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Preliminary communication

STRUCTURAL PREFERENCES AND P—P COUPLING CONSTANTS IN SOME FIVE-COORDINATE COBALT(I) COMPLEXES

R. MASON*, G.R. SCOLLARY**,
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
D.L. DUBOIS*** and D.W. MEEK*
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

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Summary

Phosphorus-31 NMR and X-ray crystallography show that the two similar chelating triphosphine ligands $PhP(CH_2CH_2PPh_2)_2$(2—2-P_3) and $PhP(CH_2CH_2CH_2PPh_2)_2$(3—3-P_3) form cobalt(I) complexes having trigonal-bipyramidal and square-pyramidal structures, respectively. The structures and P—P coupling constants of $[Co(3\text{—}3\text{-}P_3)(P(OMe)_3)CO]BF_4\cdot 1THF$ and $[Co(2\text{—}2\text{-}P_3)(P(OMe)_3)_2]BF_4$ are given, and the change from square-pyramidal geometry in $[Co(3\text{—}3\text{-}P_3)P(OMe)_3)CO]^+$ to trigonal-bipyramidal in $[Co(2\text{—}2\text{-}P_3)(P(OMe)_3)_2]^+$ may be rationalized in terms of a decreased "chelate bite angle" for the $PhP(CH_2CH_2PPh_2)_2$ ligand.

One of the particular advantages of using poly(tertiary phosphine) ligands is that certain coordination stereochemistries become definable through judicious use of such parameters as "chelate bite" angle and sterically demanding substituent groups [1]. With the flexible ligands $PhP(CH_2CH_2PPh_2)_2$ and $PhP(CH_2CH_2CH_2PPh_2)_2$, it is possible to vary the chelate ring size and thereby the chelate bite angle simply by changing the number of methylene groups in the connecting chains.

Our objective here is to delineate the effects which chelate ring size has on the preferred stereochemistries of five-coordinate cobalt(I) complexes. Several cationic species of the types $[Co(triphosphine)(CO)_2]^+$, $[Co(triphosphine)L(CO)]^+$ and $[Co(triphosphine)L_2]^+$ (triphosphine = $PhP(CH_2CH_2PPh_2)_2$(2—2-P_3) or $PhP(CH_2CH_2CH_2PPh_2)_2$(3—3-P_3); L = PPh_3, PEt_3, $PPhMe_2$, PPh_2Me or $P(OMe)_3$) have been synthesized and characterized analytically [2]. Phosphorus-31 NMR

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*To whom correspondence should be addressed.

**Present address: Melbourne State College, 757 Swanston Street, Carlton, 3053 (Australia).

***NDEA Title-IV Predoctoral Fellow, 1971—1974.

on these complexes have provided a large number of phosphorus—phosphorus coupling constants and some indications of their structures in solution [2]. In contrast to the situation with square-planar and octahedral complexes [3—6]*, there is a dearth of information on the magnitudes of P—P coupling constants in non-fluxional five-coordinate complexes. This study provides a definitive correlation between the P—P coupling constants and the structural results for two five-coordinate cobalt(I) complexes.

$[Co(3\text{—}3\text{-}P_3)(P(OMe)_3)CO]BF_4 \cdot 1THF$ crystallizes in the triclinic system (space group $P\bar{1}$) with a 14.310(1), b 11.080(2), c 11.099(3) Å, α 68.30(2)°, β 90.78(2)°, γ 75.04(1)°; $Z = 2$; ρ_{obs} 1.38, ρ_{calc} 1.36 g cm^{-3}. Fourier and least squares methods on 3123 independent integrated reflection intensities (Cu-K_α; automatic diffractometry; $I_o \geq 3\sigma I_o$; and solution of the phase problem by heavy atom methods) have provided atomic positional and thermal parameters with convergence to a present unweighted discrepancy index, R_F, of 0.117. The high discrepancy index reflects an (as yet) inadequate model for the disordered tetrafluoroborate anion and the tetrahydrofuran molecule. The square-pyramidal stereochemistry around cobalt is shown in Fig. 1; estimated standard deviations in the metal—ligand bond lengths average 0.005 Å. The cobalt ion is positioned 0.41 Å above the basal plane defined by the three phosphorus atoms of the triphosphine and the carbon atom of the carbonyl ligand. The three metal—phosphorus bond lengths in the basal plane are not significantly different, in

