orange-red solid which was sublimed at 50 °C under high vacuum (10^{-4} mmHg) to a dry ice–acetone-cooled probe. At −80 °C the sublimate is yellow but upon warming to room temperature changes to orange (1.25 g, 93%). As with **2**, **12** is best stored at −30 °C under N_2.

[η^3-(1-Me-C_3H_4)Rh(dmpe)] (13). This was prepared by the identical procedure used for **4**. Isolation via sublimation at 50 °C under high vacuum (10^{-4} mmHg) to a dry ice–acetone-cooled probe gave a yellow solid, which upon warming to room temperature turned to an orange oil and solidified. The yield was 92%.

[η^3-(1-Me-C_3H_4)Rh(dptpe)] (14). This was synthesized by the procedure outlined for **7** in 82% yield as bright yellow microcrystals.

[η^3-(1-Me-C_3H_4)Rh(dppp)] (15). This was synthesized by the procedure outlined for **6** to give **15** as an orange-yellow waxy solid in 70% yield. An analytical sample was obtained by recrystallization from hexane at low temperatures.

[η^3-(1-Me-C_3H_4)Rh(chiraphos)] (16). This was synthesized by the procedure outlined for **7** in 75% yield as a yellow-orange powder, mp 179–181 °C dec (darkened at 130 °C).

[η^3-(1-Me-C_3H_4)Rh(dmope)] (17). This was synthesized by the procedure outlined for **11** to give **17** as a yellow waxy solid.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada, by the Research Corp., and by the UBC Department of Chemistry. We thank Johnson-Matthey for a generous loan of hydrated rhodium trichloride.

Registry No. **2**, 81177-96-0; **4**, 81177-97-1; **5**, 81177-98-2; **6**, 81177-99-3; **7**, 81178-00-9; **8**, 81178-01-0; **9**, 81178-02-1; **10**, 81178-03-2; **11**, 80105-91-5; *syn*-**12**, 70428-75-0; *syn*-**13**, 81178-04-3; *anti*-**13**, 81204-42-4; *syn*-**14**, 81178-05-4; *anti*-**14**, 81204-43-5; *syn*-**15**, 81178-06-5; *anti*-**15**, 81204-44-6; *syn*-**16**, 81178-07-6; *anti*-**16**, 81244-78-2; *syn*-**17**, 81178-08-7; *anti*-**17**, 81204-45-7; [(COD)RhCl]$_2$, 12092-47-6; 2-methylallyl chloride, 563-47-3; 3-butenyl bromide, 5162-44-7.

Contribution from the Chemistry Division of the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, and the Departments of Chemistry, Carleton College, Northfield, Minnesota 55057, and University of Georgia, Athens, Georgia 30602

Poly(tertiary phosphines and arsines). 18. Preparation and Structure of bis{μ-[(methylamino)bis(dimethoxyphosphine)]}-bis(dicarbonylcobalt), a Binuclear Complex with Approximate Square-Pyramidal and Trigonal-Bipyramidal Coordination of Cobalt Atoms in the Same Molecule[1]

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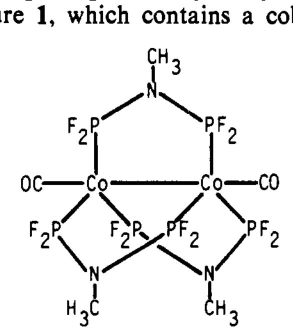
Received November 10, 1981

The ligand $CH_3N[P(OCH_3)_2]_2$ reacts readily with $Co_2(CO)_8$ to form the violet-brown complex $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. A single-crystal X-ray diffraction study of this complex shows a structure with a cobalt–cobalt bond 2.698 (1) Å long bridged by two $CH_3N[P(OCH_3)_2]_2$ ligands. The two cobalt atoms are both five-coordinate and have identical sets of ligands, each of the two being bonded to the other cobalt atom, to two carbonyl groups, and to two trivalent phosphorus donors. However, the two cobalt atoms are not equivalent; one has trigonal-bipyramidal coordination and the other has square-pyramidal coordination. The trigonal-bipyramidal cobalt atom has the other cobalt atom and a carbonyl group in the axial positions. The square-pyramidal cobalt atom has a carbonyl group in the apical position. The difference in coordination of the two cobalt atoms probably results from the packing of a fluxional molecule which has a symmetrical average structure in solution. Although the ν(CO) frequencies in the infrared spectrum in solution all appear in the terminal region, the complex in the crystal contains a carbonyl group in a borderline semibridging position with Co–C distances of 1.756 (7) and 2.812 (7) Å, probably as the result of the crystal packing. The atoms of the $Co_2(CO)_4$ unit in the complex are essentially coplanar, and the least-squares best plane through these atoms is an approximate mirror plane for the molecule.

Introduction

The reaction of the small-bite bidentate fluorophosphine $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ gives the binuclear derivative $[CH_3N(PF_2)_2]_3Co_2(CO)_2$, shown by X-ray diffraction analysis to have structure **1**, which contains a cobalt–cobalt bond



1

bridged by three $CH_3N(PF_2)_2$ ligands.[3,4] The $[CH_3N(PF_2)_2]_3Co_2$ structural unit in this complex is chemically very stable; it is retained not only upon substitution of terminal carbonyl groups with Lewis base ligands (phosphines, phosphites, isocyanides, etc.[4]) but also upon reduction to give the radical anion and dianion[5] and upon bromination to give the tetrabromide $[CH_3N(PF_2)_2]_3Co_2Br_4$.[6]

These observations on $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ stimulate interest in the cobalt carbonyl derivatives of other small-bite bidentate trivalent phosphorus ligands of the general type $RN(PX_2)_2$. This paper describes the preparation and the X-ray crystal-structure analysis of bis{μ-[(methylamino)bis(dimethoxyphosphine)]}-bis(dicarbonylcobalt), a binuclear cobalt carbonyl complex containing the ligand $CH_3N[P(OCH_3)_2]_2$.

(1) For part 17 of this series see: King, R. B.; Bakos, J.; Hoff, C. D.; Markó, L. *J. Org. Chem.* **1979**, *44*, 3095.
(2) (a) Oak Ridge National Laboratory. (b) Carleton College. (c) University of Georgia.

(3) Newton, M. G.; King, R. B.; Chang, M.; Pantaleo, N. S.; Gimeno, J. *J. Chem. Soc., Chem. Commun.* **1977**, 531.
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Experimental Section

General aspects of the experimental and spectroscopic techniques were similar to those used in previous work from the University of Georgia[4] except that mass spectra were taken at 70 eV on a Dupont 21-490 mass spectrometer located in the School of Pharmacy. Relative intensities for the ions in the mass spectra are listed in parentheses after the formulas of the ions.

