pulsion between the fluorine free valence electrons and the *two* sterically active free electron pairs on the N_α atom (indicated by broken lines in IV). In contrast to CF_3N_3, the CH_3 group in CH_3N_3 appears to be in an intermediate position between eclipsed and staggered,[7b] (25 ± 7° from the eclipsed position), which may be explained in the following manner: resonance structure II should result in a staggered configuration (V) and resonance structure III in an eclipsed (VI) configuration. Since, as discussed above, the bond lengths indicate that structure II contributes more strongly to the structure of CH_3N_3 than to that of CF_3N_3, the observation of an intermediate torsional angle is not surprising.

Linearity of the N_3 Group and CF_3 Tilt Angle. In CF_3N_3 the N_3 group is slightly (10°) bent away from the CF_3 group, and the CF_3 group is tilted away from the N_3 group by 5.8°. This is readily explained by the repulsion between the fluorine free valence electron pairs and the π-bond electron system of the N_3 group. A comparison of these values with those in CH_3N_3 would be most interesting, but unfortunately no experimental values are presently available for CH_3N_3. It is interesting to note that the angles of the N_3 group found for HN_3, ClN_3, NCN_3, and CF_3N_3 are all very similar. However, it should be kept in mind that most of these values carry rather large uncertainties.

Torsional Effects on the Structure. The present data for the excited torsional states do not allow a determination of the structural changes upon excitation of ν_{15}. It is clear from model calculations, however, that several parameters must change their value in order to reproduce the rotational constants of the excited states. Thus heavy relaxation, not only in the trifluoromethyl group but also in the tilt and the $CN_\alpha N_\beta$ angle, is assumed to take place.

Acknowledgment. We are grateful to Dr. G. Pawelke for providing a sample of CF_3N_3 for the RFMWDR measurements. D.C. and H.O. acknowledge financial support by the Fonds der Chemie. K.O.C. and C.J.S. thank the Office of Naval Research and the U.S. Army Research Office for financial support.

Registry No. CF_3N_3, 3802-95-7.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera distances (50 and 25 cm) for two sets of plates (2 pages). Ordering information is given on any current masthead page.

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Rhodium(I) Carbonyl Complexes of (Diphenylphosphino)acetic Acid

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Received March 6, 1984

Rhodium(I) and (diphenylphosphino)acetic acid (HA) form trans square-planar complexes $Rh(CO)X(HA)_2$ (X = Cl, Br, I) and Rh(CO)A(HA), in which HA acts as a P-monodentate ligand and A^- as a P,O-chelating ligand. All the complexes are fairly reactive and readily undergo oxidative-addition reactions. In the solid state, the latter complex forms several crystalline modifications. The X-ray crystal structure determination of α-carbonyl((diphenylphosphino)acetato-*P*,*O*)((diphenylphosphino)acetic acid-*P*)rhodium(I), α-Rh(CO)A(HA), demonstrated a distorted square-planar arrangement around rhodium with Rh–C = 1.773 (11) Å, Rh–P(monodentate) = 2.346 (2) Å, Rh–P(chelating) = 2.302 (2) Å, Rh–O = 2.064 (6) Å, and P–Rh–P = 170.8 (1)°. The distortion due to the chelating A^- anion renders the carbon monoxide sterically more accessible than in complexes of monodentate phosphines. There is a short Rh–H interaction of 2.80 (7) Å with a phenyl ortho hydrogen atom of the HA ligand, which forces the rhodium atom 0.03 Å out of the plane of the donor atoms. Two formula units of the complex are hydrogen bonded, forming a centrosymmetrical dimer. The complex crystallizes in space group $P\bar{1}$ with $a = 9.783$ (4) Å, $b = 11.702$ (6) Å, $c = 13.120$ (6) Å, $\alpha = 76.87$ (4)°, $\beta = 81.21$ (4)°, $\gamma = 71.77$ (4)°, and $Z = 2$. The structure was refined anisotropically to $R = 0.053$ on the basis of 2367 unique reflections.

