

**CARBONYL ADDUCTS OF  
BIS(1,4-BIS(DIPHENYLPHOSPHINO)BUTANE)RHODIUM(I) CATION.  
CRYSTAL AND MOLECULAR STRUCTURE OF  
[Rh<sub>2</sub>(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>)<sub>3</sub>(CO)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>**

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### Summary

The reaction of CO with CH<sub>2</sub>Cl<sub>2</sub> solutions of [Rh(dppb)<sub>2</sub>]<sup>+</sup>X<sup>−</sup>, where X = BF<sub>4</sub> or PF<sub>6</sub> and dppb = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>, yields the binuclear complex [Rh<sub>2</sub>(dppb)<sub>3</sub>(CO)<sub>4</sub>]<sup>2+</sup> and uncoordinated dppb. This complex was isolated in the solid state as the PF<sub>6</sub> salt and characterized by single crystal X-ray diffraction. The structure consists of two trigonal bipyramidal RhP<sub>3</sub>(CO)<sub>2</sub> cores bridged by a dppb ligand via axial coordination sites. The CO ligands are *cis* and occupy equatorial sites and the chelating dppb ligands span equatorial and axial sites of their respective coordination cores. One binuclear molecule (Rh<sub>2</sub>(dppb)<sub>3</sub>(CO)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> is contained in the *P* $\bar{1}$  unit cell such that an inversion center exists in the center of the backbone of the bridging dppb ligand. The unit cell dimensions are *a* = 12.385(2), *b* = 15.286(2), *c* = 12.353(4) Å, α = 99.77(2), β = 107.03(2), γ = 103.66(1)°, and *V* = 2100 Å<sup>3</sup>. A total of 5780 observed reflections were used to solve the structure and the final *R* value was 0.060. The formation of the binuclear complex in acetone solution was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR. The complex is fluxional at 25°C but exhibits a complicated pattern at −65°C in addition to a sharp singlet due to uncoordinated dppb ligand.

### Introduction

Recent studies on the catalytic properties of metal complexes with chelating diphosphine ligands Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>*n*</sub>PPh<sub>2</sub> have shown considerable rate differences

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as a function of the diphosphine chelate ring size [1–5]. Studies in our lab on the homogeneous catalytic decarbonylation of aldehydes using  $\text{Rh}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2^+$  complexes with  $n = 1-4$  showed that the rate was a maximum for  $n = 3$  [1,6,7]. For example, at  $115^\circ\text{C}$  using catalyst concentrations of  $0.001\text{ M}$  the rates for decarbonylation of benzaldehyde in turnovers  $\text{hour}^{-1}$  are 0.40, 3.6, 11.0 and 1.2 for  $n = 1, 2, 3$  and  $4$ , respectively [6,7]. These rate differences presumably result from a complicated variation in effective ligand basicity, metal complex stereochemistry, and the stability of intermediates [7]. In order to understand such effects we are examining these catalytic decarbonylation reactions by in situ spectroscopy (high temperature IR and NMR) and by the isolation and characterization of reaction intermediates. It is also important in general to determine the structural differences between  $\text{Rh}^I\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  complexes as a function of  $n$  since many such systems behave as excellent homogeneous catalysts for various reactions [1,2,4,8–10].

For the decarbonylation of aldehydes, the only observable intermediates are carbonyl adducts of  $\text{Rh}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2^+$  where  $n = 1, 3$  and  $4$ . In the  $n = 2$  case, carbonyl adducts have not been observed [11]. Simple mono carbonyl adducts  $[\text{Rh}(\text{diphosphine})_2\text{CO}]\text{BF}_4$  are isolated for  $n = 1$  and  $3$ . These complexes are trigonal bipyramidal (TBP) or distorted TBP in solid and solution as determined by  $^{31}\text{P}$  NMR for  $n = 3$  [11,12] and by single crystal X-ray diffraction for  $n = 1$  [12]. In the case of  $n = 4$  (dppb ligand), the reaction of CO with  $[\text{Rh}(\text{dppb})_2]\text{BF}_4$  has been examined and several carbonyl complexes are formed. One of these showed two distinct  $\nu(\text{CO})$  stretching frequencies in the IR and was found to be the binuclear complex  $[\text{Rh}_2(\text{dppb})_3(\text{CO})_4](\text{BF}_4)_2$  in the solid state by single crystal X-ray diffraction (vide infra). It is interesting that only impure samples of “ $[\text{Rh}(\text{dppb})_2\text{CO}]\text{Cl}$ ” have previously been reported and complex  $^{31}\text{P}$  NMR patterns led to uncertain structural conclusions [11]. The X-ray structural characterization of this binuclear complex is reported here. With the exception of one brief abstract [13], to our knowledge this is the first single crystal X-ray structural characterization of a dppb metal complex.

## Experimental

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded at  $40.5\text{ MHz}$  using a Varian Associates XL-100-FT instrument and chemical shifts are referenced to external standard  $85\%\text{ H}_3\text{PO}_4$  with positive shifts ( $\delta$ ) in ppm downfield. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrometer. Hydrated  $\text{Rh}^{\text{III}}$  chloride was obtained on loan from Johnson-Matthey, Inc., and 1,4-bis(diphenylphosphino)butane (dppb) was purchased from Strem Chemicals and used without further purification.

### Synthesis of compounds

$[\text{Rh}(\text{dppb})_2]\text{BF}_4$ .  $\text{Rh}_2\text{Cl}_2(\text{COD})_2$  (COD = 1,5-cyclooctadiene) [14] (140 mg,  $0.57\text{ mmol}$ ) was stirred in  $25\text{ ml}$  of acetone under a purified  $\text{N}_2$  atmosphere. Upon addition of  $\text{AgBF}_4$  (128 mg,  $0.66\text{ mmol}$ ) to this slurry, the rhodium complex dissolved and a white precipitate formed leaving a pale yellow solution. This solution was refluxed for  $30\text{ min}$  and filtered. The filtrate was added to a toluene solution ( $30\text{ ml}$ ) of dppb ( $2.6\text{ g}$ ,  $5\text{ mmol}$ ) giving a dark red solution.

Slow evaporation of the acetone yielded deep red crystals. All manipulations were carried out under a  $N_2$  atmosphere using standard Schlenk techniques.  $[Rh(dppb)_2]BF_4$  may be recrystallized from dichloromethane-diethyl ether solution. The  $PF_6^-$  salt was prepared in a similar manner. Anal. Found: C, 64.65; H, 5.58. Calcd. for  $RhC_{56}H_{56}P_4BF_4$ : C, 64.51; H, 5.38%.  $^{31}P\{^1H\}$  NMR at  $25^\circ C$  (acetone- $d_6$ ):  $\delta$  21.0 ppm, d,  $J(Rh-P) = 137$  Hz \*.

