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X-Ray Crystal Structures of Dinuclear Platinum(II) and Palladium(II) Complexes containing Metallated Tri-tert-Butylphosphine $[MCl(Bu^t_2PCMe_2CH_2)]_2$ (M = Pt or Pd)

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The intramolecular metallation occurring by the oxidative addition of metals such as platinum or palladium to carbon–hydrogen bonds of the sterically bulky tertiary alkyl- or arylphosphines has been studied extensively in recent years [1–4]. This process is believed to be promoted by the formation of five membered rings which presumably relieves the steric crowding resulting from the presence of the bulky phosphine ligands. Recently, we described the intramolecular metallation of tri-tert-butylphosphine in platinum(II) and palladium(II) hydride complexes leading to the formation of chloro-bridged dinuclear complexes $[MCl(Bu^t_2PCMe_2CH_2)]_2$ [5, 6], *1* (where M = Pt or Pd). We have used these dinuclear complexes in the formation of a variety of new mixed ligand mononuclear complexes [*e.g.*, MCl(P–C)L [7–9]; M(π-C_5H_5)(P–C); Pt(σ-C_5H_5)(P–C)L [10]; $\{Pt(P–C)L'L''\}^+$ [11]] and dinuclear complexes [*e.g.*, $M_2Cl(OCH_3)(P–C)_2$ [12, 13]; $M_2(Pz)_2(P–C)_2$ [14]; $Pt_2(H)_2(P–C)_2$ [15]]. In view of the importance of complexes *1*, we decided to characterize them by X-ray crystallography and the results are being presented here.

The chloro-bridged platinum dimer, *1* (M = Pt), was prepared in high yield from the reaction of $PtCl_2(PhCN)_2$ with tri-tert-butylphosphine in methylene chloride according to the method we reported earlier [8]. The complex was recrystallized from benzene/hexane to give colorless crystals. The palladium dimer was obtained from the metallation reaction of PdH(Cl)(PBu^t_3)$_2$ in CH_2Cl_2 and recrystallized from CH_2Cl_2/hexane [8].

X-Ray Crystal Data

Unit cell parameters and intensity data were obtained using a Syntex $P2_1$ four-circle diffractometer. A semi-empirical absorption correction using ψ0 scans was applied to the measured intensities. Sheldrick's SHELX-76 program was used for solution and refinement of the structure. The temperature factors of all non-hydrogen atoms were refined anisotropically. Hydrogen positions were either calculated by the program or located from difference Fouriers. Their temperature factors were refined isotropically.

