

Structural Studies on Some Potential 20- and 22-Valence Electron Complexes of Platinum(0)

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There are few exceptions to the "18-electron rule"¹ which summarizes the stoichiometry of many coordination complexes based on low-valent transition metal ions. The new compounds (triphos)(biphos)Pt(0) and (triphos)₂Pt(0) (triphos = CH₃C(CH₂PPh₂)₃, biphos = Ph₂PCH₂CH₂CH₂PPh₂) are nominally 20- and 22-electron species, respectively; these complexes can be synthesized readily by treating an aqueous ethanol solution of PtCl₂(triphos) with one equivalent of the appropriate tertiary phosphine ligand and an excess of sodium borohydride. We have investigated the solid state and/or solution stereochemistries of (triphos)(biphos)Pt(0) and (triphos)₂Pt(0) in order to comment on the validity of the noble gas rule for low-valent complexes containing strong Lewis bases (e.g., phosphines) as ligands.

Crystals of {CH₃C(CH₂PPh₂)₃}₂Pt (from benzene) are triclinic with *a* = 15.018(5), *b* = 25.937(9), *c* = 22.722(8) Å, α = 104.16(2)°, β = 115.80(2)°, γ = 88.65(2)°; space group = A $\bar{1}$ with Z = 4. The X-ray diffraction analysis was based on the integrated intensities of 4783 independent reflections, (MoK α automatic diffractometry, I₀ ≥ 3σ(I₀), solution of the phase problem by conventional heavy atom methods), a least squares refinement of atomic coordinates, anisotropic Debye–Waller factors for the platinum and phosphorus atoms and isotropic thermal parameters for the carbon atoms (the twelve phenyl rings being refined as rigid bodies with carbon–carbon bond distances of 1.40 Å and regular six-fold symmetry) converging to an unweighted discrepancy index, R_F, of 0.084.

Figure 1 shows the essential stereochemistry and demonstrates that the complex has an 18-valence electron structure, since only two of the three phosphorus atoms of each triphosphine ligand are coordinated to the platinum; the coordination geometry around platinum is a distorted tetrahedron. The mean "bite angle" (i.e., P–Pt–P) of the chelating ligands is 97.0(3)°, a value which could have been reasonably

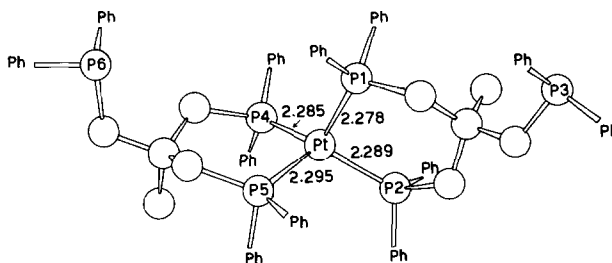
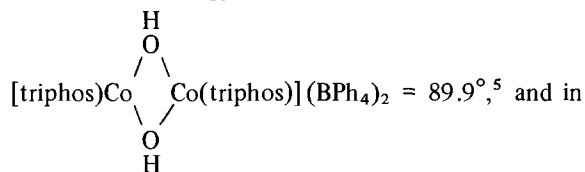


Fig. 1. The structure of {CH₃C(CH₂PPh₂)₃}₂Pt(0). Atoms of the phenyl groups have been omitted for reasons of clarity. Estimated standard deviations in the Pt–P bond lengths average 0.008 Å.

anticipated from steric considerations to have been larger than that observed in related complexes of triphos, e.g., the mean value of the P–M–P angles in (triphos)NiI = 94.3,² in (triphos)Ni(C₂F₄) = 92.5°,³

