Syntheses of Palladium(0) and Platinum(0) Olefin Complexes; Molecular Structures of $[Pt(C_2F_4)(C_2H_4)_2]$ and Tris(bicyclo[2.2.1]heptene)platinum

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Summary The syntheses of $[Pt(C_2F_4)(C_2H_4)_2]$, $[M(C_7H_{10})_3]$ (M = Pd, Pt; C_7H_{10} = bicyclo[2.2.1]heptene), $[Pd(1,5\text{-}C_8H_{12})_2]$, $[Pd(C_2H_4)_{3\text{ or }4}]$ and $[ML(C_2H_4)_2]$ (M = Pd, L = PCy_3; M = Pt, L = PMe_3, PCy_3, Cy = cyclohexyl) are described, and a trigonal planar geometry is established for the complexes $[Pt(C_2F_4)(C_2H_4)_2]$, $[M(C_7H_{10})_3]$, and $[Pt(PMe_3)(C_2H_4)_2]$.

Recently we described a new synthesis of bis(cyclo-octa-1,5-diene)platinum and its ready conversion into tris(ethylene)platinum.[1] We now report structural studies on three-co-ordinate species, and the use of $Li_2C_8H_8$ to prepare tris(bicyclo-2.2.1-heptene)palladium and bis(cyclo-octa-1,5-diene)palladium.

From a theoretical study Hoffmann and Rösch[2] predicted that the complex $[Ni(C_2H_4)_3]$ would adopt a trigonal-planar structure. Structural confirmation of this prediction rested on a single crystal *X*-ray diffraction study[3] of tris(bicyclo[2.2.1]heptene)nickel. Since a structural study of our related $[Pt(C_2H_4)_3]$ presented difficulties, one of the ethylenes was displaced with tetrafluoroethylene in petroleum ether solution to give the more stable species tetrafluoroethylenebis(ethylene)platinum (I) [^1H n.m.r. (CF_3Ph, −25°) τ 6·60 (s with ^{195}Pt satellites, J_{PtH} 45 Hz), ^{19}F n.m.r. (C_6D_6–toluene −30°; rel. CCl_3F) 123·6 p.p.m. (s with ^{195}Pt satellites, J_{PtF} 248 Hz), ^{13}C n.m.r. (C_6D_6–toluene; rel. Me_4Si) −65·9 p.p.m. ($^{13}CH_2{=}CH_2$, ^1H decoupled, J_{PtC} 38 Hz) and −100·8 p.p.m. ($^{13}CF_2{=}CF_2$, ^{19}F decoupled, J_{PtC} 470 Hz); at −80 °C the ^{13}C spectrum was unchanged].

Crystal data: monoclinic, $A2/a$, $Z = 4$, $a = 8{\cdot}884(4)$, $b = 7{\cdot}552(2)$, $c = 12{\cdot}934(6)$ Å; $\beta = 109{\cdot}51(3)°$; $R = 0{\cdot}085$ for 765 reflections (Syntex $P2_1$ four circle diffractometer).

The three olefinic double bonds (Figure 1) lie in the co-ordination plane of the platinum atom with Pt–C distances for Pt–C(F_2) and Pt–C(H_2) at 1·97(3) Å and 2·25(3) Å, respectively. Although within 2 e.s.d.'s of each other at the current stage of refinement the C=C bond lengths reflect the variation in Pt–C distances, being 1·44(4) Å in the co-ordinated C_2F_4 and 1·36(4) in the C_2H_4.

In order to confirm the molecular geometry of the species $[M(olefin)_3]$, tris(bicyclo[2.2.1]heptene)platinum (II) [white crystals, m.p. 144—145° decomp., ^1H n.m.r. (C_6D_6) τ 6·64 (s with ^{195}Pt satellites, C*H*=C*H*, J_{PtH} 64 Hz), 7·04 (s, C*H*), 8·44 (complex m, CH_2·CH_2) and 9·76 (AB system, bridging CH_2); ^{13}C n.m.r. (C_6D_6) −28·6 p.p.m. (H-*C*, J_{PtC} 44 Hz), −39·5 (bridging CH_2, J_{PtC} 49Hz), −42·8 ($CH_2{\cdot}CH_2$, J_{PtC} 14 Hz) and −68·0 (CH=CH, J_{PtC} 189 Hz)] was synthesized by treating bis(cyclo-octa-1,5-diene)platinum with bicyclo[2.2.1]heptene, or more directly by reaction of $[PtCl_2(1,5\text{-}C_8H_{12})]$ with $Li_2C_8H_8$ in Et_2O in the presence of excess bicyclo[2.2.1]heptene.