Preparation of $CH_3N[P(OCH_3)_2]_2$. A mixture of 43.4 g (54.9 mL, 1.36 mol) of absolute methanol and 141.7 g (195 mL, 1.4 mol) of triethylamine was added over a period of 2 h to a rapidly stirred mixture of 81.5 g (50 mL, 0.35 mol) of $CH_3N(PCl_2)_2$[7] and 1000 mL of absolute diethyl ether cooled in an external bath at −78 °C. After the addition was complete, the reaction mixture was warmed to room temperature. The precipitated triethylammonium chloride was then removed by filtration. Evaporation of the diethyl ether from the filtrate followed by vacuum distillation gave 38 g (50% yield) of colorless liquid $CH_3N[P(OCH_3)_2]_2$, bp 110 °C (20 mm). Proton NMR: δ 3.27 (t, J = 7 Hz, 12 H, CH_3O protons) and 2.30 (t, J = 5 Hz, 3 H, CH_3N protons). Phosphorus-31 NMR: 145.3 ppm downfield from 85% H_3PO_4. Mass spectrum (probe 80 °C): $CH_3N[P(OCH_3)_2]_2^+$ = $(CH_3)_5NP_2O_4^+$ (18), $(CH_3)_4NP_2O_4^+$ (27), $(CH_3)_3NP_2O_4^+$ (20), $CH_3NP_2(OCH_3)_3^+$ (16), $(CH_3)_2NP_2O_4^+$ (19), $CH_3NP(OCH_3)_2^+$ (16), $CH_3NP(O)OCH_3^+$ (13), $CH_3NPOCH_3^+$ (100), CH_3OP^+ (24), CH_2NP^+ (38). Anal. Calcd for $C_5H_{15}NO_4P_2$: C, 27.9; H, 7.0. Found: C, 27.9; H, 6.9.

Preparation of $\{Ch_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. A solution of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ in 150 mL of redistilled tetrahydrofuran was treated with 1.3 g (6.05 mmol) of $CH_3N[P(OCH_3)_2]_2$ at 0 °C. Immediate gas evolution occurred. The reaction mixture was filtered. Evaporation of the filtrate followed by washing the residue with cold diethyl ether gave 1.73 g (90% yield) of violet-brown crystalline $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$, dec pt 230–240 °C. Infrared ν(CO) (CH_2Cl_2): 2060 (w), 1940 (s), and 1915 (s) cm^{-1}. Proton NMR: δ 3.63 (12 H, CH_3O protons) and 2.69 (3 H, CH_3N protons). Phosphorus-31 NMR: 163.2 ppm downfield from 85% H_3PO_4 (140 Hz width at half-height). Mass spectrum (probe 200 °C): $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_3^+$ (26), $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_2^+$ (100), $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2CO^+$ (74), $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2^+$ (85). Anal. Calcd for $C_{14}H_{30}Co_2N_2O_{12}P_4$: C, 25.4; H, 4.5; N, 4.2. Found: C, 25.2; H, 4.6; N, 3.7.

Determination of the Structure of $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. A crystal from methanol solution bounded by 10 plane faces and having maximum and minimum diameters of about 0.30 and 0.12 mm was selected. The space group $P2_1/c$ was established by X-ray precession photography. The following unit-cell parameters and standard errors were derived by the method of least squares from angle data recorded at about 20–22 °C with the Oak Ridge automatic computer-controlled X-ray diffractometer for 12 Mo Kα reflections at 30–33° 2θ (wavelength assumed to be 0.7107 Å): a = 10.809 (4) Å, b = 8.980 (4) Å, c = 27.63 (1) Å, β = 94.10 (2)°. The reasonable value 1.639 g/cm^3 was calculated for the density on the assumption of four molecules per cell of $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ (molecular weight 660.17).

Intensity data were recorded by the θ–2θ step-scan technique using niobium-filtered Mo Kα radiation for the reflections of the hkl and $\bar{h}kl$ octants of the limiting sphere for a 2θ maximum of 51°. The 2θ step was 0.05°, and the scan width was variable, increasing from an initial 1.6° at low 2θ so as to accommodate the α_1–α_2 splitting. The counting time was 40 s at the initial and final points, which were used to compute background, and 2 s at every other point of each scan. The observations included a few duplicate reflections and periodic observations of three reference reflections. The data for the reference reflections showed that over the time of the data collection, which extended to about 4 weeks because of instrumental malfunctions, the reflective power of the crystal decreased by about 16%. Subsequently when the Lorenz, polarization, and absorption corrections were applied, corrections were also made for the deterioration of the crystal. The absorption corrections were computed by the method of Busing and Levy[8] using for the linear absorption coefficient the value 15.3 cm^{-1}, calculated from tabulated mass attenuation coefficients.[9a] The maximum and minimum absorption corrections applied to the F_o^2 values were 1.441 and 1.278.

By averaging the data for the replicate reflections a set of structure-factor squares F_o^2 and statistical standard errors $\sigma_s(F_o^2)$ was derived for 4993 independent reflections. For later use in least-squares refinement, the standard errors of the observations were adjusted according to

$$\sigma^2(F_o^2) = \sigma_s^2(F_o^2) + (0.03F_o^2)^2$$

The term $(0.03F_o^2)^2$ is added to the variance to make some allowance for deficiencies in the model and for instability in the generator and counter circuitry.[10]

The solution for the structure was obtained by a straightforward application of the heavy-atom method that quickly yielded reasonable positions for all 34 atoms (excluding hydrogens) of the complex molecule, which is the asymmetric unit. Full-matrix least-squares refinement was started and continued until convergence was reached at the following values for the usual measures of goodness of fit: $R(F)$ = 0.055, $R(F^2)$ = 0.066, $R_w(F^2)$ = 0.083, σ_1 = 1.204. In the final cycles, 3011 F_o^2 values were used, each with a weight of $1/\sigma^2(F_o^2)$. The 1940 reflections having $F_o^2 < 2\sigma(F_o^2)$ were given zero weights, as were all 42 reflections having 2θ < 10°. The latter were rejected because their lower angle backgrounds had clearly not been properly measured because of the filter-edge effect, which resulted characteristically in too high a value for F_o^2. Anisotropic thermal parameters were adjusted for all atoms except the hydrogen atoms. The 30 hydrogen atoms were not found in a difference map, but they were put into reasonable fixed positions calculated at an advanced stage of refinement for ideally tetrahedral methyl groups with C–H distances set at 0.95 Å.[11] For each different methyl group the three hydrogen

