

Diphenylacetylene as a Variable Electron Donor: Syntheses and X-Ray Crystal Structures of $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{MeCN})(\text{PMe}_3)_3]\text{BPh}_4$ and $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$

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Two cationic cobalt(II) complexes were prepared as their BPh_4 -salts by the reaction of diphenylacetylene with $\text{CoBr}(\text{PMe}_3)_3$ in the presence of NaBPh_4 ; diphenylacetylene behaves as a 2-electron donor in $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{MeCN})(\text{PMe}_3)_3]\text{BPh}_4$ isolated from acetone–acetonitrile mixtures, but as a 4-electron donor in $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ obtained from acetone.

Structural characterization of the alkyne ligands and the metal–alkyne linkage in transition-metal complexes is of considerable interest because of its applications in catalytic chemistry. Although a few structures have been reported,¹ there is still uncertainty surrounding the mode of bonding of acetylenic ligands even in mononuclear complexes, since alkynes may act as two- or four-electron donors.² We report here the synthesis and X-ray structure of two new cationic cobalt(II)–diphenylacetylene complexes, which are examples of this bonding dichotomy.

The reaction of diphenylacetylene with $\text{CoBr}(\text{PMe}_3)_3$ at -35°C in the presence of an equimolecular amount of

NaBPh_4 , yields, in acetone–acetonitrile (1:1), red crystals of $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{MeCN})(\text{PMe}_3)_3]\text{BPh}_4$ (1), and in acetone, green crystals of $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ (2). Both compounds are diamagnetic† in the solid state. Only compound (1) exhibits a $\nu(\text{C}\equiv\text{C})$ i.r. band at 1780 cm^{-1} , typical of co-ordinated diphenylacetylene. No $\nu(\text{CN})$ band is detected in the spectrum of (1). Species (2) is readily converted into (1) by adding MeCN to the solution.

† $\mu_{\text{eff}} = \text{ca. } 0$ after corrections from ligand contributions, following G. Foex, 'Constantes Sélectionnées—Diamagnétisme et Paramagnétisme,' Masson, Paris, 1957.

To determine unambiguously the co-ordination geometry around the cobalt and the characteristics of the bonded C_2Ph_2 ligand, single-crystal X-ray analyses of both complexes were undertaken.† The structures of (1) and (2) are shown in Figures 1 and 2, together with the most important geometrical parameters. In complex (1), the geometry around Co is trigonal bipyramidal, with diphenylacetylene and acetonitrile in equatorial positions. Acetonitrile, which has no special σ - and π -requirements, has probably been forced into the equatorial position by the steric requirements of the other ligands, because in the closely related ethylene complex $[Co(C_2H_4)(MeCN)(PMe_3)_3]BPh_4$,³ acetonitrile occupies an axial position of the trigonal bipyramid. Like C_2H_4 , the C_2Ph_2 ligand, which is also a π -donor, is located in an equatorial site. Thus, the bonding mode of diphenylacetylene in complex (1) is similar to that of ethylene; it behaves as a two-electron donor.

In complex (2), the environment of Co is best described as pseudotetrahedral, with the centre X of the $C\equiv C$ bond occupying the fourth co-ordination site. The $C\equiv C$ bond is nearly parallel to the P(1)–P(2) direction, whereas the Co–C(10)–C(20) plane is roughly perpendicular to the X–Co–P(3) plane (dihedral angle 92.3°). This diamagnetic compound may be regarded as an eighteen-electron species with a four-electron donor acetylenic ligand.§ The CoP_3X core does not show the expected C_{3v} symmetry: the Co–P(3) bond [2.123(2) Å] is significantly shorter than the two others [av. 2.212(2) Å], indicating the particular role played by C_2Ph_2 . The four-electron donor model is also supported by simple molecular symmetry considerations. In the lower symmetry adopted by (2), the $C\equiv C$ orientation favours the overlap of the two diphenylacetylene π -orbitals with the Co orbitals, forming a σ -bond along the Co–X direction and a π -bond in the X–Co–P(3) plane. In the latter plane, the overlap of the filled π -orbital of C_2Ph_2 with an empty cobalt hybrid orbital of d_{xz} symmetry and with an empty d P(3) orbital of the same symmetry, allows electron delocalisation on the three centres C_2Ph_2 , Co, and P(3). Confirmation of this is found in the significant shortening of the Co–C and Co–P(3) distances.

As observed in other acetylenic complexes, the $C\equiv C$ bond in both complexes is lengthened [1.26(7) Å in (1) and 1.265(7) Å in (2)] compared with free C_2Ph_2 [1.198(3) Å].⁴ This distance is not sensitive to the number of electrons donated by the alkyne. Conversely, a significant difference is observed in the Co–C distances, which are distinctly longer in (1) [1.977(5) Å] than