$[Rh_2(dppb)_3(CO)_4](BF_4)_2$ .  $[Rh_2(dppb)_3(CO)_4](BF_4)_2$  was prepared in good yield by bubbling CO through a  $CH_2Cl_2$  solution of  $[Rh(dppb)_2]BF_4$  (100 mg) for 15 minutes. Bright yellow crystals of the product were obtained by layering diethyl ether on top of the  $CH_2Cl_2$  solution in a tube under an atmosphere of CO. Analytically pure samples may be obtained after washing thoroughly with ether to remove dppb and recrystallizing under a CO atmosphere. Anal. Found: C, 59.57; H, 5.22. Calcd. for  $Rh_2C_{88}H_{84}P_6O_4B_2F_8$ : C, 59.73; H, 4.79%. Infrared (KBr disk): 2020, 1965  $cm^{-1}$ . The  $PF_6^-$  salt was synthesized in an analogous manner. In solution this complex readily lost CO so  $^{31}P$  NMR spectra were recorded using acetone solutions saturated with CO.  $^{31}P\{^1H\}$  NMR at  $25^\circ C$  (acetone): broad peaks:  $\delta$  23 and 20 ppm in the presence of some uncoordinated dppb ( $\delta$  -17 ppm, broad) \*. At  $-65^\circ C$  the resonances sharpened and a very complex pattern resulted:  $\delta$  17.6 ppm, d,  $J = 22$  Hz; 20.1, mult; 22.5, mult; 24.6, s; 25.5, s; 26.7, s; 27.5, s; 28.9, s; 30.1, s; 30.9, s; 33.1, s; and free dppb at -19.3, s \*\*.

#### X-ray structure determination

A single crystal of  $[Rh_2(dppb)_3(CO)_4](PF_6)_2$  was mounted inside of a 0.2 mm capillary tube and secured with a small amount of five-minute epoxy resin. The capillary was sealed under one atmosphere of carbon monoxide. The crystal dimensions were  $0.3 \times 0.2 \times 0.2$  mm. The crystal class was determined to be triclinic by the automatic peak searching, centering and indexing programs of the Enraf-Nonius SDP-CAD4 system. The Delaunay reduction of cell parameters did not suggest a higher symmetry space group and successful solution and refinement was achieved using the centric space group  $P\bar{1}$  (vide infra). The unit cell dimensions were determined by least-squares refinement of the angular values of 25 Mo- $K_\alpha$  ( $\lambda = 0.71069$  Å) peaks centered on a CAD4 diffractometer and are  $a = 12.385(2)$ ,  $b = 15.286(2)$ ,  $c = 12.353(4)$  Å,  $\alpha = 99.77(2)$ ,  $\beta = 107.03(2)$ ,  $\gamma = 103.66(1)^\circ$ ,  $V = 2100$  Å<sup>3</sup>. The measured density of 1.48 g/cm<sup>3</sup> (flotation) agrees with the calculated density of 1.492 g/cm<sup>3</sup> using  $Z = 1$  and molecular formula:  $Rh_2P_8C_{88}H_{84}O_4F_{12}$  ( $M = 1887$ ). A total of 7554 unique reflections were measured in the scan range  $2\theta = 0-50^\circ$  on a CAD4 automatic diffractometer using graphite monochromatized Mo- $K_\alpha$  radiation and employing a variable rate  $\omega-2\theta$  scan technique. No decay was noted in the intensity of three check reflections measured at intervals of 200 sequential reflections. After correction for Lorentz, polarization and background but not for absorption ( $\mu = 6.1$  cm<sup>-1</sup>) effects, 5780 reflections were judged observed [ $F_o^2 \geq$

\* The nature of  $[Rh(dppb)_2]BF_4$  in  $CH_2Cl_2$  or acetone solution is uncertain since at low temperatures a very complicated  $^{31}P\{^1H\}$  NMR spectrum is observed; however, in the solid state the cation is four-coordinate with a coordination geometry which is intermediate between square-planar and tetrahedral as determined by single crystal X-ray analysis [15].

\*\* This spectrum was recorded after adding CO to an acetone solution of  $[Rh(dppb)_2]BF_4$ .

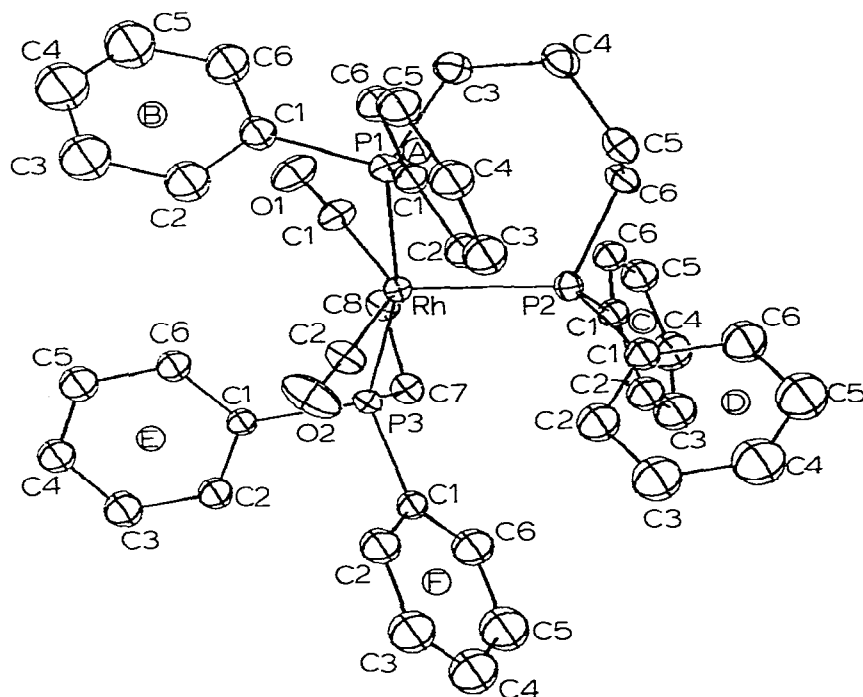


Fig. 1. ORTEP drawing of the molecular structure of  $[\text{Rh}_2(\text{dppb})_3(\text{CO})_4]^{2+}$ . Only the unique part of the structure is shown (an inversion center in the middle of the C8—C8 bond relates this unit to its equivalent counterpart. Ellipsoids are drawn with 30% probability boundaries.