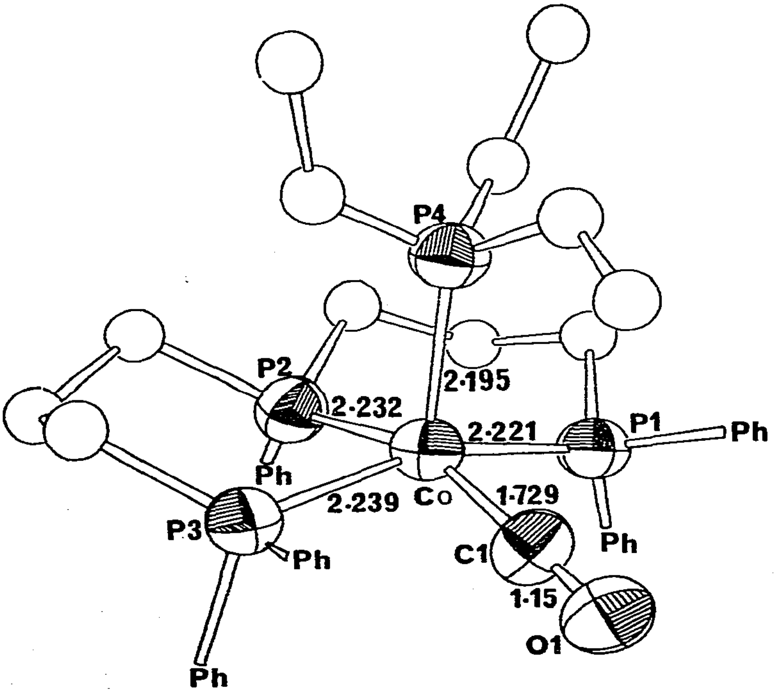

Fig. 1. A perspective of the structure of the square-pyramidal cation $[Co(PhP(CH_2CH_2CH_2PPh_2)_2)(P(OMe)_3\text{-}CO]^+$. Atoms of the phenyl and methylene groups have been omitted for the sake of clarity.

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*Reviews of ^{31}P NMR spectral data on complexes are in ref. 4—6.

contrast to the Rh—P bond distances in the structures of $[Rh(PhP(CH_2CH_2CH_2PPh_2)_2Cl]$ [7] and $[Rh(PhP(CH_2CH_2CH_2PPh_2)_2)Cl(NO)]^+$ [7]. The triphosphine ligand in the two rhodium structures has two essentially *trans* bonds ca. 0.08 Å longer than the "central" Rh—P bond; the *trans* influence, which would have provided for a difference of ~ 0.1 Å between a metal—phosphorus bond *trans* to another phosphorus atom and one *trans* to a weak Lewis base such as a carbonyl ligand, is generally more marked in the heavier transition metals. Also, the magnitude of the structural *trans* influence in octahedral and square-planar complexes may not be directly transferable to distorted square-pyramidal complexes. The two bite angles are 89.2(2)° compared to 90.3 and 90.7°, respectively, for the two rhodium complexes. Both chelate rings have chair conformations (as in the two rhodium complexes). In fact, the chelate ring has a very similar conformation to that of *cis*-decalin; torsion angles of the chelate rings are between 41 and 71°.