Introduction

The investigation of functionalized phosphines has recently received a great deal of attention[2] for both theoretical and practical reasons. The unusual combination of hard and soft donor atoms in these ligands leads to interesting structural types and/or reactivity of the complexes, which is potentially useful, e.g. in homogeneous catalysis. In our laboratory, phosphinoacetic acids of the types $(C_6H_5)_{3-n}P(CH_2CO_2H)_n$, $n = 1$–3, and $(C_6H_5)_{2-m}(HO_2CCH_2)_mPCH_2CH_2P(C_6H_5)_{2-m}(CH_2CO_2H)_m$, $m = 1, 2$, were synthesized and their complexes with a number of metal ions were studied.[3] Depending on the metal ion, acidity, and solvent, the ligands are capable of coordinating as P–, O–, PP–, PO–, and POO– donors. This work deals with rhodium(I) carbonyl complexes of (diphenylphosphino)acetic acid.

Experimental Section

Materials. The synthesis of HA has been described.[4] The $[Rh(CO)_2Cl]_2$ complex was prepared[5] from hydrated rhodium trichloride (Safina). Known methods were employed for the preparation of $[Rh(CO)_2X]_2$ (X = Br, I;[6] SCN, NO_3, CH_3CO_2, $^1/_2\,SO_4$;[7] N_3, NCO[8]) and for $Rh(CO)_2acac$.[9] Other chemicals were of CP grade and were purified by using standard methods where necessary.

Methods. The preparative work and manipulations with solutions were carried out under nitrogen. IR spectra were measured in solution

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and in Nujol mulls on Perkin-Elmer 580 and 684 and UR-20 (Zeiss) instruments. For NMR spectra, Tesla BS 487A (^{1}H, 80 MHz) and Varian XL 200 (^{31}P, 80.89 MHz) instruments were used. Shifts in ppm (downfield positive) are referenced to internal Me_4Si and external 85% H_3PO_4, respectively. X-ray powder patterns were taken on a Mikrometa (Chirana) instrument equipped with a copper source, a nickel filter, and photographic recording. Oxidative-addition reactions were monitored as changes in the ν(C≡O) region of the IR spectra in chloroform and acetone solutions. The reversible formation of SO_2 adducts followed from changes of the weight and of IR spectra of finely divided powders exposed to gaseous SO_2 at various partial pressures.

Synthesis of the Complexes. Rh(CO)X(HA)$_2$ (X = Cl, Br, I). At 50 °C, 6 mmol of HA in 10 mL of benzene was added to 1 mmol of $[Rh(CO)_2X]_2$ (X = Cl, Br, I) in 20 mL of benzene (for X = I, 7 mL). The solution was refluxed until crystallization of the product commenced, and the mixture was then allowed to cool to room temperature. The crystals (yield ca. 90%) were filtered off, washed with benzene, and dried at 110 °C (0.2 kPa) (valid for all subsequent complexes). For X = SCN, NO_3, CH_3CO_2, $^1/_2$ SO_4, N_3, and NCO the complexes could not be obtained because of successive reactions.

α-Rh(CO)A(HA). To 1 mmol of Rh(CO)$_2$acac in 25 mL of diethyl ether, was added a solution of 2.5 mmol of HA in ether dropwise with stirring. After the mixture was allowed to stand for 1 h, the product was filtered off, washed with 10 mL of ether, and recrystallized from 100 mL of boiling ethyl acetate in 93% total yield.

β-Rh(CO)A(HA). A 1-mmol sample of α-Rh(CO)A(HA) was dissolved with heating in 35 mL of 70% aqueous acetone (v/v). The filtered solution (it is necessary to remove all particles of the α-modification) was vacuum evaporated to ca. 20 mL until the product suddenly crystallized. After washing with a little 70% acetone, the product was recrystallized from 70% acetone by evaporation and seeding with a crystal of the crude product. The choice of the correct seeding crystal of the β-modification is a matter of chance but can be facilitated by microscopic examination of the crystal habit. Yield: 90%.

