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Preliminary communication

An unusual cyclopropenyl complex. The formation and structure of $[Pt\{C_3(C_6H_5)_3\}\{P(C_6H_5)_3\}_2][PF_6]\cdot C_6H_6$

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SUMMARY

Addition of $(C_3Ph_3)(PF_6)$ in CH_2Cl_2 to a benzene solution of $Pt(C_2H_4)(PPh_3)_2$ gives $[Pt(C_3Ph_3)(PPh_3)_2][PF_6]$ which is shown by X-ray diffraction to be a complex containing a localized cyclopropenyl ring system.

The π-aromatic triphenylcyclopropenyl cation, $C_3Ph_3^+$, has proven to be a versatile ligand[1] in its reactions with transition metal complexes. In compounds[2] such as $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3Ph_3)$ the three-membered carbocyclic ring bonds to the nickel atom in a symmetrical fashion. However, when this cation is added to the reactive d^8 species *trans*-$IrCl(CO)[P(CH_3)_3]_2$ a C–C bond in the cyclopropenium ring is cleaved to form the Ir^{III} adduct $Ir(C_3Ph_3)Cl(CO)[P(CH_3)_3]_2^+$. Herein we report the preparation and crystal structure determination of $[Pt(C_3Ph_3)(PPh_3)_2][PF_6]\cdot C_6H_6$ in which the $C_3Ph_3^+$ moiety coordinates in a different manner than previously reported.

When a stoichiometric quantity of $(C_3Ph_3)(PF_6)$ in CH_2Cl_2 is added to a benzene solution of $Pt(C_2H_4)[P(C_6H_5)_3]_2$ an orange complex results. Recrystallization from a C_6H_6/CH_2Cl_2 mixture affords single crystals of $[Pt\{C_3(C_6H_5)_3\}\{P(C_6H_5)_3\}_2][PF_6]\cdot C_6H_6$. (Anal. Found: C, 59.82; H, 4.04; Pt, 17.72; P, 8.17. $PtC_{57}H_{45}P_3F_6$ calcd.: C, 60.40; H, 3.98; Pt, 17.20; P, 8.20%.)

Crystals of this complex occur in the monoclinic space group $P2_1/n$. The unit cell contains four molecules and has the dimensions $a = 12.276(2)$, $b = 24.148(3)$, $c = 18.491(1)$ Å, β 91.22(1)°. Intensity data were collected by the moving-crystal, moving-counter technique using Cu-K_α radiation ($2\theta_{Cu\text{-}K_\alpha} \leqslant 110°$). The intensities were corrected for absorption and the transmission coefficients ranged from 0.21 to 0.36. Standard heavy

