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Preparation and X-Ray Crystal Structure of Pyrazolide-bridged Binuclear Complex of Platinum Containing Metalated Tri-t-butyl Phosphine

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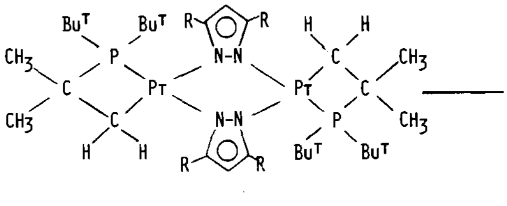
Various recent studies have shown that the chemistry of metal complexes of tertiary phosphines is markedly affected by the steric effects of the substituents on the phosphorus atom [1]. Thus, the stabilization of low coordination complexes has been made possible by the use of ligand bulk, and stable ML_2 complexes (M = Pd, Pt; L = bulky phosphines), have been isolated [2–9]. Recently, we have prepared some bis(tri-t-butylphosphine) platinum and palladium complexes of the type $MH(X)Bu_3{}^tP)_2$ (M = Pt, Pd; X = Cl, Br, I, CF_3CO_2 [10, 11] and $PtH_2(Bu_3{}^tP)_2$. The existence of these complexes is surprising because they contain two tri-t-butylphosphines (cone angle 182°) (*1*); ligand intermeshing or the phenomenon [12] of variable cone angle which gives a minimum cone angle of 130° for $Bu_3{}^tP$ presumably account for this. Not surprisingly these complexes were found to undergo rapid intramolecular metalation in solution giving the internally metalated complexes, $MX(Bu_2{}^tPCMe_2CH_2)(Bu_3{}^tP)$ (*1*). Here we describe the reaction of this complex *1* (M = Pt and X = Cl) with pyrazole leading to the formation of the corresponding pyrazolide-bridged binuclear complex containing the metalated tri-t-butyl phosphine.

$$[Pt_2Cl_2Bu_2{}^tPCMe_2CH_2)_2] + 2C_3H_2R_2N_2 \xrightarrow{2NaOH}$$



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(R = H or CH_3).

When a solution of 2 mol equivalent of sodium hydroxide is added to a suspension of chloro-bridged binuclear complex (*1*) mixed with pyrazole or 3,5-dimethylpyrazole in 1:2 molar ratio in methanol, a clear solution forms within a few minutes, which then produces a crystalline white solid on prolonged reaction (1–2 hr, eqn. 1). The solid analyzes for $[Pt_2(Bu_2{}^tPCMe_2CH_2)_2(PZ)_2]$ (*2*) (PZ = $C_3H_3N_2$ or $C_5H_7N_2$).

The proton NMR spectrum of the complex (*2*) (R = CH_3) shows six sets of doublets at δ 1.38 (JPH = 11.6 Hz) and 1.56 (JPH = 12.7 Hz) (due to t-butyl protons, $PBu_2{}^t$), δ 1.47 (JPH = 12.3 Hz) and 2.15 (JPH = 14.0 Hz) (due to methyl protons; P-CMe_2) and δ 1.55 (JPH = 12.4 Hz) and 1.85 ppm (JPH = 13.8 Hz) (due to methylene protons; P–C–CH_2) in approximate ratios 9:3:0.7. The platinum satellite signals of the methylene protons could not be determined due to overlapping with other signals. The two sets of doublets due to each of the t-butyl and methyl groups are of equal intensity. Similarly, the signals due to the methyl protons of the 3,5-dimethyl pyrazole are also found as two equally intense singlets. These data suggesting the presence of either two isomers of the complex in equal proportions or, more likely, the chemical non-equivalence of these groups within the same metalated phosphine due to different chemical environments. The ^{31}P NMR spectrum shows only one sharp singlet due to the metalated phosphine ($\delta P = -11.06$ ppm; JPtP = 3124 Hz), suggesting the presence of only one isomeric species. The magnetic non-equivalence of the two t-butyl groups, methyl groups and methylene protons of the same phosphine ligand is probably a consequence of the non-planarity of the chelate ring. Upon construction of the molecular models, indeed it has been found that in comparison with the starting chloro-bridged complex, (*1*), the symmetry is lower in the pyrazolide-bridged complex (*2*), where no plane of symmetry could be found to contain all P, C and Pt atoms. As a consequence, the two unmetalated t-butyl groups and also the methyl groups are magnetically non-equivalent. In a *trans*-complex (*2*), the methyl groups of the bridging pyrazolato- groups will also be non-equivalent. In order to obtain more definitive evidence for the configuration of the dimer (*2*), an X-ray crystal structure determination was carried out.