γ-Rh(CO)A(HA). A 1-mmol sample of α-Rh(CO)A(HA) was dissolved in 70 mL of warm acetone; the solution was filtered, cooled to 10 °C, and mixed with 10 mL of toluene. After vacuum evaporation of the solution at 10 °C to ca. 10 mL, the resulting crystalline product was filtered off and washed with 5 mL of acetone. Yield: 94%.

Rh(CO)A(HA)·s (s = Benzene, Dioxane). A 1-mmol sample of α-Rh(CO)A(HA) was refluxed for 15 min with 20 mL of benzene (8 mL of dioxane). The cooled suspension was filtered and the solid washed with a little benzene (with ethyl acetate for the dioxane solvate). Yield: 96% and 75%, respectively.

All the complexes gave correct analyses for Rh, P, C, H, H$^+$, and X. See supplementary material for analytical data.

Crystal Structure Determination and Refinement. Single crystals of α-Rh(CO)A(HA) were obtained by slow cooling of the saturated solution in hot 90% aqueous acetone. The crystal data are summarized in Table I. The techniques used for data collection on a Syntex P2$_1$ diffractometer, for data reduction, and for solution and refinement of the structure were the same as described previously.[10] Final atomic coordinates and important distances and angles are given in Tables II and III. Tables of observed and calculated structure factors, anisotropic thermal parameters, and further distances, angles, and planes are available as supplementary material.

Results and Discussion

The syntheses of the complexes employ well-known procedures but are critically dependent on the experimental conditions. The solid complexes are pale yellow to orange, crystalline, air-stable substances. On being heated in the air, they begin to decompose at about 170 °C without melting. Desolvation of benzene and dioxane was not observed even at 110 °C (0.2 kPa). Similar to other rhodium(I) compounds,[11] the solid complexes react with sulfur dioxide, forming reversible adducts, the composition of which depends on the temperature and partial pressure of the gas. The X-ray powder diagrams indicate that the Rh(CO)X(HA)$_2$ complexes are isostructural. On the other hand, the various forms of Rh(CO)A(HA) yield distinctly different powder patterns.

Table I. Summary of Crystal Data and Intensity Collection[a]

compd	$Rh(CO)(Ph_2PCH_2CO_2)(Ph_2PCH_2CO_2H)$
formula	$C_{29}H_{25}O_5P_2Rh$; M_r 618.37
cryst dimens	0.15 × 0.20 × 0.20 mm^3
cell params	$a = 9.783$ (4) Å, $b = 11.702$ (6) Å, $c = 13.120$ (6) Å, $V = 1384$ (1) Å^3, $\alpha = 78.67$ (4)°, $\beta = 81.21$ (4)°, $\gamma = 71.77$ (4)°, $Z = 2$, $d_{calcd} = 1.483$, $d_{obsd} = 1.494$ (2) g cm^{-3}, space group $P\bar{1}$, temp 20 °C
radiation	Mo Kα ($\lambda = 0.7107$ Å), graphite monochromated
scan mode	θ–2θ, with scan speed 1.5–29.30° min^{-1} and 2θ range 0–45°
data collcd	$h \in \langle -9,10 \rangle$; $k \in \langle 0,12 \rangle$; $l \in \langle -13,13 \rangle$
stds	3 every 47 reflcns; no significant intensity variation obsd
abs coeff	7.60 cm^{-1}; no cor for abs; abs factor constant in the whole range of θ
no. of reflcns measd	3622
no. of data used ($I \geqslant 1.96\sigma_1(I)$)	2367
max height in final diff map	0.43 e Å^{-3}
function minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
R, R_w	0.053, 0.054
w^b	$1/\sigma^2(F_o)$

[a] Cell parameters were derived from a least-squares fit of 20 reflections with $\theta = 5$–11°. Full-matrix least-squares refinement was done in two blocks. Anomalous scattering factors of Rh and P were taken from ref 20. [b] Derived from $\sigma(F_o)/F_o = {}^1/_2[\sigma_2(I)/I]$, $\sigma_2(I) = [\sigma_1{}^2(I) + (0.04I)^2]^{1/2}$.