Table I. Fractional Coordinates for $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ with Estimated Standard Deviations[a]

atom	x	y	z
Co(1)	0.15709 (7)	0.35154 (9)	0.412 65 (3)
Co(2)	0.272 92 (7)	0.217 18 (9)	0.341 18 (3)
P(1)	0.014 01 (14)	0.398 46 (19)	0.356 31 (6)
P(2)	0.288 47 (14)	0.229 99 (20)	0.459 29 (5)
P(3)	0.446 31 (14)	0.234 11 (19)	0.383 48 (5)
P(4)	0.213 59 (14)	0.406 48 (18)	0.298 15 (6)
O(1)	0.287 00 (51)	0.639 91 (57)	0.418 60 (19)
O(2)	−0.026 47 (43)	0.328 55 (57)	0.483 26 (17)
O(3)	0.099 17 (43)	−0.011 54 (56)	0.367 07 (18)
O(4)	0.368 90 (50)	0.037 91 (59)	0.265 84 (18)
O(5)	−0.087 33 (35)	0.522 38 (51)	0.368 58 (15)
O(6)	−0.082 10 (34)	0.271 87 (48)	0.337 57 (15)
O(7)	0.298 83 (38)	0.273 26 (58)	0.515 52 (14)
O(8)	0.274 07 (36)	0.052 47 (46)	0.467 61 (15)
O(9)	0.542 59 (35)	0.096 13 (53)	0.377 90 (15)
O(10)	0.547 17 (36)	0.365 08 (51)	0.380 06 (15)
O(11)	0.295 38 (36)	0.554 67 (47)	0.305 94 (15)
O(12)	0.199 35 (37)	0.392 37 (49)	0.239 34 (14)
N(1)	0.064 96 (43)	0.458 04 (54)	0.304 40 (17)
N(2)	0.434 25 (38)	0.237 61 (53)	0.443 96 (16)
C(1)	0.238 59 (61)	0.526 92 (84)	0.414 76 (22)
C(2)	0.046 26 (57)	0.330 63 (71)	0.454 28 (23)
C(3)	0.164 47 (57)	0.086 08 (77)	0.358 98 (22)
C(4)	0.330 18 (57)	0.110 55 (75)	0.295 27 (24)
C(5)	−0.047 59 (75)	0.668 4 (10)	0.385 29 (31)
C(6)	−0.151 96 (62)	0.191 21 (92)	0.371 24 (31)
C(7)	0.312 54 (79)	0.424 9 (10)	0.530 86 (27)
C(8)	0.165 21 (65)	−0.009 85 (83)	0.486 16 (27)
C(9)	0.501 11 (70)	−0.053 49 (91)	0.386 01 (27)
C(10)	0.578 65 (63)	0.419 27 (93)	0.334 20 (28)
C(11)	0.259 46 (82)	0.698 52 (87)	0.284 84 (34)
C(12)	0.308 69 (76)	0.376 3 (10)	0.213 06 (26)
C(13)	−0.022 35 (62)	0.520 72 (90)	0.265 08 (25)
C(14)	0.543 58 (58)	0.205 29 (81)	0.478 82 (23)

[a] The estimated standard deviations are given by the numbers in parentheses, whose digits correspond to the least significant digits of the adjacent coordinates. This convention for specifying esd's is used throughout the paper.

(7) King, R. B.; Gimeno, J. *Inorg. Chem.* **1978**, *17*, 2390.
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(10) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70.

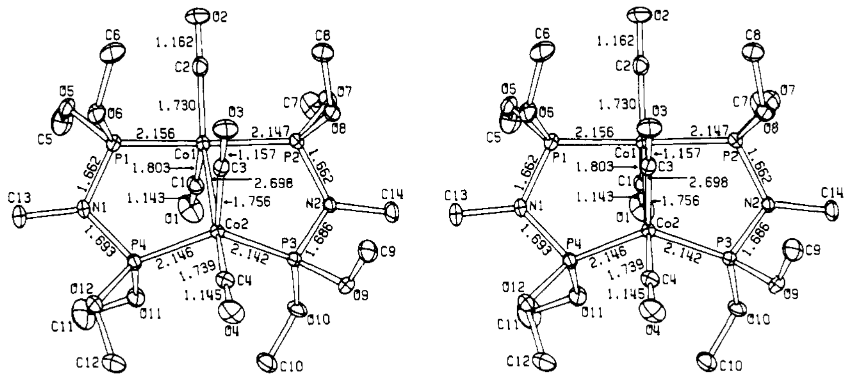

Figure 1. Nonperspective stereoscopic drawing of the molecule of $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. The atoms are represented by their vibrational ellipsoids of 20% probability.[12e] The bond lengths (Å) of most interest are included.

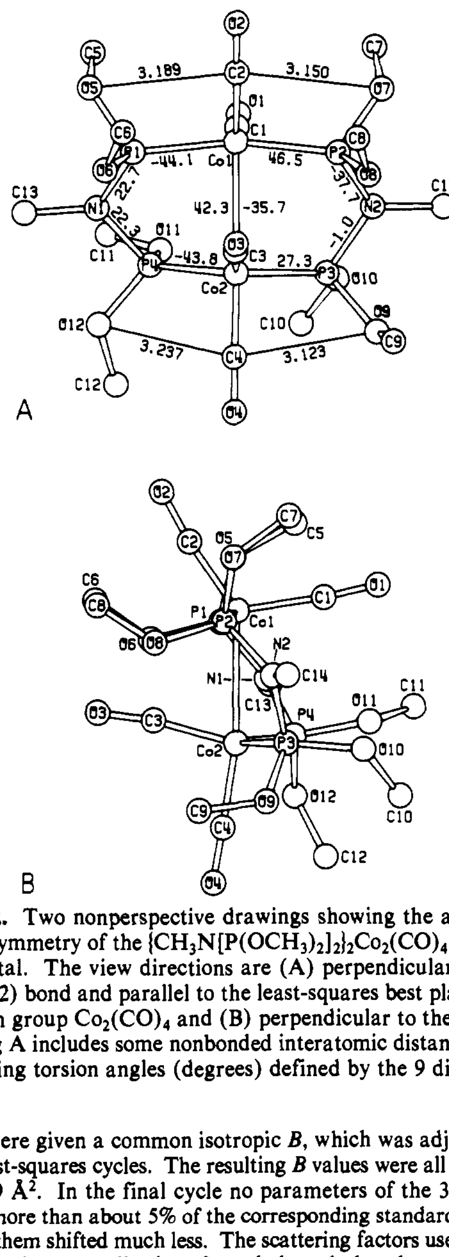

Figure 2. Two nonperspective drawings showing the approximate mirror symmetry of the $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ molecule in the crystal. The view directions are (A) perpendicular to the Co(1)–Co(2) bond and parallel to the least-squares best plane through the atom group $Co_2(CO)_4$ and (B) perpendicular to the best plane. Drawing A includes some nonbonded interatomic distances (Å) and the 10 ring torsion angles (degrees) defined by the 9 different ring bonds.