The complex crystallizes in the orthorhombic system, space group Pbca with eight formula units per unit cell; the lattice constants are *a* = 26.949(3), *b* = 16.917(3), *c* = 17.065(3) Å. Intensity data were

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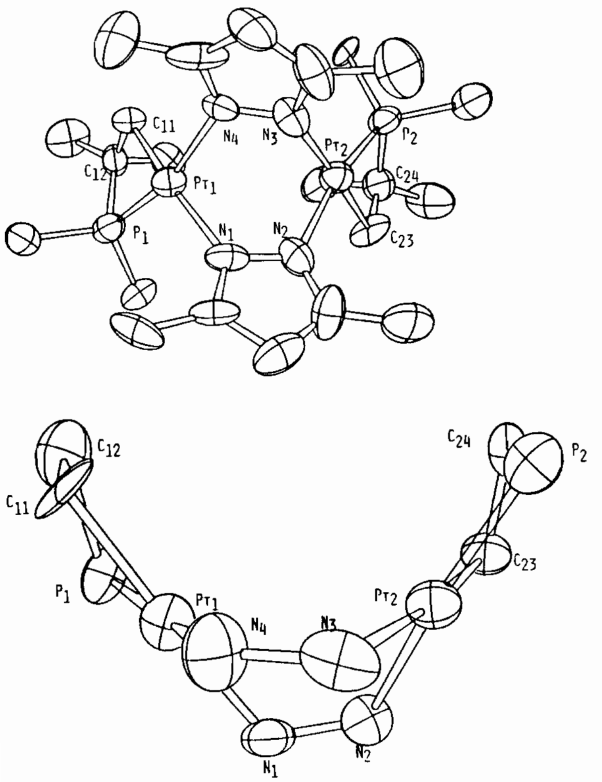

Figs. 1 and 2. ORTEP drawings of the complex $[Pt_2(C_5H_7N_2)_2(Bu_2{}^tPCMe_2CH_2)_2]$. The methyl carbons of the non-metalated t-butyl groups are omitted for clarity. Principal bond lengths (Å) are: Pt1–P1 = 2.224(7), Pt1–N1 = 2.159(18), Pt1–C11 = 2.038(20), Pt1–N4 = 2.095(18), P1–C12 = 1.864(23), C11–C12 = 1.561(29), N1–N2 = 1.388(27), N3–N4 = 1.381(25), Pt2–N2 = 2.065(19), Pt2–N3 = 2.079(18), Pt2–P2 = 2.207(6), Pt2–C23 = 2.080(23), P2–C24 = 1.891(27), C23–C24 = 1.534(36); and angles (°): N1–Pt1–P1 = 109.4(0.5), C11–Pt1–P1 = 69.8(0.6), C11–Pt1–N1 = 172.6(0.8), N4–Pt1–P1 = 164.0(0.5), N4–Pt1–N1 = 86.6(0.7), N4–Pt1–C11 = 94.5(0.8), C12–P1–Pt1 = 87.4(0.7), C12–C11–Pt1 = 103.2(1.3), C11–C12–P1 = 90.6(1.3), N2–N1–Pt1 = 116.4(1.4), Pt2–N2–N1 = 122.0(1.4), N3–Pt2–N2 = 82.9(0.8), N3–Pt2–P2 = 110.8(0.5), C23–Pt2–N2 = 96.5(0.9), P2–Pt2–N2 = 166.2(0.6), C23–Pt2–P2 = 69.9(0.7), C23–Pt2–N3 = 176.3(0.8), C24–P2–Pt2 = 88.6(0.8), C23–C24–P2 = 91.2(1.6).

collected on a $P2_1$ four-circle automated diffractometer with MoKα-radiation. A total of 6938 independent reflections were measured. Intensities were corrected for Lorentz, polarization and absorption effects. The structure was determined by heavy-atom techniques and refined by full-matrix least squares procedures. The final conventional R value is 0.080.

A perspective view of the molecule (*2*) is presented in Fig. 1 where the most relevant atoms are labeled. Figure 2 demonstrates that the six membered-ring formed by the two-pyrazolide groups bridged between two platinums, is in the boat form and the metalated t-butyl phosphine chelates are away from the pyrazolate groups.

In the compound the two Pt atoms are four-coordinated and are surrounded in a distorted square-planar fashion by two nitrogens of the pyrazolato-groups and phosphorus and carbon atoms of metalated phosphine. In the molecule, the two phosphorus may be considered in *sym–trans* positions. As proposed above, the chelate rings of the metalated phosphine are not planar and thus the t-butyl groups, methyl groups and methyl protons are magnetically non-equivalent. The bond distance of 2.159 Å between Pt1–N1 (nitrogen *trans* to carbon) is observed to be longer than that of Pt1–N4 (2.095 Å; nitrogen *trans*- to phosphorus) indicating the higher *trans*- effect of carbon compared to that of phosphorus.

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