$3.00\sigma(F_0^2)]$  and were used in all subsequent calculations \*. Conventional heavy atom techniques were used to solve the structure, and refinement with all non-hydrogen atoms thermally anisotropic by full-matrix least-squares methods (334 variables), converted  $R$  and  $R_w$  to their final values of 0.060 and 0.086, respectively \*\*. The error in an observation of unit weight was 2.24 using a

\* The intensity data were processed as described in ref. 29. The net intensity  $I$  is given as

$$I = \frac{K}{NPI} (C - TB)$$

where  $K = 20.1166$  (attenuator factor),  $NPI$  = ratio of fastest possible scan rate to scan rate for the measurement,  $C$  = total count,  $B$  = total background count and  $T$  = ratio of total count time to background count time and is 2. The standard deviation in the net intensity is given by

$$\sigma^2(I) = \left( \frac{K}{NPI} \right)^2 [C + 4B + (pI)^2]$$

where  $p$  is a factor used to downweight intense reflections. The observed structure factor amplitude  $F_0$  is given by

$$F_0 = (I/Lp)^{1/2}$$

where  $Lp$  = Lorentz and polarization factors. The  $\sigma(I)$ 's were converted to the estimated errors in the relative structure factors  $\sigma(F_0)$  by

$$\sigma(F_0) = \frac{1}{2} \frac{\sigma(I)}{I} F_0.$$

All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described in ref. 30.

\*\* The function minimized was  $\sum w(|F_0| - |F_c|)^2$  where  $w = 1/\sigma^2(F_0)$ . The unweighted and weighted

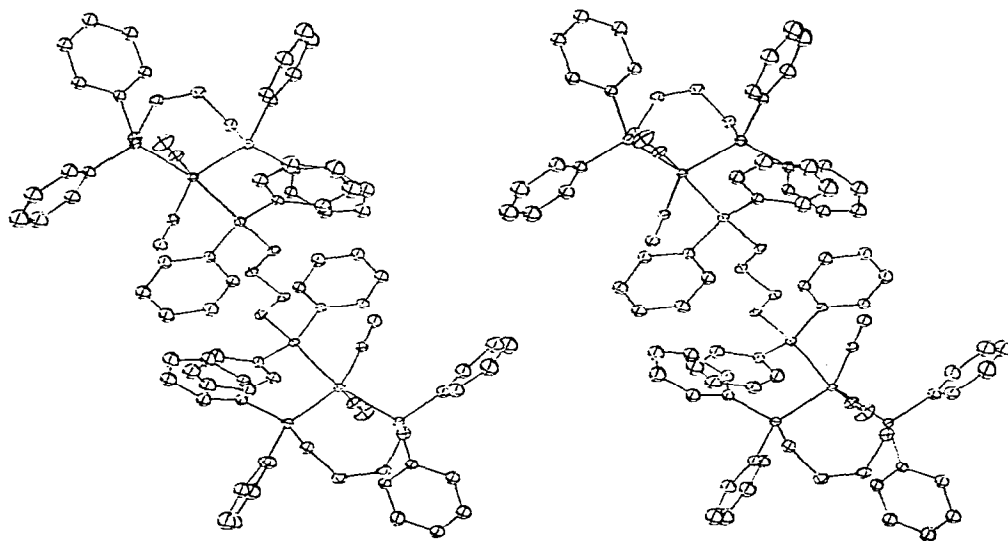


Fig. 2. ORTEP stereoview of  $[\text{Rh}_2(\text{dppb})_3(\text{CO})_4]^{2+}$ .

value of 0.04 for  $p$  in the  $\sigma(I)$  equation. The largest peak in the final difference Fourier map was  $1.3 \text{ e}^-/\text{\AA}^3$  and was located midway between C4D and C5D. No new chemically significant features were noted in this map and since hydrogen positions were not readily located, they were not included in the model.

The final atomic coordinates with their estimated standard deviations and the final thermal parameters are given in Table 1 \*. Scattering factor tables and anomalous dispersion terms (included for all refined atoms) were obtained from ref. 31, Tables 2.2B and 2.3.1, respectively. Hydrogen atoms were not located nor included in any calculations. Figure 1 presents an ORTEP perspective of the asymmetric unit which consists of one-half the molecular formula. The molecule possesses an inversion center in the middle of the bridging dppb ligand. Figure 2 presents an ORTEP stereoview of the entire binuclear molecule.

\* Supplementary material is available from the authors on request.

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residuals are defined as follows:

$$R = (\sum \|F_0\| - \|F_c\|) / \sum \|F_0\|$$

and

$$R_w = [(\sum w(\|F_0\| - \|F_c\|)^2) / (\sum w\|F_0\|^2)]^{1/2}$$

The error in an observation of unit weight is

$$[\sum w(\|F_0\| - \|F_c\|)^2 / (NO - NV)]^{1/2}$$

where  $NO$  and  $NV$  are the number of observations and variables, respectively.