In solution, the complexes are fairly reactive and readily undergo oxidative-addition reactions with molecules such as halogenated hydrocarbons, halogens, chlorosulfonyl compounds, and tetracyanoethylene, yielding rhodium(III) complexes. The oxidative addition is followed by chelation of the A$^-$ ligand, mostly resulting in an inseparable mixture of products, including various geometrical isomers.

In general, the complexes are characterized by the lack of solubility in noncoordinating solvents, apparently as a result of intermolecular hydrogen bonding through the carboxyl group of the ligand. On the other hand, in solvents of higher polarity that are capable of breaking the hydrogen bonds, traces of water present cause the elimination of HX, producing Rh(CO)A(HA) with an increasing tendency from X = Cl to I. All measurements in solution therefore required careful (and in some cases compromising) choice of solvent.

The properties of the complexes are summarized as supplementary material. They are consistent with a square-planar Rh(I) core with trans phosphine ligands: ν(C≡O), δ_h(C≡O), and δ_v(C≡O) in the IR spectra at 1963–1980, 542–554, and 555–572 cm^{-1}, respectively,[12] the apparent triplet of the methylene protons at 3.02–3.63 ppm ($J \approx 4$ Hz) in the ^{1}H NMR spectra,[13] and ^1J(Rh,P) values of 126.9–129.1 Hz in the ^{31}P NMR spectra.[14,15] The ν(C═O) and ν_{as}(OCO) bands in the IR spectra are indicative of free CO_2H (ca. 1340 and ca. 1710 cm^{-1}) and chelating PCH_2CO_2 groups (1268 and ca. 1590 cm^{-1}).

The polarity of the solvent seems to be the main factor controlling the formation of the various modifications of Rh-

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Table II. Atomic Coordinates (for non-H, $\times 10^4$; for H, $\times 10^3$)[a]