In the molecular structure of (II) (Figure 2) [*Crystal data:*

orthorhombic, $P2_12_12_1$, $Z = 4$, a = 5·720(1), b = 10·740(4), c = 28·771(12) Å; R = 0·106 for 1695 reflections] the double bonds of the three bicyclo[2.2.1]heptene ligands lie in the co-ordination plane of the platinum atom, at a mean Pt–C distance of 2·22(3) Å. The maximum deviation from this plane is currently 0·06 Å. The bridgehead carbon atoms C(7) and C(21) lie 2·3 Å to one side of this plane, and the third bridgehead carbon C(14) is 2·3 Å on the opposite side, all lying approximately 3·2 Å from the platinum atom. The C=C bonds have a mean bond length of 1·38(4) Å, which is essentially the same as found for co-ordinated ethylene in (I). The remaining C–C bond lengths in the co-ordinated bicyclo[2.2.1]heptene ligands are those expected for singly bonded carbon atoms. The average dihedral angle at the bend of the C_7 rings, *i.e.* between planes C(1),C(2),C(3),C(6) and C(3),C(6),C(5),C(4) *etc.*, is 105°.

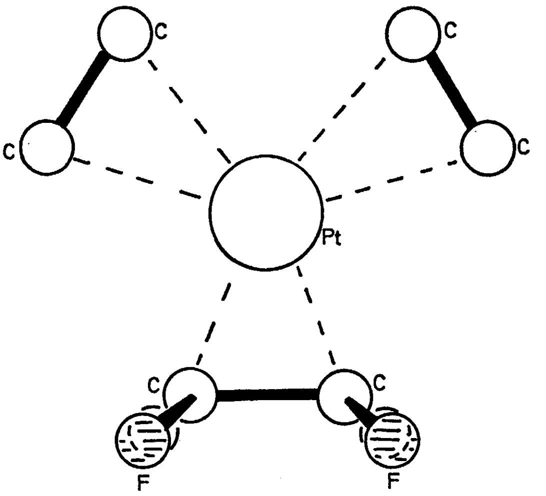

FIGURE 1 Molecular structure of [$Pt(C_2F_4)(C_2H_4)_2$]

Reaction (−30°) of [$PdCl_2(1,5\text{-}C_8H_{12})$] with $Li_2C_8H_8$ in Et_2O in the presence of excess bicyclo[2.2.1]heptene gave white crystals of tris(bicyclo[2.2.1]heptene)palladium (III),[4] stable in the solid state at 0°, except under vacuum. In solution, (III) decomposes to palladium metal unless an excess of ligand is present. Crystals of (III) have the same morphology as the platinum complex (II), and *X*-ray photographs indicate they are not only isomorphous but also isostructural. Cell constants are almost identical and the space group is also $P2_12_12_1$ with four molecules per unit cell [a = 5·705(1), b = 10·784(5) and c = 28·770(15) Å].

Thus in both of the 3-co-ordinate species (I) and (II) where Pt^0 is stabilised by olefinic ligands with different steric and electronic requirements, and also in the case of the Pd^0 complex (III), a trigonal planar structure is preferred.

Reaction (−40°) of [$PdCl_2(1,5\text{-}C_8H_{12})$] with a solution ($Et_2O$) of $Li_2C_8H_8$ in the presence of excess ethylene and cyclo-octa-1,5-diene gave after filtration and evaporation (low temperature) white crystals of the sparingly soluble complex bis(cyclo-octa-1,5-diene)palladium(IV).[4] Treatment of (IV) with bicyclo[2.2.1]heptene gave (III). Ethylene (1 atm., −30°) displaces cyclo-octa-1,5-diene from (IV), as was observed[1] with [$Pt(1,5\text{-}C_8H_{12})_2$], to give a highly reactive white crystalline complex (V), showing a ^1H n.m.r. resonance ([$^2H_8$]-toluene, −60°) at τ 6·62(s). This complex is probably tris(ethylene)palladium,[4] although present evidence does not exclude its formulation as [$Pd(C_2H_4)_4$]. Addition of tricyclohexylphosphine to (V) gave tricyclohexylphosphine-bis(ethylene)palladium (VI) [^1H n.m.r. resonance ([$^2H_8$]-toluene, −35°) at τ 6·79 (s, $CH_2{=}CH_2$)].