TABLE 1  
POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

| Atom | X          | Y          | Z          | B <sub>11</sub> | B <sub>22</sub> | B <sub>33</sub> | B <sub>12</sub> | B <sub>13</sub> | B <sub>23</sub> |
|------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Rh   | 0.30953(4) | 0.21356(3) | 0.22314(4) | 2.02(1)         | 1.93(1)         | 1.75(1)         | 0.47(1)         | 0.55(1)         | 0.19(1)         |
| P1   | 0.3215(1)  | 0.0620(1)  | 0.2255(1)  | 2.89(5)         | 2.10(5)         | 2.36(5)         | 0.75(4)         | 0.86(4)         | 0.33(4)         |
| P2   | 0.4720(1)  | 0.2637(1)  | 0.1526(1)  | 2.40(5)         | 2.35(5)         | 2.35(5)         | 0.62(4)         | 0.95(4)         | 0.33(5)         |
| P3   | 0.2650(1)  | 0.3563(1)  | 0.2466(1)  | 1.91(4)         | 2.01(5)         | 1.87(5)         | 0.49(4)         | 0.37(4)         | 0.16(4)         |
| P4   | 0.2643(2)  | 0.7308(1)  | 0.3885(2)  | 5.37(8)         | 3.66(7)         | 4.15(8)         | 1.39(6)         | 1.37(7)         | 1.12(7)         |
| F1   | 0.2573(7)  | 0.7823(5)  | 0.5068(6)  | 12.8(4)         | 8.4(4)          | 6.0(3)          | 1.5(3)          | 3.6(3)          | -0.1(3)         |
| F2   | 0.3722(5)  | 0.8184(4)  | 0.4034(6)  | 6.9(3)          | 6.8(3)          | 9.9(4)          | -0.5(2)         | 2.3(3)          | 1.6(3)          |
| F3   | 0.1776(6)  | 0.7804(5)  | 0.3239(7)  | 9.4(3)          | 9.5(3)          | 10.0(4)         | 4.6(2)          | -0.6(3)         | 2.5(3)          |
| F4   | 0.1543(6)  | 0.6470(4)  | 0.3723(7)  | 12.7(4)         | 5.8(3)          | 12.5(4)         | -2.2(3)         | 6.1(3)          | 1.4(3)          |
| F5   | 0.2658(7)  | 0.6827(6)  | 0.2690(5)  | 19.4(4)         | 10.3(4)         | 9.9(3)          | 1.8(3)          | 10.3(2)         | -1.6(3)         |
| F6   | 0.3506(6)  | 0.6849(5)  | 0.4543(9)  | 10.5(3)         | 13.1(3)         | 21.7(6)         | 6.7(2)          | 2.2(4)          | 10.6(3)         |
| O1   | 0.3891(5)  | 0.2425(4)  | 0.4887(4)  | 6.9(3)          | 3.8(2)          | 2.9(2)          | 0.9(2)          | 1.4(2)          | 0.8(2)          |
| O2   | 0.0641(4)  | 0.1152(4)  | 0.0460(6)  | 2.7(2)          | 4.8(2)          | 7.4(4)          | 0.7(2)          | -0.8(2)         | -0.9(3)         |
| C1   | 0.3663(6)  | 0.2356(4)  | 0.3908(5)  | 4.1(2)          | 2.3(2)          | 2.2(2)          | 0.8(2)          | 1.0(2)          | 0.3(2)          |
| C2   | 0.1562(5)  | 0.1545(4)  | 0.1114(6)  | 2.6(2)          | 2.5(2)          | 3.8(3)          | 0.7(2)          | 0.6(2)          | -0.0(2)         |
| C3   | 0.4693(5)  | 0.0498(5)  | 0.2924(6)  | 3.2(2)          | 3.7(2)          | 3.3(3)          | 1.4(2)          | 0.8(2)          | 1.1(2)          |
| C4   | 0.5361(5)  | 0.0333(4)  | 0.2039(7)  | 3.7(2)          | 3.3(2)          | 4.6(3)          | 1.8(2)          | 1.8(2)          | 0.9(2)          |
| C5   | 0.5353(5)  | 0.0987(5)  | 0.1234(6)  | 3.2(2)          | 3.5(2)          | 4.1(3)          | 1.5(2)          | 1.5(2)          | 0.6(2)          |
| C6   | 0.5859(5)  | 0.2043(4)  | 0.1904(6)  | 2.5(2)          | 3.1(2)          | 4.1(3)          | 1.2(2)          | 1.2(2)          | 0.9(2)          |
| C7   | 0.3840(5)  | 0.4620(4)  | 0.3426(5)  | 2.3(2)          | 2.0(2)          | 2.5(2)          | -0.0(2)         | 0.3(2)          | -0.4(2)         |
| C8   | 0.4543(5)  | 0.4516(4)  | 0.4640(5)  | 2.2(2)          | 2.3(2)          | 2.0(2)          | -0.0(2)         | -0.1(2)         | -0.3(2)         |
| C1A  | 0.2533(5)  | -0.0324(4) | 0.0899(5)  | 2.9(1)          |                 |                 |                 |                 |                 |
| C2A  | 0.2236(5)  | -0.0159(5) | -0.0182(5) | 3.3(1)          |                 |                 |                 |                 |                 |
| C3A  | 0.1728(6)  | -0.0937(5) | -0.1208(7) | 4.3(2)          |                 |                 |                 |                 |                 |
| C4A  | 0.1597(6)  | -0.1828(5) | -0.1044(7) | 4.4(2)          |                 |                 |                 |                 |                 |
| C5A  | 0.1908(6)  | -0.1983(5) | 0.0017(7)  | 4.3(2)          |                 |                 |                 |                 |                 |

TABLE 1 (continued)

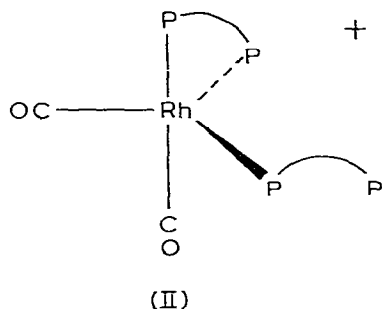
| Atom | X         | Y          | Z          | $B(\text{\AA}^2)$ | Atom | X          | Y         | Z           | $B(\text{\AA}^2)$ |
|------|-----------|------------|------------|-------------------|------|------------|-----------|-------------|-------------------|
| C6A  | 0.2388(6) | -0.1231(5) | 0.1048(6)  | 3.7(1)            | C3D  | 0.2818(8)  | 0.2112(7) | -0.2013(9)  | 6.0(2)            |
| C1B  | 0.2404(5) | 0.0204(5)  | 0.3171(6)  | 3.4(1)            | C4D  | 0.3683(9)  | 0.2106(8) | -0.2501(10) | 7.0(2)            |
| C28  | 0.1151(7) | -0.0114(6) | 0.2689(8)  | 5.0(2)            | C5D  | 0.4834(9)  | 0.2294(7) | -0.1836(9)  | 6.6(2)            |
| C3B  | 0.0491(9) | -0.0408(7) | 0.3400(9)  | 6.5(2)            | C6D  | 0.5198(7)  | 0.2484(6) | -0.0588(8)  | 4.9(2)            |
| C4B  | 0.1119(9) | -0.0375(8) | 0.4560(10) | 7.3(3)            | C1E  | 0.1464(5)  | 0.3529(4) | 0.3100(5)   | 2.4(1)            |
| C5B  | 0.2303(9) | -0.0037(7) | 0.5028(9)  | 6.5(2)            | C2E  | 0.0934(5)  | 0.4229(5) | 0.3056(6)   | 3.2(1)            |
| C6B  | 0.2983(7) | 0.0231(6)  | 0.4351(7)  | 4.8(2)            | C3E  | 0.0057(6)  | 0.4243(5) | 0.3563(7)   | 4.2(1)            |
| C1C  | 0.5661(5) | 0.3846(4)  | 0.2063(5)  | 2.7(1)            | C4E  | -0.0287(6) | 0.3568(5) | 0.4087(7)   | 3.9(1)            |
| C2C  | 0.5475(6) | 0.4498(5)  | 0.1421(7)  | 4.0(1)            | C5E  | 0.0227(6)  | 0.2851(5) | 0.4136(7)   | 4.2(1)            |
| C3C  | 0.6193(7) | 0.5436(6)  | 0.1876(8)  | 5.3(2)            | C6E  | 0.1111(5)  | 0.2813(4) | 0.3619(6)   | 3.2(1)            |
| C4C  | 0.7078(7) | 0.5705(6)  | 0.2957(8)  | 5.0(2)            | C1F  | 0.2068(5)  | 0.3929(4) | 0.1128(5)   | 2.6(1)            |
| C5C  | 0.7265(6) | 0.5058(5)  | 0.3598(7)  | 4.1(1)            | C2F  | 0.1004(6)  | 0.3348(5) | 0.282(7)    | 4.2(1)            |
| C6C  | 0.6548(5) | 0.4137(4)  | 0.3157(6)  | 3.2(1)            | C3F  | 0.0520(8)  | 0.3627(6) | -0.0737(8)  | 5.7(2)            |
| C1D  | 0.4321(5) | 0.2436(4)  | -0.0067(6) | 3.1(1)            | C4F  | 0.1071(8)  | 0.4455(7) | -0.0899(9)  | 6.3(2)            |
| C2D  | 0.3140(6) | 0.2269(5)  | -0.0764(7) | 4.5(2)            | C5F  | 0.2135(9)  | 0.5029(7) | -0.0070(9)  | 6.7(2)            |
|      |           |            |            |                   | C6F  | 0.2626(7)  | 0.4783(6) | 0.0969(7)   | 4.8(2)            |