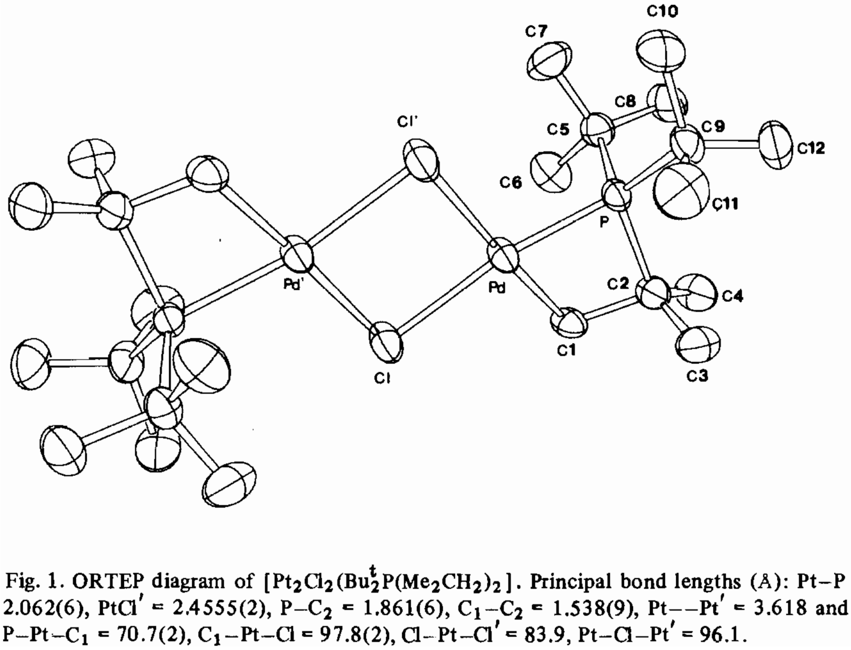

Fig. 1. ORTEP diagram of $[Pt_2Cl_2(Bu^t_2P(Me_2CH_2)_2]$. Principal bond lengths (Å): Pt–P = 2.187(2), Pt–Cl = 2.409(2), Pt–C_1 = 2.062(6), PtCl$'$ = 2.4555(2), P–C_2 = 1.861(6), C_1–C_2 = 1.538(9), Pt––Pt$'$ = 3.618 and bond angles (°): P–Pt–Cl = 168.3(1), P–Pt–C_1 = 70.7(2), C_1–Pt–Cl = 97.8(2), Cl–Pt–Cl$'$ = 83.9, Pt–Cl–Pt$'$ = 96.1.

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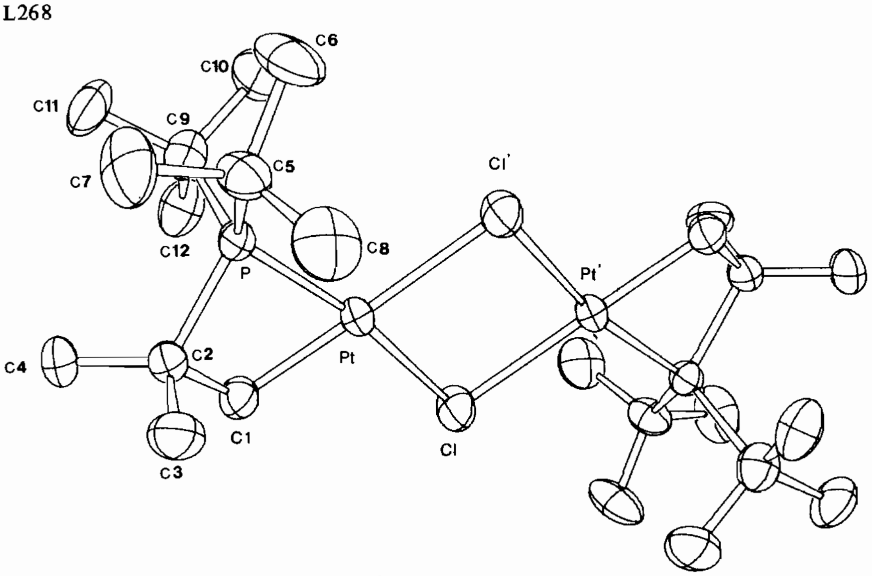

Fig. 2. ORTEP diagram of $[Pd_2Cl_2(Bu^t_2PCMe_2CH_2)_2]$. Principal bond lengths (Å): Pd–Cl = 2.469(1), Pd–P = 2.207(1), Pd–C_1 = 2.058(4), Pd–Cl = 2.427(1), P–C_2 = 1.889(4), C_1–C_2 = 1.565(5), Pd––Pd′ = 3.554, and bond angles (°): P–Pd–Cl′ = 107.2(0), C_1–Pd–Cl′ = 177.1(1), C_1–Pd–P = 70.1(1), Cl–Pd–Cl′ = 86.9, Pd–Cl–Pd′ = 93.1.

$[PtCl(Bu^t_2PCMe_2CH_2)]_2$

The complex crystallized in the monoclinic space group $P2_1/C$ with a = 7.702(3), b = 15.101(3), c = 13.433(3) Å; β = 105.30(2)°; Z = 2 (MoKα radiation). The structure was solved using conventional heavy-atom techniques and refined to a final R_F of 0.029 for 2670 reflections having $F \geqslant 3\sigma_F$ and 145 variable parameters.

The complex is a dimer located about a crystallographically imposed inversion center. The four membered chelating ring is observed to be non-planar. The bridging chlorines are bound assymmetrically to the platinums with the two unique Pt–Cl distances differing by 0.046 Å which is explainable on the basis of the relative *trans*-influence of a σ-bonded carbon atom and coordinated phosphorus. Pertinent bond distances and angles are presented in Fig. 1.

$[PdCl(Bu^t_2PCMe_2CH_2)]_2$

Monoclinic, a = 7.710(3), b = 15.198(3), c = 13.411(3) Å, β = 105.66(2)°; Z = 2. This dimer is also located about a crystallographically imposed inversion center, with a space group $P2_1/C$. 2677 reflection intensities (MoKα; $F \geqslant 3\sigma_F$) with 145 variable parameters, formed the basis of X-ray structure analysis (solved by conventional heavy-atom techniques) which converged to R_F = 0.033.