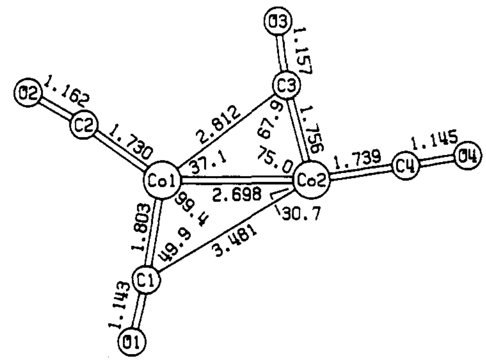

Figure 3. View of the atom group $Co_2(CO)_4$ perpendicular to its least-squares best plane, showing the borderline semibridging by carbonyl group C(3)–O(3). Distances (Å) and angles (degrees) are labeled.

atoms were given a common isotropic B, which was adjusted in the final least-squares cycles. The resulting B values were all in the range 8.2–17.9 $Å^2$. In the final cycle no parameters of the 317 adjusted shifted more than about 5% of the corresponding standard errors, and most of them shifted much less. The scattering factors used, including the anomalous contributions for cobalt and phosphorus, were from the standard source.[9b]

The final positional and thermal parameters except those of the hydrogen atoms are given in Tables I and II. The coordinates and thermal parameters of the hydrogen atoms and a listing of observed and calculated structure factors with standard errors are available.

The standard Oak Ridge National Laboratory crystallographic computer programs[12] were used in this work.

Results and Discussion

The ligand used in this work, $CH_3N[P(OCH_3)_2]_2$, apparently has not been reported. It was prepared by the following rather conventional reaction:

$$CH_3N(PCl_2)_2 + 4CH_3OH + 4(C_2H_5)_3N \rightarrow CH_3N[P(OCH_3)_2]_2 + 4[(C_2H_5)_3NH]Cl$$

This reaction is completely analogous to the reaction used to convert $Cl_2PCH_2CH_2PCl_2$ into $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$.[13] The ligand $CH_3N[P(OCH_3)_2]_2$ was characterized by elemental analyses, proton and phosphorus-31 NMR spectra, and the mass spectrum.

The reaction of $Co_2(CO)_8$ with $CH_3N(PF_2)_2$ at room temperature rapidly results in evolution of 75% of the available CO to give $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ (**1**).[3,4] However, the analogous reaction of $Co_2(CO)_8$ with $CH_3N[P(OCH_3)_2]_2$ results in substitution of only half of the CO groups to give $\{[CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. The single phosphorus-31 NMR resonance of this complex is rather broad, presumably because of the cobalt-59 quadrupole moment. Though the breadth possibly could obscure relatively small chemical-shift

(11) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(12) The following programs were used: (a) For preliminary processing of reflection data, programs DATATAPE, DATALIB, and DATASORT by H. A. Levy and R. D. Ellison. (b) For least-squares refinement, program XFLS-4 (1979) by W. R. Busing, H. A. Levy, and others. (c) For calculation of bond lengths, angles, and best planes, ORFFE4 (1977) by W. R. Busing and H. A. Levy. (d) Fast Fourier package, ORFFP3 (1977), by H. A. Levy was also utilized. (e) Johnson, C. K. "Ortep-II, Fortran Thermal-Ellipsoid Plot Program for Crystal-Structure Illustrations", ORNL Report 5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(13) King, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961.

Table II. Anisotropic Thermal Parameters[a] U_{ij} (Å^2) for $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0.0279 (4)	0.0289 (5)	0.0273 (5)	0.0015 (4)	0.0008 (3)	0.0017 (4)
Co(2)	0.0273 (4)	0.0278 (5)	0.0260 (4)	0.0008 (4)	0.0009 (3)	0.0012 (4)
P(1)	0.0264 (9)	0.0343 (10)	0.0370 (10)	0.0017 (8)	−0.0014 (7)	0.0004 (8)
P(2)	0.0321 (9)	0.0373 (10)	0.0261 (9)	−0.0001 (8)	0.0017 (7)	0.0066 (8)
P(3)	0.0265 (8)	0.0381 (11)	0.0293 (9)	−0.0032 (8)	0.0019 (7)	0.0086 (8)
P(4)	0.0320 (9)	0.0330 (10)	0.0291 (9)	−0.0006 (8)	−0.0009 (7)	0.0042 (8)
O(1)	0.1043 (43)	0.0408 (32)	0.0739 (38)	−0.0303 (34)	−0.0132 (32)	−0.0001 (30)
O(2)	0.0584 (32)	0.0845 (41)	0.0584 (34)	0.0056 (29)	0.0332 (27)	0.0044 (30)
O(3)	0.0585 (33)	0.0482 (33)	0.0740 (37)	−0.0224 (28)	0.0161 (28)	0.0010 (28)
O(4)	0.1058 (44)	0.0651 (38)	0.0496 (34)	0.0206 (33)	0.0286 (31)	−0.0153 (29)
O(5)	0.0327 (25)	0.0459 (31)	0.0563 (31)	0.0134 (23)	0.0024 (22)	0.0011 (25)
O(6)	0.0334 (24)	0.0458 (29)	0.0537 (28)	−0.0109 (23)	−0.0092 (21)	0.0017 (25)
O(7)	0.0557 (29)	0.0670 (35)	0.0308 (25)	0.0043 (28)	−0.0006 (21)	0.0027 (26)
O(8)	0.0371 (26)	0.0389 (29)	0.0550 (30)	−0.0033 (22)	0.0034 (22)	0.0206 (23)
O(9)	0.0314 (24)	0.0586 (34)	0.0490 (29)	0.0132 (24)	0.0088 (21)	0.0114 (25)
O(10)	0.0426 (27)	0.0670 (34)	0.0384 (27)	−0.0251 (25)	−0.0009 (22)	0.0189 (25)
O(11)	0.0417 (27)	0.0370 (29)	0.0589 (31)	−0.0098 (22)	−0.0027 (22)	0.0152 (24)
O(12)	0.0480 (27)	0.0650 (34)	0.0306 (25)	0.0108 (25)	0.0040 (21)	0.0108 (23)
N(1)	0.0357 (29)	0.0372 (32)	0.0338 (31)	0.0078 (26)	−0.0036 (24)	0.0109 (26)
N(2)	0.0260 (25)	0.0362 (31)	0.0283 (27)	−0.0049 (24)	−0.0059 (20)	0.0095 (24)
C(1)	0.0477 (42)	0.0479 (48)	0.0291 (37)	0.0018 (37)	−0.0006 (30)	0.0027 (35)
C(2)	0.0421 (38)	0.0387 (42)	0.0433 (41)	0.0097 (33)	0.0008 (32)	0.0040 (34)
C(3)	0.0359 (38)	0.0430 (45)	0.0375 (38)	0.0063 (35)	−0.0010 (30)	−0.0030 (35)
C(4)	0.0460 (40)	0.0453 (47)	0.0357 (40)	−0.0029 (35)	0.0069 (32)	0.0021 (35)
C(5)	0.0780 (57)	0.0525 (57)	0.0963 (68)	0.0281 (47)	0.0009 (48)	−0.0077 (50)
C(6)	0.0408 (43)	0.0809 (64)	0.0947 (63)	−0.0265 (43)	0.0091 (43)	0.0055 (50)
C(7)	0.1090 (70)	0.0630 (63)	0.0522 (51)	−0.0166 (53)	−0.0118 (46)	−0.0127 (45)
C(8)	0.0506 (47)	0.0605 (53)	0.0762 (56)	−0.0144 (41)	0.0120 (41)	0.0235 (44)
C(9)	0.0732 (55)	0.0525 (56)	0.0743 (59)	0.0253 (46)	0.0173 (45)	0.0200 (45)
C(10)	0.0552 (48)	0.0921 (65)	0.0597 (51)	−0.0203 (44)	−0.0009 (39)	0.0375 (47)
C(11)	0.1062 (70)	0.0376 (52)	0.1172 (77)	−0.0093 (49)	−0.0128 (57)	0.0255 (51)
C(12)	0.0793 (57)	0.0962 (70)	0.0527 (50)	0.0097 (52)	0.0278 (45)	0.0203 (47)
C(13)	0.0480 (44)	0.0874 (61)	0.0495 (48)	0.0169 (43)	−0.0121 (36)	0.0243 (44)
C(14)	0.0393 (38)	0.0722 (54)	0.0486 (43)	−0.0090 (38)	−0.0172 (32)	0.0240 (40)