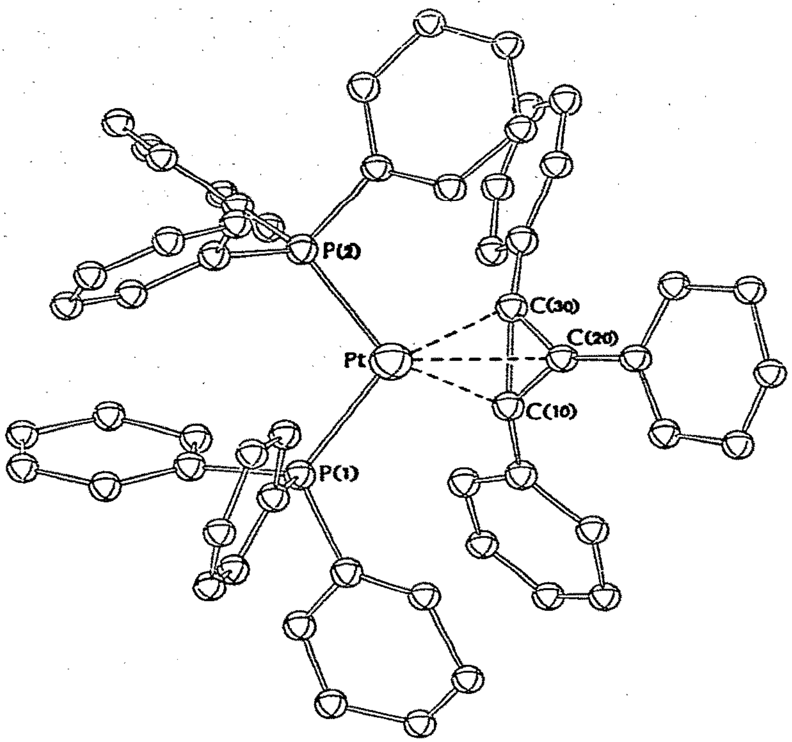

Fig. 1. The $[Pt(C_3Ph_3)(PPh_3)_2]^+$ ion. Some pertinent angles and their standard deviations are: P(1)–Pt–P(2), 104.5(1)°; C(10)–Pt–C(30), 44.2(5)°; P(1)–Pt–C(10), 106.6(3)°; P(2)–Pt–C(30), 104.3(3)°; C(10)–C(20)–C(30), 69.1(9)°; C(20)–C(30)–C(10), 54.7(8)°; C(20)–C(10)–C(30), 56.2(8)°.

atom techniques were used to solve the structure. Full-matrix least-squares refinement has led to a current value for R of 0.079 where $R = \Sigma || F_o | - | F_c || / \Sigma | F_o |$.

Figure 1 gives a view of the cation. A dihedral angle of 6.8° was found between the Pt,P(1),P(2) and the Pt,C(10),C(30) portions of the molecule. However, a mean molecular plane can be defined by atoms P(1),P(2),Pt,C(10) and C(30) since none of these atoms deviates by more than 0.15 Å from this plane. Atom C(20) of the cyclopropenyl ring lies 0.95 Å above this essentially planar portion of the molecule. The C_3 ring is roughly perpendicular to the Pt,P(1),P(2) plane as evidenced by the dihedral angle of 111° found between these two segments of the molecule. The Pt–P(1) and Pt–P(2) distances of 2.285(3) Å and 2.322(3) Å respectively are in the middle of the range[3] found for phosphorus to Pt^0 and Pt^{II} bonds.

Perhaps the most interesting feature of this molecule is the unsymmetrical relationship of the C_3 ring to the metal. Carbon atoms C(10) and C(30) are equidistant from the platinum atoms (Pt–C(av.) = 2.09(1) Å) while the Pt–C(20) distance of 2.48(1) Å indicates a much weaker platinum–carbon interaction. The former two Pt–C bond lengths compare favorably with the average value[4] of 2.11(1) Å in the platinum(0)-1,2-dimethylcyclopropene adduct, $Pt(C_3H_2Me_2)(PPh_3)_2$. As in other metallocenes of this type, unequal metal—carbon interactions are mirrored[5] in the C—C distances. The C(10)—C(30) distance of 1.58(2) Å is significantly longer than the average value of 1.39(2) Å (C(10)—C(20) = 1.38(2) Å and C(20)—C(30) = 1.40(2) Å) determined for the other two bond lengths in the three-membered ring. This latter distance is essentially equal to the distance[6] of 1.373(5) Å in the uncomplexed cation, $(C_3Ph_3)(ClO_4)$. Moreover, the C(10)—C(30) distance is comparable to the coordinated C—C double bond length of 1.50(2) Å determined in the cyclopropene[4] complex $Pt(C_3H_2Me_2)(PPh_3)_2$.

We suggest that both the coordination geometry of the C_3 ring and the lengthening of the C(10)—C(30) bond can best be described using the model for bonding of olefins[7][★] to zerovalent transition metals. If we assume that the major bonding interactions involve atoms Pt,P(1),P(2),C(10) and C(30) and that the C_3 ring occupies one coordination position then there is trigonal symmetry around the platinum(0) atom. Using this scheme, we find that $[Pt(C_3Ph_3)(PPh_3)_2]^+$ can be regarded as a complex of a localized double bond in the cyclopropenyl ring. This is in contrast to the trihapto complexes[2] $(h^3\text{-}C_3Ph_3)Ni(h^5\text{-}C_5H_5)$ and $(h^3\text{-}C_3Ph_3)NiCl(Py)_2$, Py = pyridine, which involve a delocalized cyclopropenyl ring system. It should be recognized that the above description is an approximation. An alternative to this view would be to consider this compound as a π-allyl complex. However, because of the C—C and Pt—C bond length patterns we deem the allyl description to be less appropriate.

Finally, it is interesting to note that when $C_3Ph_3^+$ is added to the coordinatively unsaturated d^8 complex, *trans*-$IrCl(CO)[P(CH_3)_3]_2$, carbon—carbon bond cleavage occurs whereas no ring fission and concomitant oxidation takes place in the reaction of this carbocyclic ring with the d^{10} complex $Pt(C_2H_4)(PPh_3)_2$.

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