The form of the anisotropic thermal parameter is:  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$ .

## Discussion

The reaction of CO with  $[\text{Rh}(\text{dppb})_2]\text{X}$  where  $\text{X} = \text{BF}_4$  or  $\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  solution at  $25^\circ\text{C}$  results in the loss of a dppb ligand and the formation of a binuclear dppb-bridged tetracarbonyl complex  $[\text{Rh}_2(\text{dppb})_3(\text{CO})_4](\text{X})_2$ , I, which is isolated in the solid state.  $^{31}\text{P}\{^1\text{H}\}$  NMR at  $-65^\circ\text{C}$  of the resulting yellow solution shows the presence of uncomplexed phosphorous ( $\delta -19.3$  ppm) and a complicated pattern centered at approx.  $\delta 26$  ppm (see Experimental). At room temperature the resonances are broadened due to exchange between coordinated and uncoordinated dppb. The complex  $^{31}\text{P}$  pattern may be due to the presence of several compounds in solution but upon crystallization, induced by adding diethyl ether, the binuclear complex I is obtained along with crystals of dppb. Crystals of I are bright yellow and are obtained in high yield providing all operations are carried out under an atmosphere of CO. This complex is most easily identified by its infrared spectrum which exhibits two strong  $\nu(\text{CO})$  bands (KBr disk, 2020 and  $1965\text{ cm}^{-1}$ ). I contains two TBP  $\text{RhP}_3(\text{CO})_2$  coordination cores with *cis* CO ligands and bridged by a dppb ligand via axial TBP sites (*vide infra*).

It is not surprising that a previous  $^{31}\text{P}$  NMR analysis of this system (as the chloride salt) was inconclusive due to the complexity of the spectra [11]. It is noteworthy that reaction of  $[\text{Rh}_2(\text{COD})_2\text{Cl}_2]$  with CO and two equivalents of diop (diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane) in toluene yields  $[\text{Rh}(\text{diop})_2(\text{CO})_2]\text{Cl}$ , II, which contains one monodentate and one bidentate diop as determined by  $^{31}\text{P}$  NMR and infrared spectroscopy (IR,  $\nu(\text{CO}) = 1974$  and  $1927\text{ cm}^{-1}$ ) [11].



The single crystal X-ray structure of I as the  $\text{PF}_6$  salt has been determined. The crystal structure consists of one binuclear molecule in each centric  $P\bar{1}$  unit cell. The molecule possesses an inversion center in the middle of the bridging dppb ligand backbone. Figures 1 and 2 illustrate the overall molecular geometry. The Rh centers are well separated ( $8.437\text{ \AA}$ ) and therefore will exhibit chemistry characteristic of five-coordinate monomeric complexes. The dications and  $\text{PF}_6$  anions are well separated. The shortest interionic contacts are  $2.973(8)$  and  $3.286(6)\text{ \AA}$  for  $\text{O1}\cdots\text{F6}$  and  $\text{O2}\cdots\text{C2A}$ , respectively. The inner-coordination core of the dication is shown in Fig. 3 along with selected distances and angles. Distances and angles within the dication are presented in Table 2.

The geometry of the coordination core around Rh is close to ideal trigonal



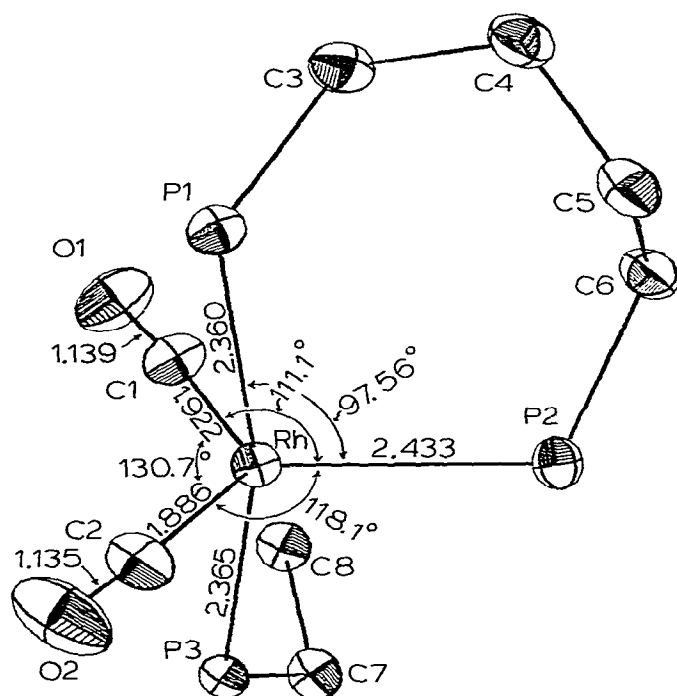


Fig. 3. ORTEP drawing of the coordination core around Rh with selected distances and angles.