[a] The temperature factor is of the form $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots + 2a^*b^*hkU_{12} + \ldots)]$.

Table III. Bond Lengths (Å) in $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2CO_4$

Co(1)-Co(2)	2.698 (1)	P(1)-O(5)	1.614 (4)
Co(1)-P(1)	2.156 (2)	P(1)-O(6)	1.601 (4)
Co(1)-P(2)	2.147 (2)	P(2)-O(7)	1.598 (4)
Co(2)-P(3)	2.142 (2)	P(2)-O(8)	1.620 (4)
Co(2)-P(4)	2.146 (2)	P(3)-O(9)	1.633 (4)
Co(1)-C(1)	1.803 (8)	P(3)-O(10)	1.611 (4)
Co(1)-C(2)	1.730 (7)	P(4)-O(11)	1.604 (4)
Co(2)-C(3)	1.756 (7)	P(4)-O(12)	1.627 (4)
Co(2)-C(4)	1.739 (7)	C(5)-O(5)	1.445 (9)
C(1)-O(1)	1.143 (7)	C(6)-O(6)	1.436 (8)
C(2)-O(2)	1.162 (7)	C(7)-O(7)	1.431 (9)
C(3)-O(3)	1.157 (7)	C(8)-O(8)	1.431 (7)
C(4)-O(4)	1.145 (7)	C(9)-O(9)	1.439 (8)
P(1)-N(1)	1.662 (5)	C(10)-O(10)	1.422 (8)
P(4)-N(1)	1.693 (5)	C(11)-O(11)	1.458 (9)
P(2)-N(2)	1.662 (4)	C(12)-O(12)	1.438 (8)
P(3)-N(2)	1.686 (5)	C(13)-N(1)	1.497 (7)
		C(14)-N(2)	1.499 (7)

differences among the phosphorus atoms, the single peak suggests complexation of all four phosphorus atoms in an equivalent manner, implying fourfold molecular symmetry, at least in solution on the NMR time scale. The mass spectrum contains the bimetallic ions $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_n^+$ (n = 3, 2, 1, and 0) but not the molecular ion (n = 4). The infrared spectrum in dichloromethane solution exhibits terminal ν(CO) frequencies but no bridging or semibridging ν(CO) frequencies. The lower degree of CO substitution in $Co_2(CO)_8$ by $CH_3N[P(OCH_3)_2]_2$ relative to $CH_3N(PF_2)_2$ under comparable conditions can be attributed to the larger size and lower electronegativity of the CH_3O substituents relative to the F substituents.

The results of the X-ray structure analysis are presented in Figures 1–4 and in Tables III–V. Figures 1–3 show drawings of the molecule, with some numerical data included, and Figure 4 shows the packing of the molecules. Bond lengths with esd's are in Table III, and valence angles with esd's are in Table IV.

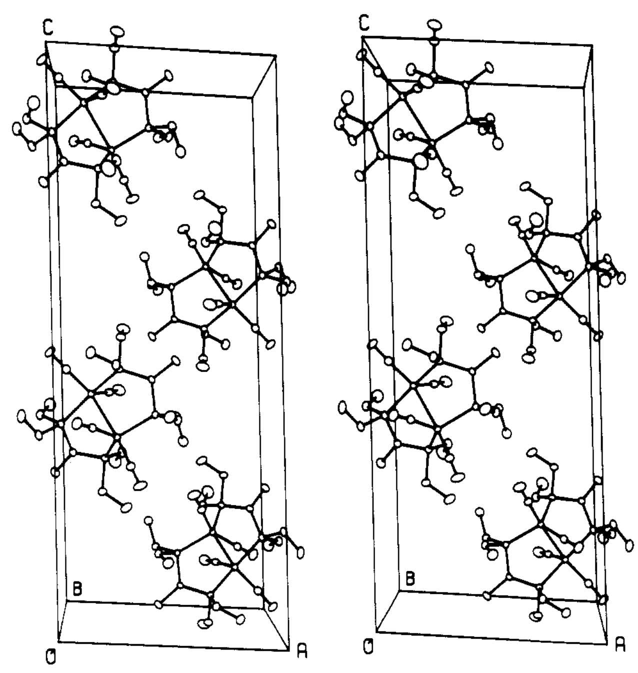

Figure 4. Stereoscopic drawing showing the packing of the molecules in the crystal structure of $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$.