atom	x	y	z	$(U_{eq}$ or $U)$, Å^2
Rh	185.6 (8)	4058.7 (7)	2887.7 (6)	0.0336 (3)
P1	−1731 (2)	5740 (2)	3145 (2)	0.0346 (9)
P2	1947 (2)	2169 (2)	2845 (2)	0.0358 (9)
O1	−818 (6)	3263 (5)	4238 (5)	0.047 (3)
O2	−2699 (6)	3355 (5)	5426 (5)	0.049 (3)
O3	1640 (7)	−932 (6)	4427 (6)	0.064 (4)
O4	3794 (7)	−626 (6)	3939 (7)	0.078 (4)
O5	1404 (8)	5297 (7)	910 (6)	0.077 (4)
C1	−2260 (11)	5258 (8)	4527 (7)	0.043 (4)
C2	−1920 (9)	3874 (8)	4753 (7)	0.041 (4)
C3	−1562 (9)	7264 (7)	3021 (6)	0.036 (4)
C4	−2788 (10)	8251 (8)	3175 (8)	0.047 (4)
C5	−2655 (12)	9405 (9)	3114 (9)	0.058 (5)
C6	−1309 (14)	9594 (10)	2881 (9)	0.065 (5)
C7	−101 (12)	8650 (11)	2710 (9)	0.066 (5)
C8	−216 (10)	7478 (9)	2794 (8)	0.052 (5)
C9	−3252 (8)	5926 (7)	2422 (6)	0.034 (4)
C10	−4656 (10)	6138 (11)	2884 (8)	0.060 (5)
C11	−5790 (11)	6251 (13)	2297 (9)	0.078 (6)
C12	−5515 (11)	6165 (11)	1273 (10)	0.065 (5)
C13	−4122 (13)	5897 (10)	804 (8)	0.062 (5)
C14	−3012 (11)	5792 (9)	1387 (8)	0.050 (4)
C15	1648 (11)	1091 (8)	4050 (8)	0.047 (4)
C16	2517 (10)	−244 (8)	4112 (7)	0.040 (4)
C17	1953 (9)	1464 (8)	1754 (7)	0.041 (4)
C18	811 (13)	1979 (11)	1095 (10)	0.067 (5)
C19	813 (18)	1458 (16)	237 (12)	0.098 (9)
C20	1891 (21)	461 (16)	11 (13)	0.108 (10)
C21	3014 (17)	−88 (12)	677 (13)	0.088 (8)
C22	3057 (12)	427 (10)	1516 (9)	0.061 (5)
C23	3779 (9)	2274 (7)	2802 (7)	0.038 (4)
C24	4266 (11)	2371 (9)	3707 (9)	0.058 (5)
C25	5563 (14)	2614 (10)	3663 (11)	0.071 (6)
C26	6385 (12)	2752 (10)	2726 (14)	0.071 (6)
C27	5963 (13)	2636 (11)	1815 (12)	0.082 (6)
C28	4618 (11)	2408 (10)	1864 (9)	0.057 (5)
C29	942 (10)	4797 (8)	1704 (9)	0.051 (5)
H1A	−316 (10)	566 (9)	479 (7)	0.038
H1B	−160 (10)	552 (8)	494 (7)	0.038
H4	−369 (10)	809 (9)	336 (8)	0.048
H5	−354 (11)	1006 (10)	330 (8)	0.057
H6	−128 (11)	1039 (10)	295 (8)	0.063
H7	79 (12)	882 (10)	250 (9)	0.067
H8	64 (11)	676 (9)	279 (8)	0.057
H10	−486 (11)	620 (9)	361 (8)	0.057
H11	−672 (12)	653 (11)	267 (9)	0.080
H12	−620 (12)	606 (10)	96 (9)	0.065
H13	−399 (11)	588 (10)	−0 (9)	0.071
H14	−207 (11)	564 (9)	106 (8)	0.049
H15A	58 (10)	126 (9)	419 (8)	0.049
H15B	188 (11)	143 (9)	460 (8)	0.049
H18	6 (12)	275 (11)	138 (9)	0.077
H19	14 (16)	188 (14)	−9 (12)	0.098
H20	178 (14)	11 (12)	−56 (11)	0.098
H21	366 (14)	−69 (12)	52 (11)	0.086
H22	370 (11)	0 (10)	200 (9)	0.061
H24	371 (12)	222 (10)	430 (9)	0.060
H25	596 (12)	269 (10)	423 (9)	0.070
H26	710 (13)	290 (11)	279 (10)	0.067
H27	644 (12)	291 (10)	114 (9)	0.073
H28	431 (12)	243 (10)	125 (8)	0.060
H(O3)	196 (12)	−169 (10)	443 (9)	0.062

[a] U_{eq} corresponds to non-hydrogen atoms; U, to hydrogen atoms. $U_{eq} = {}^1/_3[U_{11} + U_{22} + U_{33} + 2(U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)]$.

Table III. Important Bond Distances (Å) and Angles (deg)[a]

Rh–P1	2.302 (2)	P1–Rh–O1	81.4 (2)
Rh–P2	2.346 (2)	P1–Rh–C29	95.7 (3)
Rh–O1	2.064 (6)	P1–Rh–P2	170.8 (1)
Rh–C29	1.773 (11)	P2–Rh–O1	89.5 (2)
Rh–H18	2.80 (7)	P2–Rh–C29	93.4 (3)
P1–C1	1.818 (9)	O1–Rh–C29	176.5 (4)
P1–C3	1.811 (8)	C1–P1–C3	105.7 (4)
P1–C9	1.816 (9)	C1–P1–C9	107.1 (4)
P2–C15	1.833 (10)	C3–P1–C9	105.9 (4)
P2–C17	1.806 (9)	C15–P2–C17	107.1 (4)
P2–C23	1.826 (10)	C15–P2–C23	107.2 (4)
C29–O5	1.174 (14)	C17–P2–C23	105.7 (4)
C2–C1	1.515 (13)	Rh–C29–O5	178.2 (7)
C2–O1	1.282 (11)	O1–C2–O2	121.7 (7)
C2–O2	1.253 (11)	O3–C16–O4	124.7 (8)
C16–C15	1.518 (13)	O3–H(O3)–O2^i	174 (8)
C16–O3	1.317 (12)		
C16–O4	1.190 (13)		
O3–H(O3)	0.86 (11)		
O3–O2^i	2.669 (9)		

[a] Symmetry code: (i) $-x, -y, 1 - z$.