Occupation of the apical site in the $[Co(3\text{—}3\text{-}P_3)(P(OMe)_3)CO]^+$ cation by the trimethylphosphite ligand is, at first consideration, surprising. Calculations by Rossi and Hoffmann [8] have shown that a strong π-acceptor ligand should prefer the apical site of a square pyramid for an $L_{ap}\text{—}M\text{—}L_{ba}$ angle greater than ca. 100°. In our case, the angles lie between 98.6(2)° and 107.6(5)°. Generally, carbon monoxide is assumed to be a stronger π-acceptor ligand than trimethylphosphite. Although we realize that our mixed ligand complex is of lower symmetry than that used by Rossi and Hoffmann in their calculations, it seems reasonable to conclude that either the π-acceptor nature of these two ligands is reversed or steric effects dictate that the larger ligand occupies the apical site.

$[Co(2\text{—}2\text{-}P_3)(P(OMe)_3)_2]BF_4$ crystallizes in the monoclinic system (space

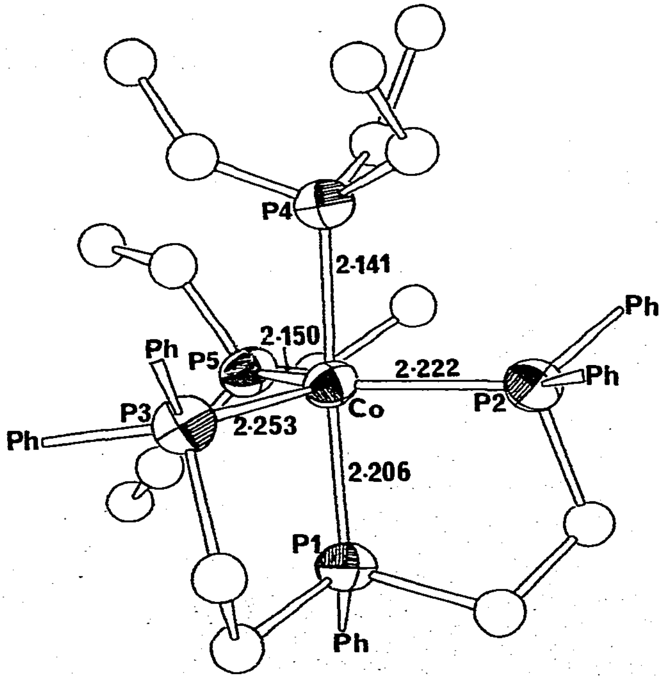

Fig. 2. A perspective of the structure of the trigonal-bipyramidal cation $[Co(Ph(PCH_2CH_2PPh_2)_2)(P(OMe)_3)_2]^+$. Atoms of the phenyl and methylene groups have been omitted for clarity.

group $P2_1/c$) with a 13.18(4), b 11.49(3), c 29.66(6) Å and β 101.59(2)°; $Z = 4$. The diffraction analysis was based on the integrated intensities of 2256 reflections (Mo-K_α; automatic diffractometry; $I_o \geq 3\sigma(I_o)$; and solution of the phase problem by the symbolic addition method). The refinement was similar to that described above and has converged to an unweighted discrepancy index, R_F, of 0.100.

The geometry of the cation is effectively trigonal bipyramidal, as shown in Fig. 2; the average estimated standard deviations in the Co—P bond lengths is 0.007 Å. The cobalt is displaced from the trigonal plane by 0.09 Å towards the axial phosphite group. The two Co—P (phosphite) bond lengths are not significantly different. Although the axial Co—P (chelate) bond is shorter than the two equatorial Co—P (chelate) bonds, there is a difference of 0.03 Å (4σ) in the equatorial Co—P (chelate) bond lengths. The mean bite angle is 85.0(2)° and this compares favourably with the mean value of 84.7° in [Ni(2—2-P_3)$(NCS)_2$]*. Within the equatorial plane, the P—Co—P angles are between 111.2(2) and 126.0(2)°. The two chelate rings adopt different conformations. One, involving