The X-ray diffraction analysis confirms the binuclear structure for $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ (see Figure 1.) The Co(1)–Co(2) distance of 2.698 (1) Å corresponds to a metal–metal bond and is quite close to the Co–Co distances found in complexes containing the $[CH_3N(PF_2)_2]_3Co_2$ unit,

Table IV. Bond Angles (Deg) in $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$

Co(1) and Co(2) Angles Referred to Square Pyramid of Minimum Repulsion[a]			
Apical-Basal Angles (Ideal Angle = 104°)			
C(1)-Co(1)-P(1)	100.2 (2)	C(3)-Co(2)-P(3)	118.0 (2)
C(1)-Co(1)-C(2)	115.7 (3)	C(3)-Co(2)-C(4)	96.6 (3)
C(1)-Co(1)-P(2)	97.1 (2)	C(3)-Co(2)-P(4)	120.5 (2)
C(1)-Co(1)-Co(2)	99.4 (2)	C(3)-Co(2)-Co(1)	75.0 (2)
Lateral Basal-Basal Angles (Ideal Angle = 87°)			
P(1)-Co(1)-C(2)	90.4 (2)	P(3)-Co(2)-C(4)	95.4 (2)
C(2)-Co(1)-P(2)	90.3 (2)	C(4)-Co(2)-P(4)	98.0 (2)
P(2)-Co(1)-Co(2)	83.7 (1)	P(4)-Co(2)-Co(1)	85.2 (1)
Co(2)-Co(1)-P(1)	84.6 (1)	Co(1)-Co(2)-P(3)	90.1 (2)
Diagonal Basal-Basal Angles (Ideal Angle = 152°)			
P(1)-Co(1)-P(2)	160.5 (1)	P(3)-Co(2)-P(4)	117.5 (1)
Co(2)-Co(1)-C(2)	144.9 (2)	C(4)-Co(2)-Co(1)	188.6 (2)
Co(1) and Co(2) Angles Referred to Trigonal Bipyramid			
Axial-Axial Angles (Ideal Angle = 180°)			
P(1)-Co(1)-P(2)	160.5 (1)	C(4)-Co(2)-Co(1)	171.4 (2)
Axial-Equatorial Angles (Ideal Angle = 90°)			
P(1)-Co(1)-Co(2)	84.6 (1)	C(4)-Co(2)-P(3)	95.4 (2)
P(1)-Co(1)-C(1)	100.2 (2)	C(4)-Co(2)-P(4)	98.0 (2)
P(1)-Co(1)-C(2)	90.4 (2)	C(4)-Co(2)-C(3)	96.6 (3)
P(2)-Co(1)-Co(2)	83.7 (1)	Co(1)-Co(2)-P(3)	90.1 (1)
P(2)-Co(1)-C(1)	97.1 (2)	Co(1)-Co(2)-P(4)	85.2 (1)
P(2)-Co(1)-C(2)	90.3 (2)	Co(1)-Co(2)-C(3)	75.0 (2)
Equatorial-Equatorial Angles (Ideal Angle = 120°)			
Co(2)-Co(1)-C(1)	99.4 (2)	P(3)-Co(2)-P(4)	117.5 (1)
Co(2)-Co(1)-C(2)	144.9 (2)	C(3)-Co(2)-P(3)	120.5 (2)
C(1)-Co(1)-C(2)	115.7 (2)	P(4)-Co(2)-C(3)	118.0 (2)
Other Angles			
Co(1)-P(1)-N(1)	114.9 (2)	Co(2)-P(3)-N(2)	114.6 (2)
Co(1)-P(1)-O(5)	116.4 (2)	Co(2)-P(3)-O(9)	115.7 (2)
Co(1)-P(1)-O(6)	120.7 (2)	Co(2)-P(3)-O(10)	126.1 (2)
N(1)-P(1)-O(5)	103.4 (2)	N(2)-P(3)-O(9)	101.7 (2)
N(1)-P(1)-O(6)	101.4 (2)	N(2)-P(3)-O(10)	98.3 (2)
O(5)-P(1)-O(6)	97.1 (2)	O(9)-P(3)-O(10)	96.3 (2)
Co(1)-P(2)-N(2)	115.1 (2)	Co(2)-P(4)-N(1)	114.1 (2)
Co(1)-P(2)-O(7)	117.2 (2)	Co(2)-P(4)-O(11)	116.3 (2)
Co(1)-P(2)-O(8)	121.3 (2)	Co(2)-P(4)-O(12)	119.7 (2)
N(2)-P(2)-O(7)	103.7 (2)	N(1)-P(4)-O(11)	106.7 (2)
N(2)-P(2)-O(8)	100.3 (2)	N(1)-P(4)-O(12)	95.8 (2)
O(7)-P(2)-O(8)	95.9 (3)	O(11)-P(4)-O(12)	102.2 (2)
P(1)-N(1)-P(4)	112.1 (3)	P(2)-N(2)-P(3)	113.2 (3)
P(1)-N(1)-C(13)	121.1 (4)	P(2)-N(2)-C(14)	123.1 (4)
P(4)-N(1)-C(13)	125.6 (4)	P(3)-N(2)-C(14)	121.4 (4)
Co(1)-C(1)-O(1)	175.9 (6)	Co(2)-C(3)-C(3)	172.1 (5)
Co(1)-C(2)-O(2)	174.5 (6)	Co(2)-C(4)-O(4)	178.4 (6)
P(1)-O(5)-C(5)	120.1 (4)	P(3)-O(9)-C(9)	119.1 (4)
P(1)-O(6)-C(6)	120.5 (4)	P(3)-O(10)-C(10)	120.5 (4)
P(2)-O(7)-C(7)	121.2 (4)	P(4)-O(11)-C(11)	123.6 (4)
P(2)-O(8)-C(8)	121.7 (4)	P(4)-C(12)-C(12)	119.3 (4)

[a] See text.

Table V. Least-Squares Best Plane through the Group $Co_2(CO)_4$ and Deviations (Å) of the Atoms from the Plane

Equation:[a] $6.9533x - 3.3628y + 17.139z = 7.0052$ Å

Co(1)	−0.018	Co(2)	0.014
C(1)	−0.005	C(3)	−0.006
C(2)	−0.004	C(4)	−0.016
O(1)	0.018	O(3)	0.019
O(2)	−0.007	O(4)	−0.007

[a] The variables x, y, and z here are fractional coordinates.

for example, the distances 2.716 (1), 2.769 (1), 2.740 (3), and 2.717 (5) Å in $[Ch_3N(PF_2)_2]_3Co_2(CO)_2$, $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, and $[CH_3N(PF_2)_2]_3Co_2Br_4$, respectively.[3,7,14] The reasons are not clear for the minor variations in the Co–Co bond distances in these five dicobalt complexes of bridging small-bite bidentate phosphorus ligands.