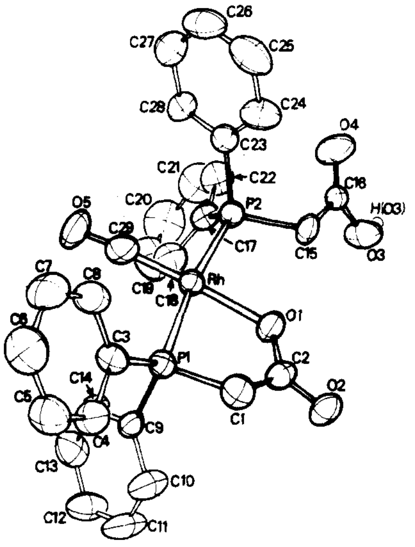

Figure 1. ORTEP drawing of the structure of α-Rh(CO)A(HA). Hydrogen atoms (omitted for clarity) are given the numbers of their bonding partners.

(CO)A(HA). The individual forms including the solvates, however, give identical solution spectra after prolonged standing (the UV spectra are featureless). The differences must therefore be inherent in the crystal structures.

The structure of α-Rh(CO)A(HA) is depicted in Figure 1. The set of four donor atoms is planar but distorted significantly from the square, due mainly to chelate bonding of the A$^-$ ligand. The rhodium atom is located 0.03 Å under the plane (viewed as in Figure 1) because of interaction with the phenyl ortho hydrogen H18 of the HA ligand. The Rh–H18 distance of 2.80 (7) Å and the geometry of the P1P2RhH18 moiety are normal for this structural type[16] and indicate that the complex cannot be considered as square pyramidal as the angles involving H18 are far from ideal (H18RhP2 = 63° etc.). Further comparisons with known structures of (diphenylphosphino)acetates and of other related compounds are presented as supplementary material. The geometry of the monodentate and chelating ligand remains essentially unchanged in the series involving complexes of Pd, Pt, and Rh. As a consequence of the distortion due to the chelate ring, however, the carbon monoxide becomes sterically more accessible in this complex than in complexes of monodenate phosphines, which should play a role in the reactivity of the complex. The phosphine ligands are otherwise fairly normal with respet both to the overall geometry and to the distance and angles of the carboxyl groups[17] in particular. The mutual conformation of the phosphines with respect to the P1P2 axis is nearly eclipsed, the corresponding CPPC torsional angles being less than 20°. The hydrogen-bonding mode, however,

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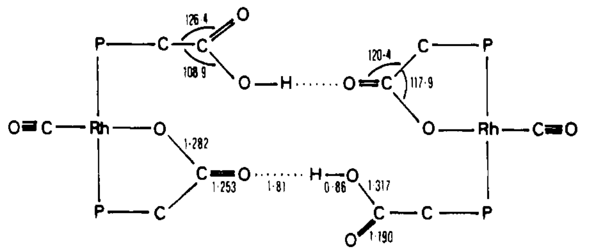
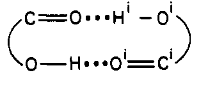


Figure 2. Hydrogen bonding in α-Rh(CO)A(HA).

is unique for the complex studied. By means of two intermolecular hydrogen bonds, the crystal structure consists of centrosymmetrical dimers (Figure 2), which are packed in the structure at van der Waals distances without any further significant intermolecular interaction. The central moiety of the double hydrogen bridge



comprises a plane within ±0.04 Å, which intersects the planes involving Rh and Rh^i at angles of ±20°. Hence, the whole dimer possesses a "chair" arrangement consisting of three planes, which contain Rh, the inversion center, and Rh^i. As a result, the RhA chelate ring adopts the δ-envelope conformation, which minimizes the strain involved between the planes.