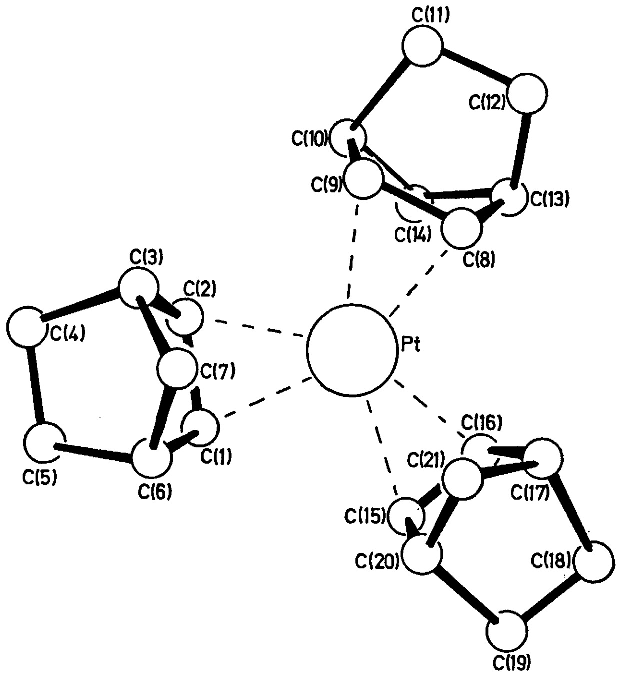

FIGURE 2 Molecular structure of [$Pt(C_7H_{10})_3$].

A similar reaction with tris(ethylene)platinum and one molar equivalent of tricyclohexylphosphine or trimethylphosphine gave respectively crystalline complexes, tricyclohexylphosphinebis(ethylene)platinum(VII) [^1H n.m.r. (C_6H_6, 35°) τ 7·22 (s with ^{195}Pt satellites, $CH_2{=}CH_2$, J_{PtH} 58 Hz) and 8·42 (br.m)] and trimethylphosphinebis(ethylene)platinum(VIII) [^1H n.m.r. (C_6H_6, 35°) τ 7·32 (s with ^{195}Pt satellites, $CH_2{=}CH_2$, J_{PtH} 57 Hz) and 8·78 (d with ^{195}Pt satellites, PMe_3, J_{PtH} 8·5 Hz, J_{PtH} 21·5 Hz), ^{13}C n.m.r. ([$^2H_8$]-toluene, C_2H_4 resonances only, +30°) −36·7 p.p.m. (s with ^{195}Pt satellites, J_{PtC} 152 Hz); at −40° two resonances were observed at −33·6 p.p.m. (d with ^{195}Pt satellites, J_{PC} 15·0 Hz, J_{PtC} 158 Hz) and −38·6 p.p.m. (d with ^{195}Pt satellites, J_{PC} 6·0 Hz, J_{PtC} 137 Hz)].

These observations show that at room temperature (VIII) [and presumably (VI) and (VII)] is a fluxional molecule, where it is likely the co-ordinated ethylene rotates about an axis through the metal and perpendicular to the C–C bond. The low temperature ^{13}C spectrum of (VIII) shows that the 'frozen out' structure is again a trigonal planar arrangement. It is interesting to note that the activation energy for ethylene rotation in (I) is clearly lower than in (VIII).

(*Received, 24th March* 1975; *Com.* 353.)

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[3] C. Kruger and Y. H. Tsay, Abstracts VIth Internat. Conference Organometallic Chemistry (Amherst) **1973**, 80; see K. Fischer K. Jonas, and G. Wilke, *Angew. Chem. Internat. Edn.*, **1973**, **12**, 565.

[4] This complex was obtained using palladium atoms in an independent study by R. M. Atkins, R. Mackenzie, P. L. Timms, and T. W. Turney, to be published.