TABLE 2

SELECTED DISTANCES AND ANGLES IN  $[\text{Rh}_2(\text{dppb})_3(\text{CO})_4]^{2+}$

| Distances (Å)    |           |                    |          |                       |          |
|------------------|-----------|--------------------|----------|-----------------------|----------|
| Rh-P1            | 2.360(1)  | P1-C3              | 1.843(5) | P3-C7                 | 1.841(4) |
| Rh-P2            | 2.433(1)  | P1-C1A             | 1.839(5) | P3-C1E                | 1.851(4) |
| Rh-P3            | 2.365(1)  | P1-C1B             | 1.817(5) | P3-C1F                | 1.836(4) |
| Rh-C1            | 1.922(5)  | P2-C6              | 1.843(4) | P1-P2                 | 3.606(2) |
| Rh-C2            | 1.886(4)  | P2-C1C             | 1.824(4) | P1-C1                 | 2.884(4) |
| C1-O1            | 1.139(6)  | P2-C1D             | 1.834(5) | P1-C2                 | 2.921(5) |
| C2-O2            | 1.135(5)  | C7-C8              | 1.553(6) | P3-P2                 | 3.580(1) |
| C3-C4            | 1.574(7)  | C8-C8 <sup>a</sup> | 1.560(7) | P3-C1                 | 3.007(5) |
| C4-C5            | 1.525(7)  | C1-C2              | 3.461(7) | P2-C2                 | 3.715(5) |
| C5-C6            | 1.565(6)  |                    |          | P2-C1                 | 3.602(5) |
| Angles (degrees) |           |                    |          |                       |          |
| P1-Rh-P2         | 97.56(4)  | P2-Rh-C1           | 111.1(1) | Rh-P2-C6              | 113.7(1) |
| P1-Rh-C1         | 84.0(1)   | P2-Rh-C2           | 118.1(2) | Rh-P2-C1C             | 119.5(1) |
| P1-Rh-C2         | 86.2(1)   | C1-Rh-C2           | 130.7(2) | Rh-P2-C1D             | 116.1(2) |
| P1-Rh-P3         | 165.70(4) | Rh-P1-C3           | 117.5(1) | Rh-P2-C7              | 118.2(1) |
| P3-Rh-P2         | 96.49(4)  | Rh-P1-C1A          | 120.3(1) | Rh-P3-C1E             | 112.0(2) |
| P3-Rh-C1         | 88.5(1)   | Rh-P1-C1B          | 106.8(1) | Rh-P3-C1F             | 116.9(1) |
| P3-Rh-C2         | 89.6(1)   | C1A-P1-C1B         | 102.4(2) | C1E-P3-C1F            | 102.1(2) |
| Rh-C1-O1         | 173.0(2)  | Rh-C2-O2           | 176.6(5) | C1C-P2-C1D            | 102.6(2) |
| P1-C3-C4         | 114.2(4)  | P2-C6-C5           | 110.8(3) | P3-C7-C8              | 114.8(3) |
| C3-C4-C5         | 115.0(4)  | C4-C5-C6           | 113.6(4) | C7-C8-C8 <sup>a</sup> | 107.9(4) |

<sup>a</sup> Atom C8\* is related to C8 by an inversion center.

TABLE 3

## TABLE OF WEIGHTED LEAST-SQUARES PLANES

The equation of the plane is of the form:  $AX + BY + CZ - D = 0$  where A, B, C and D are constants and X, Y and Z are orthogonalized coordinates

| Plane no. | A       | B       | C       | D       | Atom                  | X       | Y       | Z       | Distance | esd   |
|-----------|---------|---------|---------|---------|-----------------------|---------|---------|---------|----------|-------|
| 1         | 0.4130  | -0.9083 | -0.0667 | -1.4605 | <i>Atoms in plane</i> |         |         |         |          |       |
|           |         |         |         |         | C1                    | 2.2719  | 2.3134  | 4.4602  | 0.000    | 0.006 |
|           |         |         |         |         | C2                    | 0.9736  | 1.9573  | 1.2717  | -0.000   | 0.007 |
|           |         |         |         |         | P2                    | 4.3412  | 3.4540  | 1.7417  | 0.000    | 0.002 |
|           |         |         |         |         | <i>Other atoms</i>    |         |         |         |          |       |
|           |         |         |         |         | Rh                    | 2.2553  | 2.4945  | 2.5470  | -0.044   | 0.000 |
|           |         |         |         |         | O1                    | 2.1747  | 2.1186  | 5.5785  | 0.062    | 0.006 |
|           |         |         |         |         | O2                    | 0.2117  | 1.5713  | 0.5248  | 0.086    | 0.006 |
|           |         |         |         |         | P1                    | 2.9419  | 0.2365  | 2.5741  | 2.289    | 0.002 |
|           |         |         |         |         | P3                    | 1.1045  | 4.5432  | 2.8143  | -2.398   | 0.001 |
| 2         | -0.3319 | -0.0873 | -0.9393 | -3.3672 | <i>Atoms in plane</i> |         |         |         |          |       |
|           |         |         |         |         | Rh                    | 2.2553  | 2.4945  | 2.5470  | 0.009    | 0.000 |
|           |         |         |         |         | P1                    | 2.9419  | 0.2365  | 2.5741  | -0.048   | 0.002 |
|           |         |         |         |         | P2                    | 4.3412  | 3.4540  | 1.7417  | -0.011   | 0.002 |
|           |         |         |         |         | P3                    | 1.1045  | 4.5432  | 2.8143  | -0.039   | 0.001 |
|           |         |         |         |         | <i>Other atoms</i>    |         |         |         |          |       |
|           |         |         |         |         | C1                    | 2.2719  | 2.3134  | 4.4602  | -1.778   | 0.006 |
|           |         |         |         |         | C2                    | 0.9736  | 1.9573  | 1.2717  | 1.679    | 0.007 |
|           |         |         |         |         | O1                    | 2.1747  | 2.1186  | 5.5785  | -2.779   | 0.005 |
|           |         |         |         |         | O2                    | 0.2117  | 1.5713  | 0.5248  | 2.667    | 0.007 |
| 3         | 0.9978  | 0.0648  | -0.0107 | 2.8675  | <i>Atoms in plane</i> |         |         |         |          |       |
|           |         |         |         |         | C1A                   | 2.9294  | -0.7547 | 1.0257  | -0.004   | 0.007 |
|           |         |         |         |         | C2A                   | 2.8931  | -0.1816 | -0.2077 | 0.010    | 0.007 |
|           |         |         |         |         | C3A                   | 2.9159  | -1.0244 | -1.3788 | -0.010   | 0.008 |
|           |         |         |         |         | C4A                   | 3.0160  | -2.3989 | -1.1913 | -0.001   | 0.009 |
|           |         |         |         |         | C5A                   | 3.0731  | -2.9502 | 0.0191  | 0.008    | 0.008 |
|           |         |         |         |         | C6A                   | 2.0229  | -2.1469 | 1.1967  | -0.003   | 0.008 |
|           |         |         |         |         | <i>Other atoms</i>    |         |         |         |          |       |
|           |         |         |         |         | P1                    | 2.9419  | 0.2365  | 2.5741  | 0.056    | 0.002 |
|           |         |         |         |         | <i>Atoms in plane</i> |         |         |         |          |       |
| 4         | 0.3588  | -0.8904 | -0.2801 | 0.2022  | C1B                   | 1.7571  | -0.6600 | 3.6196  | 0.002    | 0.007 |
|           |         |         |         |         | C2B                   | 0.4943  | -0.9856 | 3.0688  | -0.007   | 0.009 |
|           |         |         |         |         | C3B                   | -0.4744 | -1.6381 | 3.8811  | -0.001   | 0.011 |
|           |         |         |         |         | C4B                   | -0.1283 | -1.9421 | 5.2046  | 0.023    | 0.012 |
|           |         |         |         |         | C5B                   | 1.0471  | -1.5822 | 5.7388  | -0.025   | 0.011 |
|           |         |         |         |         | C6B                   | 2.0367  | -0.9788 | 4.9664  | 0.009    | 0.009 |

