Ni). The analogous methylthio complexes $[M(SCH_3)L]BPh_4$ have been obtained using CH_3SH as a reactant, in place of H_2S.

All complexes have been characterized by appropriate physical methods. The x-ray structures of the complexes $[M(SH)(pp_3)]BPh_4$ (M = Fe, Ni) and $[Co(SCH_3)(np_3)]$-$BPh_4 \cdot (CH_3)_2CO$ have been determined.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand np_3 was prepared by the method previously described.[6] The ligand pp_3 was purchased from the Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification.

Preparation of the Complexes. All reactions were carried out at room temperature under dry nitrogen atmosphere using deoxygenated solvents.

All of the compounds reported in Table I were prepared by the following procedure. The ligand (1 mmol) in 10 mL of acetone (or of DMF) was added at ambient temperature to a solution of the metal(II) tetrafluoroborate hexahydrate (1 mmol) in 30 mL of ethanol. Hydrogen sulfide (or methyl mercaptan) was bubbled into this solution until a definite, generally sudden, change of color took place. Addition of 1 mmol of sodium tetraphenylborate, dissolved in 10 mL of ethanol, led to precipitation of crystals which were filtered off, washed with ethanol first and then with petroleum ether, and were finally dried in a current of nitrogen.

Attempts to prepare the np_3 iron derivatives by the above procedure failed, as precipitation of the metal sulfide took place.

The analytical data for the complexes are listed in Table I.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of the UV–visible spectra have been described previously.[7]

Collection and Reduction of X-Ray Intensity Data. Data were collected following essentially the same procedure for the complexes $[Fe(SH)(pp_3)]BPh_4$ (I), $[Co(SCH_3)(np_3)]BPh_4 \cdot (CH_3)_2CO$ (II), and $[Ni(SH)(pp_3)]BPh_4$ (III). The analogous mercaptocobalt complex could not be investigated because suitable crystals were not obtained. Details of crystal data and intensity collection are reported in Table II. The three compounds are isomorphous to each other and belong to the triclinic system; the centric space group $P\bar{1}$ was initially assumed