The four membered chelating ring of metallated phosphine is observed to be non-planar. The relative *trans*-influence of the σ-bonded carbon atom and the coordinated phosphorus is reflected in the non-equivalent palladium–chlorine bridge bonds which differ by 0.042 Å. Pertinent bond distances and angles are given in Fig. 2.

Upon comparing the structures of the platinum and palladium dimers, it is clearly observed that these are isomorphous structures (both have the same space group with similar unit cell dimensions). Interestingly, however, some of the bond distances in palladium dimers are observed to be slightly bigger than that of platinum. For example, Pd–Cl (2.427) > Pt–Cl (2.409), Pd–Cl′ (2.469) > Pt–Cl′ (2.455) and Pd–P (2.207) > Pt–P (2.187). Another interesting difference was observed in the 300 mHz proton NMR spectra of these complexes recorded in $CDCl_3$. Although the structures of both the complexes show non-planar four member metallated phosphine rings, no effect of this non-planarity can be observed in the ^1H NMR spectrum of the palladium complex. The proton NMR spectrum of palladium complex consists of only three sets of doublets at δ 1.54 ppm (JPH = 1.40 Hz), 1.45 ppm (JPH = 14.0 Hz) and 1.08 ppm (JPH = 2.6 Hz) in 9:3:1 ratios, due to tertiary butyl (P–Bu^t_2), methyl (C–Me_2) and methylene (Pd–CH_2) protons respectively. This suggests that in solution the non-planar nature of the ring does not create any non-equivalency in the protons of these groups. On the other hand, the platinum complex shows a complicated spectrum which consists of at least three sets of doublets due to t-butyl and methyl protons at δ 1.51 ppm (JPH = 13.6 Hz), 1.48 ppm (JPH = 13.6 Hz) and 1.43 (JPH = 14.3 Hz) and one quartet (AA′XX′ spin system) at δ 1.38 ppm (JPH = 7.4 Hz) due to methylene protons. This pattern implies that the non-planarity of the ring causes the non-equivalence in the t-butyl, methyl and methylene groups' protons. This difference in the proton NMR of the platinum and palladium is probably due to the labile nature of the palladium phosphine complex [8].

References

1 G. W. Parshall, *Acc. Chem. Res., 3,* 139 (1970); *8,* 113 (1975).

2 C. E. Jones, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.,* 992 (1974);
M. D. Empsall, P. N. Heys and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 257 (1978) and references therein.

3 A. J. Cheney, B. E. Mann, B. L. Shaw and R. M. Slade, *J. Chem. Soc., A,* 3833 (1971);
R. Mason, M. Textor, N. Al-Salem and B. L. Shaw, *J. Chem. Soc., Chem. Commun.,* 292 (1976).

4 A. J. Cheney and B. L. Shaw, *J. Chem. Soc., A,* 754, 860 (1972).

5 H. C. Clark, A. B. Goel, R. G. Goel and W. O. Ogini, *J. Organometal. Chem., 157,* C16 (1978).

6 H. C. Clark, A. B. Goel, R. G. Goel, S. Goel and W. O. Ogini, *Inorg. Chim. Acta, 31,* L441 (1978).

7 H. C. Clark, A. B. Goel, R. G. Goel and S. Goel, *Inorg. Chem., 19,* 3220 (1980).

8 H. C. Clark, A. B. Goel and S. Goel, *Inorg. Chem., 18,* 2803 (1979).

9 A. B. Goel, S. Goel and H. C. Clark, *Syn. React. Inorg. Metal-Org. Chem., 11,* 289 (1981).

10 A. B. Goel, S. Goel, D. VanDerveer and H. C. Clark, *Inorg. Chim. Acta, 53,* L117 (1981).

11 A. B. Goel, S. Goel and H. C. Clark, *Inorg. Chem.* (submitted for publication).

12 H. C. Clark and A. B. Goel, *J. Organometal. Chem., 178,* C27 (1979).

13 A. B. Goel and S. Goel, *Trans. Met. Chem., 5,* 378 (1980).

14 H. C. Clark, A. B. Goel and S. Goel, *Can. J. Chem.* (in press).

15 H. C. Clark, A. B. Goel and R. G. Goel, *J. Am. Chem. Soc.* (in press).