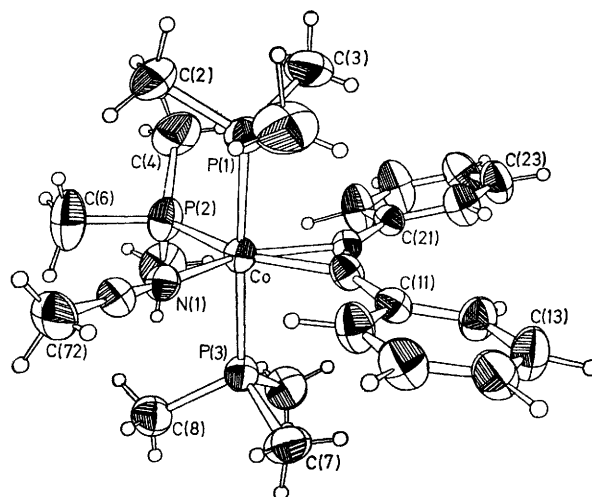


Figure 1. Structure of the $[Co(C_2Ph_2)(MeCN)(PMe_3)_3]^+$ cation (1). Important bond lengths (Å): Co–P(1), 2.256(2); Co–P(3), 2.236(2); Co–P(2), 2.263(2); Co–N(1), 1.943(4); Co–C(10), 1.977(5); Co–C(20), 1.981(5); C(10)–C(20), 1.267(7); angles ($^\circ$): P(1)–Co–P(3), 171.50(7); P(1)–Co–P(2), 93.53(6); P(1)–Co–N(1), 86.6(1); P(1)–Co–C(10), 87.2(1); P(1)–Co–C(20), 89.4; P(2)–Co–N(1), 99.5(1); P(2)–Co–C(20), 113.8(1); N(1)–Co–C(10), 109.3(2); C(10)–C(20)–C(21), 147.0(5); C(20)–C(10)–C(11), 148.8(5).

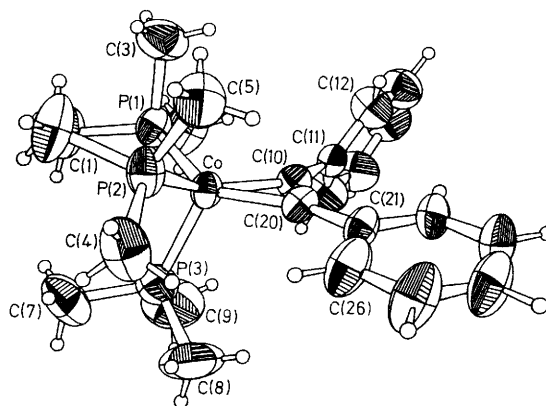


Figure 2. Structure of the $[Co(C_2Ph_2)(PMe_3)_3]^+$ cation (2). Important bond lengths (Å): Co–P(1), 2.216(2); Co–P(2), 2.208(2); Co–P(3), 2.127(2); Co–C(10), 1.847(5); Co–C(20), 1.856(5); C(10)–C(20), 1.265(7); angles ($^\circ$): P(1)–Co–P(2), 104.4(1); P(1)–Co–P(3), 98.4(1); P(1)–Co–C(10), 99.6(2); P(1)–Co–C(20), 136.9(2); P(2)–Co–P(3), 94.8(1); P(2)–Co–C(10), 137.8(2); P(2)–Co–C(20), 103.2(2); P(3)–Co–C(10), 115.6(2); P(3)–Co–C(20), 111.6(2); C(10)–C(20)–C(21), 137.5(5); C(20)–C(10)–C(11), 143.6(5).

† Crystal data: (1): monoclinic, $P2_1/c$, $a = 10.274(3)$, $b = 18.191(8)$, $c = 25.739(7)$ Å, $\beta = 107.42(3)^\circ$, $Z = 4$, $U = 4589.8$ Å³, $\mu(Cu-K\alpha) = 43.1$ cm^{−1}, $t = 22^\circ\text{C}$, $R = 0.036$ ($R_w = 0.038$) for 2821 reflections measured on an Enraf-Nonius CAD-4 diffractometer. (2): monoclinic, $P2_1/c$, $a = 12.320(6)$, $b = 22.514(11)$, $c = 19.177(9)$ Å, $\beta = 124.22(7)^\circ$, $Z = 4$, $U = 4398.3$ Å³, $\mu(Cu-K\alpha) = 44.6$ cm^{−1}, $t = 22^\circ\text{C}$, $R = 0.039$ ($R_w = 0.045$) for 2814 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ A square-pyramidal five-co-ordinate structure, with diphenylacetylene viewed as a dicarbene and cobalt in a +3 oxidation state may also be envisaged. However, no five-co-ordinate cobalt(III) complexes with phosphine ligands are known. Species (2) adds MeCN easily giving a five-co-ordinate cobalt(I) species. We thus prefer the formulation of (2) as a pseudo-tetrahedral species with C_2Ph_2 acting as a four-electron donor. Nevertheless the two hypotheses are strongly related, the carbene formulation being the extreme charged form. On the other hand, its diamagnetism precludes formulation as a sixteen-electron tetrahedral species. Up to now, all the reported four-co-ordinate cobalt(I) complexes with monodentate phosphine ligands are paramagnetic.

in (2) [1.853(5) Å]. Short metal–C bonds in W, Mo, and Ta acetylenic complexes were discussed in terms of two- and four-electron donor acetylenic ligands, but the conclusions drawn therefrom are not completely convincing since the comparisons were made between complexes with different metals, ligands or acetylenic groups, restrictions which do not exist here. The change in the $Ph-C\equiv C$ angles upon co-ordination is also noticeable; from $178.1(2)^\circ$ in the essentially linear free ligand, they average $147.9(5)^\circ$ in (1) and $140.5(5)^\circ$ in (2), as a result of a rehybridization of the acetylenic carbons.

Isolation of (1) and (2) is consistent with the known reactivity of the sixteen-electron $CoBr(PMe_3)_3$ species with small molecules, which is dominated by the formation of five-co-ordinate eighteen-electron adducts. We are currently

attempting to assess the role played by the steric hindrance of diphenylacetylene in stabilizing complex (2).

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