Since the entire molecule is the asymmetric unit in the crystal, it contains no symmetry element and cannot have any exact symmetry. However, the pattern of chemical linkages, the chemical topology, of the molecule is clearly such that one would expect it to display some symmetry when unperturbed by packing; and, as already noted above, the phosphorus-31 NMR spectrum does imply fourfold symmetry in solution. Some residual approximate symmetry might be expected in the crystal. It is of interest to note, therefore, that the least-squares best plane through the ten atoms of the group $Co_2(CO)_4$, which are shown by the data in Table V to be nearly coplanar, is an approximate mirror plane for the molecule. Figure 2 shows the approximate symmetry, which applies, surprisingly, even to the C(5), C(6), C(7), and C(8) methyl groups, though not to the other methoxy methyl groups. The degree of approximation is illustrated numerically by the ring torsion angles included in Figure 2A. If there were an exact mirror plane, there would be five pairs of ring torsion angles with individual values equal in magnitude but opposite in sign. The actual situation is rather different; in fact, it seems remarkable that the group $Co_2(CO)_4$ is so nearly plane when the departure from mirror symmetry with respect to the plane is as observed. It appears that an essentially plane group $Co_2(CO)_4$ endowed with some resistance to out-of-plane distortion is an inherent structural feature of the molecule. A similar almost plane group, $Fe_2(CO)_4$, has been found[15] in tetracarbonylbis(μ-2,2,5,5-tetramethylhex-3-yne)-diiron, $[(CH_3)_3CC{\equiv}CC(CH_3)_3]_2Fe_2(CO)_4$, another example of a complex in which the two metal atoms of a group $M_2(CO)_4$ are bridged by two ligands. In μ-carbonyl-μ-[N,N-bis(dimethoxyphosphino)methylamine]-bis(tricarbonyliron), $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$, there is a similar situation in that a group $Fe_2(CO)_5$ is almost plane.[16]

In $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ each cobalt atom is five-coordinate since each is linked to the other cobalt atom, to two phosphorus atoms, and to two carbonyl groups. However, in the crystal the two cobalt atoms are not related by symmetry, and the two coordination polyhedra are distinctly different. The situation is a most unusual one: in the same molecule two identical metal atoms with identical ligands display approximations to the two different coordination polyhedra characteristic of coordination number 5, namely, the square pyramid and the trigonal bipyramid. We believe that the polyhedra can be seen from the stereoscopic drawing of the molecule in Figure 1 to be as described. However, to make still clearer the appropriateness of the two different referent polyhedra for the two cobalt atoms, we have grouped in Table IV the 10 angles about Co(1) and the 10 about Co(2) in two different ways so as to emphasize maximally the similarity of each cobalt polyhedron first to an ideal square pyramid (point symmetry C_{4v}—$4mm$) and then to an ideal trigonal bipyramid (point symmetry D_{3h}—$\bar{6}m2$). The referent square pyramid in Table IV is not one with the metal atom in the basal plane but the somewhat more realistic one corresponding to minimum Coulombic repulsion in an equal-bond-distances, equal-charges model, for which the apical–basal angles have been calculated[17] to be 104°. The ideal diagonal[18] basal–basal angles corresponding are obviously 152°; and the lateral[18] basal–basal angles are given by arccos

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Table VI. Examples of Noncompensated Semibridging Carbonyl Groups

compd	M-C dist, Å, to semibridging CO r_1	r_2	r_2/r_1	ref
$\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$	1.756	2.812	1.60	this work
$Cp_2Mo_2(CO)_4(RC{\equiv}CR)$				22
R = HC≡CH	1.951	2.902	1.49	
R = EtC≡CEt	1.936	2.826	1.46	
R = PhC≡CPh	1.949	2.871	1.47	
$C_4H_4Fe_2(CO)_6$	1.779	2.508	1.41	23
$C_{12}H_{16}Fe_2(CO)_6$	1.753	2.321	1.32	24
$[CH_3N(PF_2)_2]_4Mo_2(CO)_3$	2.02	2.54	1.26	25
$(C_5H_5)_2V_2(CO)_5$	1.93	2.44	1.26	26
	1.94	2.40	1.23	

$(\cos^2 104°) = 87°$, according to the properties of the isosceles right spherical triangle involved.

From Table IV it is clear that the Co(1) polyhedron regarded as a tetragonal pyramid with the C(1)–O(1) group at the apex is a fair approximation to the referent ideal square pyramid. There are, of course, distortions from the ideal because the pattern of ligands on Co(1) does not conform to the equal-bond-distances, equal-charges model. Even so, the means of the four apical–basal angles, the four lateral basal–basal angles, and the two diagonal basal–basal angles are 103, 87, and 153°, respectively, close to the ideal values for the model. In contrast, the Co(2) polyhedron is better described as a distorted trigonal bipyramid, with atom Co(1) and the carbonyl group C(4)–O(4) in the axial positions. The 10 angles about Co(2) include 6 close to the ideal 90° axial–equatorial angles, 3 close to the ideal 120° equatorial–equatorial angles, and 1 close to the ideal 180° axial–axial angle. The distortions from the ideal are no more than those expected from the lack of D_{3h}—$\bar{6}m2$ symmetry of the ligand pattern on the cobalt atoms.

The existence in the crystal of the two distinctly different cobalt coordination polyhedra and the related lack of symmetry equivalence of the four phosphorus atoms contrast with the situation in dichloromethane solution, where the single phosphorus-31 NMR resonance indicates equivalence of the phosphorus atoms. Evidently the complex $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ is a stereochemically nonrigid system in which the two cobalt atoms and the four phosphorus atoms that are not equivalent in the crystal become equivalent in solution on the NMR time scale through fluxional processes,[19] just as expected since stereochemical nonrigidity is a common feature of five-coordinate complexes.[20] From Figures 1 and 2 (especially Figure 2B) and from Table IV, one can see that opening angle P(1)–Co(1)–P(2) by ~20° and closing angle P(3)–Co(2)–P(4) by ~20°, with accompanying changes in the ring conformations and other changes involving little energy, could result in a molecule having the symmetry C_{2h}—$2/m$ that would exhibit only one phosphorus-31 NMR peak and which may represent the average structure in solution on the NMR time scale. To put it the other way around, the actual molecular structure in the crystal can quite reasonably be supposed to be the result of distortion of such a symmetrical structure caused by the packing of the molecules.

An interesting feature of the molecule in the crystal is the position of the C(3)–O(3) carbonyl group relative to the two cobalt atoms (see Figure 3), which at least approaches a semibridging position.[21] The absence of evidence for semibridging in the infrared spectrum in solution is consistent with the difference in the structure of the complex between crystal and solution.

