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Preliminary communication

PREPARATION OF *cis*-BIS-ACETYLENE-BIS(PENTAFLUOROPHENYL)-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES. CRYSTAL STRUCTURE OF *cis*-[Pt(C_6F_5)$_2$ (PhC≡CPh)$_2$]

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Summary

Treatment of *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, Pt; THF = tetrahydrofuran) with PhC≡CPh has given the novel bis-acetylene-palladium(II) and -platinum(II) complexes *cis*-[M(C_6F_5)$_2$(PhC≡CPh)$_2$]; these are stable even though there seems to be no significant π-back bonding according to the X-ray structure of the platinum complex.

Palladium(II) and platinum(II) acetylene complexes are very rare and are usually prepared by displacement of olefins from palladium(II) complexes [1] or of olefins or halides from the corresponding platinum complexes [2]. We report here the syntheses of two stable bis-acetylene complexes of palladium and platinum, viz. *cis*-[M(C_6F_5)$_2$(dpa)$_2$] (M = Pd, Pt; dpa = diphenylacetylene).

Treatment of dichloromethane solutions of *cis*-[M(C_6F_5)$_2$(OC_4H_8)$_2$] (M = Pd, Pt; OC_4H_8 = tetrahydrofuran) [3] with diphenylacetylene (dpa) gives bis-acetylene derivatives which on evaporation of the solution crystallize as white solids (eq. 1).

$$cis\text{-}[M(C_6F_5)_2(OC_4H_8)_2] + 2\ dpa \rightarrow 2\ cis\text{-}[M(C_6F_5)_2(dpa)_2] + 2\ OC_4H_8 \qquad (1)$$

(1 : M = Pd;
2 : M = Pt)

Satisfactory analytical results have been obtained for both complexes [4]. They are non conducting in solution. The IR spectra show two absorptions

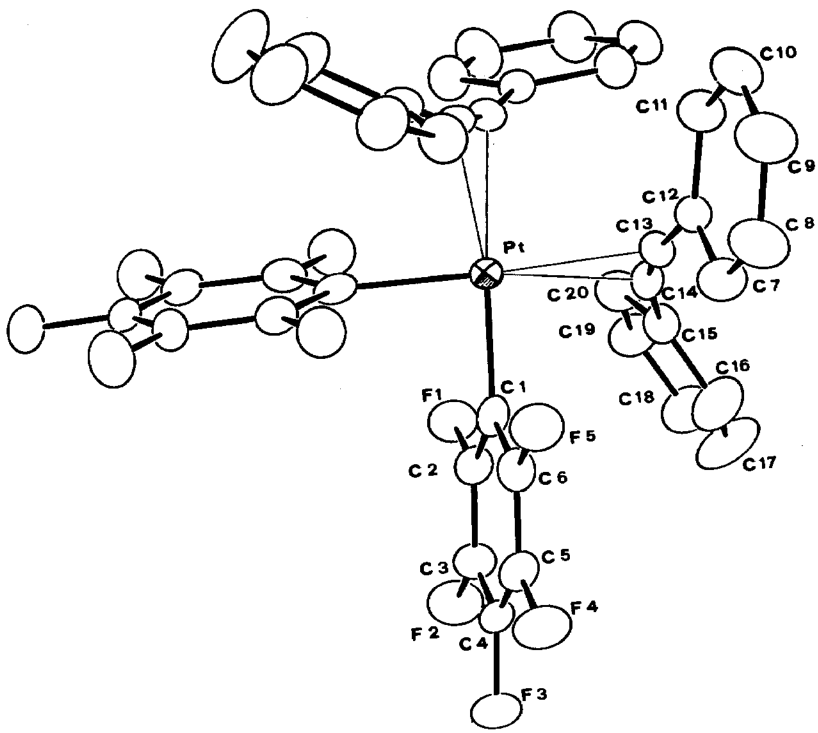

Fig. 1. ORTEP diagram of 2. Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond distances (Å) and angles (°) Pt—C(1), 2.0477(25); Pt—C(13), 2.311(4); Pt—C(14), 2.264(5); C(13)—C(14), 1.197(6); C(12)—C(13), 1.449(5); C(14)—C(15), 1.451(6). C(1)—Pt—C(1′), 86.62(10); C(12)—C(13)—C(14), 167.5(5); C(13)—C(14)—C(15), 165.2(5).

which may be assigned to the X-sensitive mode of the C_6F_5 groups (1 790s, 779s; 2 805s, 795s cm^{-1}) in agreement with a *cis*-arrangement of the two pentafluorophenyl groups [5]; however, the stretching mode $\nu(C{\equiv}C)$, which if observed would be in the range 2050—1600 cm^{-1} [6], is not seen.

The structure of 2 was determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained by slow diffusion of a n-hexane solution of dpa into a solution of *cis*-$[Pt(C_6F_5)_2(OC_4H_8)_2]$ (molar ratio 2/1) at room temperature [7]. The molecular structure is shown in Fig. 1. The molecule possesses a crystallographically-imposed C_2 axis bisecting, and in the plane of, the C(1)—Pt—C(1)′ angle. The coordination around platinum is almost square-planar, since the metal atom, the α carbon atoms of the pentafluorophenyl rings (C(1), C(1)′) and the mid points (C(0), C(0)′) of the C≡C bonds are only 0.0000(1), −0.0181(25), 0.0181(25), 0.103(7), −0.103(7) Å, respectively, away from the appropriate weighted least-squares plane. The C≡C triple bond is inclined to the normal to this plane by 21.39(28)°. The angle between both C≡C bonds is 142.84(38)°. The distances Pt—C(1) or Pt—C(1)′ are 2.0477(25) Å similar to those found for other pentafluorophenylplatinum derivatives [8, 9]. Distances Pt—C(13) and Pt—C(14) are 2.311(4) and 2.264(5) Å, respectively. The C≡C distance is 1.197(6) Å, the same as for the free PhC≡CPh (1.19 Å) [10] and the coordinated acetylene is almost linear, with angles C(14)—C(13)—C(12) and C(15)—C(14)—C(13) of 167.5(5) and 165.2(5)°, respectively. These data suggest that no significant π-back bonding is present.

Although no X-ray crystal structures of dpa-Pt^{II} or dpa-Pd^{II} complexes have been previously reported, structural data for other platinum(II) acetylene derivatives also point to negligible π-back bonding [11—14] whereas for dpa-Pt^0 complexes [15, 16], in which there is a better π-donor center, there are much greater modifications of the C≡C distance and the C≡C—C angles as a consequence of the better π-back bonding.

Studies of the syntheses of some new bis-acetylene-palladium(II) or -platinum(II) complexes and of the reactivity of some metal-acetylide compounds towards *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ are in progress, and a comprehensive theoretical study of the bonding capabilities of the *cis*-$[M(C_6X_5)_2]$ fragment is in hand.

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.