The structures of the other modifications and solvates of the Rh(CO)A(HA) complex remain elusive, partly because they were not obtained as single crystals suitable for X-ray analysis. The ν(C═O) and δ(C═O) bands safely indicate that the Rh(I) core remains intact, and therefore the differences probably involve more subtle changes, e.g., in the hydrogen bonding, relative conformation of the trans phosphine ligands, packing of the phenyl rings, or ortho hydrogen–metal interaction. This situation seems to occur frequently in rhodium(I) phosphine complexes.[16,18,19] The various forms of the complex yield different patterns for the carboxyl region in the IR spectra, which might be taken as evidence that differences in hydrogen bonding are the main reason for the existence of the modifications. In the absence of firmer evidence, however, these changes cannot be safely correlated to any distinct structure.

Registry No. Rh(CO)Cl(HA)$_2$, 92763-41-2; Rh(CO)Br(HA)$_2$, 92763-42-3; Rh(CO)I(HA)$_2$, 92763-43-4; α-Rh(CO)A(HA), 92763-44-5; [Rh(CO)$_2$Cl]$_2$, 14523-22-9; [Rh(CO)$_2$Br]$_2$, 21475-96-7; [Rh(CO)$_2$I]$_2$, 21475-95-6; Rh(CO)$_2$acac, 14874-82-9.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters of non-hydrogen atoms, distances and angles in phenyl rings, least-squares planes and deviations of atoms therefrom, analytical data, and properties of the complexes and a table comparing important distances and angles of α-Rh(CO)A(HA) with those of related complexes (27 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Magnetic Properties of (μ-Terephthalato)bis[(*N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine)aquocopper(II)] Perchlorate and (μ-Terephthalato)bis[(*N*,*N*,*N'*,*N''*,*N''*-pentaethyldiethylenetriamine)copper(II)] Perchlorate

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Received March 6, 1984

The two title compounds of formula [[Cu(pmedien)(H$_2$O)]$_2$tp](ClO$_4$)$_2$ (**1**) and [(Cu(petdien))$_2$tp](ClO$_4$)$_2$·H$_2$O (**2**) with pmedien = *N,N,N',N'',N''*-pentamethyldiethylenetriamine, petdien = *N,N,N',N'',N''*-pentaethyldiethylenetriamine, and tp = terephthalato have been synthesized and their structures solved at room temperature. **1** crystallizes in the monoclinic system, space group $P2_1/c$: $a = 8.42$ (5) Å, $b = 14.40$ (4) Å, $c = 15.99$ (5) Å, $\beta = 100.65$ (10)°, $Z = 4$. **2** crystallizes in the orthorhombic system, space group *Pbca*: $a = 28.48$ (1) Å, $b = 26.363$ (2) Å, $c = 12.591$ (5) Å, $Z = 8$. The structures of **1** and **2** consist of μ-terephthalato-bridged copper(II) binuclear complexes and noncoordinated perchlorate anions. In **1**, tp bridges in a bis monodentate fashion, and in **2**, in a bis bidentate fashion. In both compounds, the environment of the metal ions is intermediate between the square-based pyramid and the trigonal bipyramid, the trigonal-bipyramid character being more pronounced in **2**. The magnetic properties of **1**, **2**, and [[Cu(dien)(H$_2$O)]$_2$tp](ClO$_4$)$_2$ (**3**) have been investigated in the 4.2–300 K temperature range. The decrease of the product $\chi_M T$ of the molar magnetic susceptibility and the temperature upon cooling from 30 to 4.2 K in **1** and **3** is attributed to intermolecular interactions that vary according to **3** (dien) > **1** (pmedien) > **2** (petdien). The EPR spectra do not exhibit any evidence of triplet state. The unfavorable character of the terephthalato bridge to transmit the electronic effects over long distances is discussed.

Introduction

In the last few years, it has been shown that two paramagnetic centers could interact through extended bridging ligands, even if these centers were relatively far away from each other.[2] Restricting ourselves to copper(II) bimetallic complexes with a copper–copper separation larger than 5 Å, we can mention the end-to-end bis(μ-azido),[3] the μ-oxalato,[4–6]

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