|             |                |                |        |         |        |       |
|-------------|----------------|----------------|--------|---------|--------|-------|
| 5           | Other atoms    |                |        |         |        |       |
|             | P1             | 2.9419         | 0.2365 | 2.5741  | -0.079 | 0.002 |
|             | Atoms in plane |                |        |         |        |       |
|             | C1C            | 4.8758         | 5.0859 | 2.3553  | 0.005  | 0.006 |
|             | C2C            | 4.6433         | 6.2489 | 1.6223  | -0.001 | 0.008 |
|             | C3C            | 5.0290         | 7.5047 | 2.1410  | -0.004 | 0.010 |
|             | C4C            | 5.6370         | 7.5765 | 3.3752  | 0.000  | 0.009 |
|             | C5C            | 5.8700         | 6.4199 | 4.1080  | 0.007  | 0.008 |
|             | C6C            | 5.4742         | 5.1865 | 3.6039  | -0.008 | 0.007 |
|             | Other atoms    |                |        |         |        |       |
| P2          | 4.3412         | 3.4540         | 1.7417 | -0.047  | 0.002  |       |
| 6           | Atoms in plane |                |        |         |        |       |
|             | C1D            | 4.4963         | 3.6381 | -0.0760 | 0.015  | 0.007 |
|             | C2D            | 3.3464         | 3.6021 | -0.8719 | -0.007 | 0.008 |
|             | C3D            | 3.4561         | 3.7483 | -2.2978 | -0.019 | 0.010 |
|             | C4D            | 4.7066         | 3.8871 | -2.8551 | 0.027  | 0.012 |
|             | C5D            | 5.8231         | 3.9649 | -2.0962 | 0.007  | 0.011 |
|             | C6D            | 5.7535         | 3.8684 | -0.6710 | -0.026 | 0.009 |
|             | Other atoms    |                |        |         |        |       |
|             | P2             | 4.3412         | 3.4540 | 1.7417  | 0.027  | 0.002 |
|             | 7              | Atoms in plane |        |         |        |       |
| C1E         |                | -0.5822        | 4.3012 | 3.5384  | -0.009 | 0.006 |
| C2E         |                | -1.4752        | 5.3534 | 3.4877  | 0.006  | 0.007 |
| C3E         |                | -2.7499        | 5.2203 | 4.0664  | 0.001  | 0.008 |
| C4E         |                | -3.1225        | 4.0595 | 4.6646  | -0.001 | 0.008 |
| C5E         |                | -2.2443        | 2.9795 | 4.7214  | -0.007 | 0.008 |
| C6E         |                | -0.9489        | 3.0791 | 4.1310  | 0.011  | 0.007 |
| Other atoms |                |                |        |         |        |       |
| P3          |                | 1.1045         | 4.5432 | 2.8143  | -0.052 | 0.001 |
| 8           |                | Atoms in plane |        |         |        |       |
|             | C1F            | 0.7350         | 5.4934 | 1.2876  | 0.005  | 0.006 |
|             | C2F            | -0.0676        | 4.8877 | 0.3223  | -0.002 | 0.008 |
|             | C3F            | -0.3984        | 5.6112 | -0.8413 | -0.001 | 0.010 |
|             | C4F            | 0.0433         | 6.8898 | -1.0258 | -0.006 | 0.011 |
|             | C5F            | 0.8541         | 7.4913 | -0.0794 | 0.019  | 0.011 |
|             | C6F            | 1.1745         | 6.8104 | 1.1061  | -0.016 | 0.009 |
|             | Other atoms    |                |        |         |        |       |
|             | P3             | 1.1045         | 4.5432 | 2.8143  | -0.049 | 0.001 |

bipyramidal (TBP) with the two CO ligands occupying equatorial sites. The bridging dppb ligand spans axial sites of the two Rh coordination cores. The Rh atom is within 0.04 Å of the trigonal plane formed by P2, C1 and C2 (see Table 3, plane 1). The L—Rh—L angles within the trigonal plane are 111.1(1), 118.1(2), and 130.7(2)° while the axial—Rh—equatorial angles are 97.56(4), 84.0(1) and 86.2(1)° for P1—Rh—L and 96.49(4), 88.5(1) and 89.6(1)° for P3—Rh—L, all close to ideal TBP values.

The *trans* Rh—P(axial) bond distances (av. 2.363(1) Å) compare favorably with those reported for other rhodium(I) complexes which contain a *trans* P—Rh—P unit (range 2.31–2.37 Å) [12,16–20]. The Rh—P2 distance within the equatorial plane of the TBP is considerably longer (2.433(1) Å). This lengthening probably results from the combined *trans* influence of the two equatorial CO ligands. The Rh—CO distances average 1.904(5) Å which is longer than usually observed in Rh<sup>I</sup> complexes (typically 1.81–1.84 Å) [21–23]; however, this distance is similar to that observed in [Rh(dppm)<sub>2</sub>CO]·BF<sub>4</sub> where dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> [12], the C—O distances (av. 1.137(6) Å) and Rh—C—O angles (av. 174.8(5)°) are normal.