It is of interest to compare (see Table VI) the ratio of the longer Co–C(3) distance, r_2, to the shorter Co–C(3) distance, r_1, of the cobalt complex with the corresponding ratios for a number of binuclear metal complexes which are recognized from crystal-structure analyses to have semibridging carbonyl groups. The table is restricted to complexes with "noncompensated" semibridging carbonyl groups, that is, those which function singly rather than as members of compensated pairs.[21,27] Bands in the 1900–1800-cm^{-1} range, said to be the characteristic range for semibridging carbonyls,[26] have been observed in the infrared spectra recorded from mulls of the compounds $(C_5H_5)_2V_2(CO)_5$[26] and $(C_5H_5)_2Mo_2(CO)_4(RC{\equiv}CR)$.[22] Just as in the case of $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$, however, the infrared spectra of the compounds $C_4H_4Fe_2(CO)_6$[28] and $C_{12}H_{16}Fe_2(CO)_6$[29] in solution show no evidence of semibridging carbonyls. The ratio r_2/r_1 for $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ is 1.60, higher than the ratio for any other compound in Table VI and just at the value that has for practical purposes been taken as the boundary value for distinguishing between semibriding and terminal carbonyl groups.[30] The present case may therefore be regarded as one of borderline semibridging.

Semibridging has usually been explained either as the result of a charge dissymmetry[21,26,31] between two metal atoms resulting from a difference in the chemical bonding about the two and requiring the semibridging for balancing the charge distribution or as the result of an intra- or intermolecular packing effect.[21,22] The first explanation is applicable to all of the compounds in Table VI except the cobalt complex and the compounds of formula $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$,[22] in each of which each metal atom has the same set of ligands and in which, therefore, there should be no charge dissymmetry. The semibridging and some other structural asymmetry in the compounds $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$ have been attributed to "internal crowding" in the molecules;[22] and we believe that the borderline semibridging in the cobalt complex in the crystal results from similar intramolecular effects in a molecule made unsymmetrical, as already suggested above, by the packing in the crystal. Atom C(4) is in contact with atoms O(9) and O(12), at distances 3.123 (8) and 3.237 (8) Å, respectively. Carbonyl group C(4)–O(4) is thus held out of line with bond Co(1)–Co(2), and it in turn holds group C(3)–O(3) in the incipient semibridging position. The C(3)···C(4), C(3)–O(6), and C(3)–O(8) distances are respectively 2.609 (9), 3.164 (7), and 3.162 (7) Å. Note that at the Co(1) end of the molecule the atom C(2) is in contact with O(5) and O(7) at distances 3.189 and 3.150 Å, respectively, but that at this end the relative positions of the atoms are such that there is no resulting tendency toward semibridging. Implicit in this discussion is the assumption that the carbonyl group positions are determined by the positions of atoms in the two bidentate ligands instead of the reverse. This assumption seems reasonable since these atoms cannot move independently of other atoms in the

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bidentate ligands and the conformations of the rings formed by these ligands are determined by a large number of intermolecular contacts.

Acknowledgment. The research performed at Oak Ridge National Laboratory was sponsored by the Division of Material Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp. The research performed at the University of Georgia was supported partially by the U.S. Air Force Office of Scientific Research under Grant AFOSR-75-2869.

Registry No. $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$, 81011-78-1; $Co_2(CO)_8$, 10210-68-1; $CH_3N[P(OCH_3)_2]_2$, 34244-05-8; $CH_3N(PCl_2)_2$, 17648-16-7; methanol, 67-56-1.

Supplementary Material Available: A table of coordinates and thermal parameters of the hydrogen atoms and a listing of observed and calculated values of F^2, with estimated standard errors of the former (22 pages). Ordering information is given on any current masthead page.

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Intra- and Intermolecular Equilibria and Their Pertinence to the Mechanism of Cis–Trans Isomerization of L_2PtX_2 Complexes: Four- and Five-Coordinate Platinum Phosphole Complexes

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Received August 20, 1981

A series of platinum(II) complexes of the type L_2PtX_2 (L = 1-R-3,4-dimethylphosphole; R = $-CH_3$, $-n-C_4H_9$, $-t-C_4H_9$, $-C_6H_5$, $-CH_2C_6H_5$; X = Cl^-, Br^-, I^-) have been prepared and characterized by elemental analyses, physical properties, conductance measurements, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopy. All complexes are nonelectrolytes in chloroform and methanol solutions and most possess the cis geometry in solution as well as in the solid state. Variable-temperature $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy and conductance studies of the equilibrium $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ have been analyzed in terms of intra- and intermolecular equilibria of the pentacoordinate species L_3PtX_2. The formation of L_3PtX_2 is enthalpy favored and entropy disfavored. The relative thermodynamic stability of the L_3PtX_2 complexes is a function of ligand steric bulk; the smaller ligand gives the greater stability. The stereochemical rigidity of the L_3PtX_2 complexes is inversely proportional to ligand steric bulk: the larger the ligand, the more rigid the L_3PtX_2 complex. The relationship of these observations to the mechanism of cis–trans isomerization of L_2MX_2 (M = Pd, Pt) is discussed. Coordination chemical shift relationships of the form $\Delta\delta(^{31}P) = A[\delta(^{31}P_{ligand})] + B$ were found for the four-coordinate L_2PtX_2 complexes and for both of the magnetically inequivalent phosphole ligands in the five-coordinate L_3PtX_2 complexes. The complexes *cis*-$L_2PtBrCl$, which are intermediates in the bromide ligand substitution reactions of *cis*-L_2PtCl_2, were isolated and characterized. They demonstrate that anion ligand substitution of *cis*-L_2PtCl_2 complexes occurs with complete retention of configuration. This is direct evidence of the kinetic trans effect. In contrast, iodide substitution of L_2PtCl_2 to produce L_2PtI_2 is accompanied by some cis–trans isomerization, as mixtures of *cis*- and *trans*-L_2PtI_2 are formed in these reactions. This is evidence of the thermodynamic trans effect. The $L_2PtBrCl$ complexes react with excess L to form $L_3PtBrCl$ rather than $[L_3PtBr]Cl$ or $[L_3PtCl]Br$ in support of the contention that the equilibrium can be best described as $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ and not as $L_2PtX_2 + L \rightleftharpoons [L_3PtX]X$. Thus, five-coordinate complexes and not ionic four-coordinate complexes are formed in solutions of L_2PtX_2 upon addition of excess ligand (L). The implications of this in regard to consecutive anion displacement for isomerization of L_2PtX_2 complexes is discussed.

Introduction

Much effort[2–18] has been expended toward understanding the mechanisms of ligand substitution and isomerization of square-planar transition-metal complexes. While it is becoming clearer that pentacoordinate species are involved[2,4,9,16,19–21] in these processes, there is little information[18] regarding the solution structure and reactivity of pentacoordinate Pd(II) and Pt(II) ML_3X_2 complexes. Sterically undemanding ligands that possess both strong σ-donor and π-acceptor abilities are held[14,22,23] to be an important stabilizing influence on these pentacoordinate complexes. Of the few d^8 pentacoordinate species that have been characterized, most have involved phospholes[24,25] or trimethylphosphine.[26] Superficially, phosphole (I, R^1 = R = H) is very similar to the

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