in [(triphos)Fe–H–Fe(triphos)]⁺ = 88.8°,⁴ in



[Co(CH₃CO₂)(triphos)](BPh₄) = 91.0°.⁵ The remaining chelate bond angles are 115.7(3)° for P(1)–Pt–P(4), 106.7(3)° for P(1)–Pt–P(5), 125.6(3)° for P(2)–Pt–P(4) and 114.4(3)° for P(2)–Pt–P(5). The axially distorted coordination geometry is maintained in solution, as the ³¹P n.m.r. spectrum has a singlet at +168.4 ppm⁶ and a multiplet centered at +155.2 ppm, the latter being consistent with an A₂B₂ pattern which has been computer-simulated using the iterated n.m.r. parameters; δ_A = 153.00 ppm; δ_B = 157.4; J_{AB} = 49.5 Hz. The main A₂B₂ multiplet has satellite peaks due to phosphorus coupling with ¹⁹⁵Pt (33.7% natural abundance, I = 1/2) which are maintained over the temperature range –60 to +70 °C in toluene. The sharp singlet, which has no ¹⁹⁵Pt coupling, is due to the two "dangling" or non-coordinated phosphorus atoms P(3) and P(6), their chemical shift being close to the value of the free ligand (+166.6 ppm). The ³¹P n.m.r. spectrum of the compound Pt(Ph₂PCH₂CH₂CH₂PPh₂)₂, which has unsubstituted six-membered chelate rings, shows, relatedly, the four coordinated phosphorus atoms to be magnetically equivalent (singlet at +151.2 ppm⁶ with ¹⁹⁵Pt satellites at room temperature (Fig. 2), whereas below –60 °C the sharp signal broadens until it gives an A₂B₂ pattern at –115 °C similar to that of (triphos)₂Pt. Thus, in the case of (triphos)₂Pt, the

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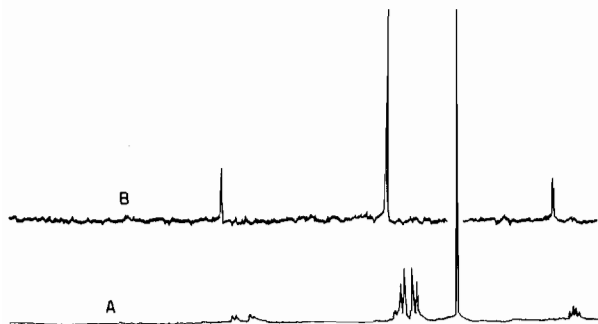


Fig. 2. (A) The ^{31}P n.m.r. spectrum of $(\text{triphos})_2\text{Pt}(0)$ in benzene at room temperature; (B) ^{31}P n.m.r. spectrum of $(\text{biphos})_2\text{Pt}(0)$ in benzene at room temperature; triphos and biphos = $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, respectively.

dangling $-\text{CH}_2\text{PPh}_2$ group restricts the conformational flexibility of the chelate chain and reduces the effective symmetry below T_d , even in solution at room temperature.

The chelate rings have chair conformations, whereas in the nickel complexes^{2,3} they are described as having a "flexible" or a twist-boat arrangement. The difference can be related to the coordination mode of the ligand; when it functions as a tridentate ligand, the metal-triphosphine unit is a tricyclic system that has a close structural analogy to [2,2,2]-bicyclo-octane, whose conformation it approximates.

The mean platinum-phosphorus bond length of 2.287(8) Å is similar to those observed in tris(triphenylphosphine)platinum(0) (where the bond lengths vary between 2.25 and 2.28 Å⁷ and in bis(tricyclohexylphosphine)platinum(0), where the mean Pt-P distance is 2.23 Å,⁸ the mean Pt-P bond length in more than twenty complexes of the type $(\text{L})\text{Pt}(\text{PPh}_3)_2$ (L = alkene, alkyne, etc.) is 2.28 Å.⁹ Also, the 2.28 Å bond length is typical for Pt(II)-P(phosphine) bonds when there is no strong *trans*-influence due to the remaining ligands.¹⁰ We shall demonstrate elsewhere that these small variations can be accounted for simply in terms of the "s" electron character of the metal-phosphorus bonds¹¹ and that the apparent shortening of metal-phosphorus bond lengths due to metal to ligand

π -bonding, even in zerovalent metal complexes, has been overemphasized in the past.

The ^{31}P n.m.r. spectrum of the twenty valence electron complex $(\text{triphos})(\text{biphos})\text{Pt}(0)$ has a sharp singlet at 168.3 ppm⁶ and a multiplet at 152.1 ppm. The spectrum indicates that triphos again functions as a bidentate ligand in the presence of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$. We conclude, generally, that polydentate ligands with stereochemical flexibility and strong Lewis base properties do not give low-valent metal complexes that do not satisfy the eighteen-electron rule. Those proven exceptions, such as nickelocene, possess ligands which, for steric and electronic reasons, do not require the highest filled molecular orbitals to be strongly antibonding with respect to the metal-ligand bonds.

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- 6 ^{31}P Chemical shifts are relative to trimethylphosphite, positive numbers being reported as upfield from the standard $(\text{MeO})_3\text{P}$.
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