The P1—Rh—P2 chelate bite angle (97.56(4)°) is somewhat larger than values observed in five-coordinate Rh<sup>I</sup> complexes of Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> = dppp. For example, in Rh(Cl)<sub>2</sub>(COPh)(dppp) the chelate bite angle is 94.23(3)° [24]. Within the dppb ligands, the phosphorous—phenyl bond distances range from 1.817(5) to 1.851(4) Å and average 1.834 Å, in good agreement with results from other diphosphine complexes [12,24–27]. The C—P—C angles range from 99.7(2) to 104.0(2) and average 102.5°. This contraction of C—P—C angle from the tetrahedral value of 109.5° is characteristic of metal phosphine complexes [28]. The remaining distances and angles within the dppb ligands are normal. There are no significant differences in bond distances and angles within the two different dppb ligands. The six phenyl rings have normal distances and angles and are planar within experimental error (Table 3).

The PF<sub>6</sub> anion refined to give normal distances and angles. The P—F distances range from 1.528(5) to 1.593(4) Å and average 1.562 Å and the F—P—F angles are consistent with octahedral geometry within experimental error.

The reaction of CO with Rh(diphosphine)<sub>2</sub><sup>+</sup> complexes is surprisingly dependent on the chelate ring size of the diphosphine ligand. The formation of Rh(dppm)<sub>2</sub>(CO)<sup>+</sup> and Rh(dppp)<sub>2</sub>(CO)<sup>+</sup>, the absence of a CO adduct of Rh(dppe)<sub>2</sub><sup>+</sup> (dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>), and the formation of the binuclear complex Rh(dppb)<sub>3</sub>(CO)<sub>4</sub><sup>2+</sup> illustrates the variety of reactivities. Since these CO adducts have also been isolated from the catalytic decarbonylation reaction mixtures containing Rh(diphosphine)<sub>2</sub><sup>+</sup> and benzaldehyde [1,6,7], an understanding of these reactivity differences is important for a determination of the catalytic reaction mechanism. Recent evidence has been obtained which shows that Rh(dppb)<sub>2</sub><sup>+</sup> does not have a simple square-planar geometry in the solid or solution phases (see Experimental) and therefore a detailed study of the stereochemistry of the Rh(diphosphine)<sub>2</sub><sup>+</sup> complexes is being undertaken.

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## References

- 1 D.H. Doughty and L.H. Pignolet, *J. Amer. Chem. Soc.*, **100** (1978) 7083.
- 2 J.-C. Poulin, T.-P. Dang and H.B. Kagan, *J. Organometal. Chem.*, **84** (1975) 87.
- 3 Y. Kawabata, T. Hayashi and I. Ogata, *J. Chem. Soc. Chem. Commun.*, (1979) 462.
- 4 B.R. James and D. Mahajan, *Canad. J. Chem.*, **57** (1979) 180.
- 5 W.S. Knowles, private communication.
- 6 D.H. Doughty, M.F. McGuiggan, H. Wang and L.H. Pignolet, in *Fundamental Research in Homogeneous Catalysis*, Vol. 3, Plenum Press, New York, 1979, 909.
- 7 D.H. Doughty, Ph.D. Thesis, Univ. of Minnesota (1979).
- 8 J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, *J. Amer. Chem. Soc.*, **99** (1977) 8055.
- 9 W.S. Knowles, M.J. Sabacky, B.D. Vineyard and D.J. Weinkauff, *J. Amer. Chem. Soc.*, **97** (1975) 2567.
- 10 B.R. James, R.S. McMillan, R.H. Morris and D.K.W. Wang, *Adv. Chem. Series*, **167** (1978) 122.
- 11 A.R. Sanger, *J. Chem. Soc. Dalton Trans.*, (1977) 120.
- 12 L.H. Pignolet, D.H. Doughty, S.C. Nowicki and A.L. Casalnuovo, *Inorg. Chem.*, **19** (1980) in press.
- 13 W.S. Knowles, *American Crystallographic Assoc.*, **6** (1978), abstract PA1.
- 14 J. Chatt and L.M. Venanzi, *J. Chem. Soc. A*, (1957) 4735.
- 15 L.H. Pignolet and M. Anderson, submitted for publication.
- 16 F. Bachechi, L. Zambonelli and L.M. Venanzi, *Helv. Chim. Acta*, **60** (1977) 2815.
- 17 R. Schlodder and J.A. Ibers, *Inorg. Chem.*, **13** (1974) 2870.
- 18 A.J. Gusev and Y.T. Struchkov, *Z. Strukt. Chim.*, **15** (1974) 282.
- 19 S.J. LaPlaca and J.A. Ibers, *J. Amer. Chem. Soc.*, **85** (1963) 3501.
- 20 P. Singh, C.B. Damman and D.J. Hodgson, *Inorg. Chem.*, **12** (1973) 1335.
- 21 M.M. Olmstead, C.H. Lindsay, L.S. Benner and A.L. Balch, *J. Organometal. Chem.*, **179** (1979) 289 and references therein.
- 22 H. Cowie, *Inorg. Chem.*, **18** (1979) 286.
- 23 C.P. Kubiak and R. Eisenberg, *J. Amer. Chem. Soc.*, **99** (1977) 6129.
- 24 M.F. McGuiggan, D.H. Doughty and L.H. Pignolet, *J. Organometal. Chem.*, **185** (1980) 241.
- 25 H.H. Wang and L.H. Pignolet, *Inorg. Chem.*, **19** (1980) in press.
- 26 M.R. Churchill and S.A. Bezman, *Inorg. Chem.*, **12** (1973) 531.
- 27 W.L. Steffen and G.J. Palenik, *Inorg. Chem.*, **15** (1976) 2432.
- 28 M.R. Churchill and T.A. O'Brien, *J. Chem. Soc. A*, (1968) 2980.
- 29 CAD4 and SDP Users Manual, Enraf-Nonius, Delft, Holland, 1978.
- 30 B.A. Frenz, The Enraf-Nonius CAD4 SDP-A Real Time System for Concurrent X-ray Data Collection and Crystal Structure Determination, in H. Schlenk, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), *Computing in Crystallography*, Delft University Press, Delft, Holland, 1978, pp. 64-71.
- 31 *International Tables for X-ray Crystallography*, Kynoch University Press, Birmingham, 1974, Tables 2.2B and 2.3.1.