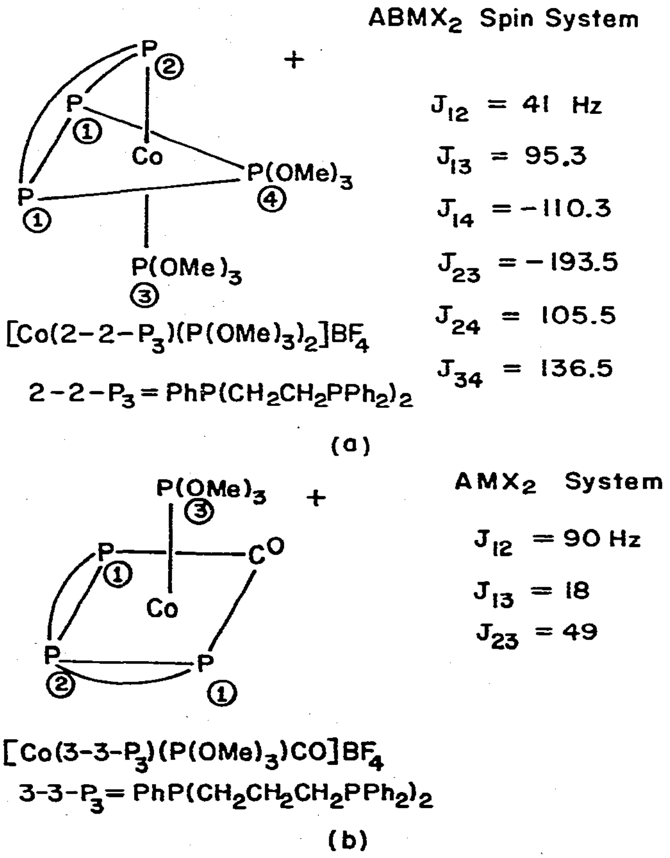

Fig. 3. A structural representation and J(PP) values of [Co(2—2-P_3)$(P(OMe)_3)_2$]BF_4 (a) and [Co(3—3-P_3)-$(P(OMe)_3)$CO]BF_4 (b).

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[*] At the present stage of refinement (R_F 0.065), the bond lengths are Ni—P (central) 2.152 and Ni—P (terminal) 2.244 and 2.220 Å [9].

the P(1)—Co—P(3) unit, approximates the standard envelope conformation, whereas the P(1)—Co—P(2) system is twisted with the two carbon atoms being displaced equally above and below the mean plane of the cobalt and two phosphorus atoms.

The change from square-pyramidal coordination geometry in [Co(3—3-P_3)-($P(OMe)_3$)CO$]^+$ to trigonal-bipyramidal in [Co(2—2-P_3)($P(OMe)_3)_2]^+$ can be attributed partly to the decrease in chelate bite angle. As a consequence of the smaller bite angle in 5-membered chelate rings, the central phosphorus atom must either be pulled in close to the metal in a square-pyramidal geometry (as would appear to be the case in [Ni(2—2-P_2)$(NCS)_2$] [9] or be free to adopt a position more equivalent to the terminal phosphorus atoms as in a trigonal-bipyramidal geometry.

On the basis of ^{31}P NMR data, other cobalt(I) complexes in the three series [Co(triphosphine)$(CO)_2]^+$, [Co(triphosphine)L(CO)$]^+$, and [Co(triphosphine)$L_2]^+$ appear to adopt either a square-pyramidal or a trigonal-bipyramidal structure depending on whether the triphosphine ligand is 3—3-P_3 or 2—2-P_3, respectively. Figure 3 gives the P—P coupling constants and the structural locations of the different phosphorus nuclei in [Co(2—2-P_3)($P(OMe)_3)_2$]BF_4 (Fig. 3a) and [Co(3—3-P_3)($P(OMe)_3$CO]BF_4 (Fig. 3b). The largest P—P coupling in [Co(2—2-P_3)-($P(OMe)_3)_2$]BF_4 involves a *trans* coupling along the axis of the trigonal bipyramid; however, the *cis* couplings J_{34}, J_{13}, and J_{24} are also relatively large. Additional ^{31}P NMR and structural studies are being undertaken to investigate other factors that affect the structural preference and the J(PP) values in five-coordinate complexes of flexible polyphosphine ligands.

Acknowledgments

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