## Ligand Lability in and Electron Transfer of $[Co(py)_6]^+$ ; Cyclotrimerisation of Alkynes and Synthesis, Structure, and Properties of $(\eta^6-C_6Ph_6)Co(\eta^2-C_2Ph_2)$ (py = pyridine)

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In pyridine the ionic Co<sup>1</sup> complex  $[Co(py)_6][BPh_4]$  (py = pyridine) catalyses the cyclotrimerisation of but-2-yne and hex-l-yne at room temperature; under the same conditions, diphenylacetylene promotes an irreversible disproportionation of the Co<sup>1</sup> complex to give  $[Co(py)_6][BPh_4]_2$  and  $(\eta^6-C_6Ph_6)Co(\eta^2-C_2Ph_2)$ , this compound having been structurally characterised and its reaction with CO investigated.

We recently described the synthesis of the zwitterionic  $Co(\eta^6-BPh_4)(py)_2$  which in pyridine yields the complex cation  $[Co(py)_6]^+$  (1).<sup>1</sup> Unusual chemical properties have already been reported for (1) *e.g.* it promotes  $CO_2$  deoxygenation in non-aqueous media.<sup>1</sup> We report now that under an inert atmosphere, the addition of but-2-yne or hex-l-yne to a 0.03 M solution of (1) in pyridine (alkyne/Co, molar ratio = 30) brings about an instantaneous colour change from intense blue to dark maroon and, in the case of hex-l-yne, heat evolution is observed. G.l.c. quantitative analysis and mass spectrometry of the organic products showed a quantitative cyclotrimerisation to alkyl substituted benzenes and, in the case of hex-l-yne,

the two isomeric products 1,2,4-tri-n-butylbenzene and 1,3,5tri-n-butylbenzene were formed in the ratio 2/1. No other cationic Co<sup>1</sup> co-ordination compounds display such catalytic activity: tertiary phosphine complexes simply add alkynes,<sup>2</sup> while [Co(bpy)<sub>3</sub>]<sup>+</sup> (bpy = 2,2'-bipyridyl), formed by adding bpy in a 3/1 molar ratio to (1) in pyridine,<sup>1</sup> was found to be unreactive. Rather, (1) mimics the organometallic derivative cyclopentadienylbis(ethylene)cobalt in promoting catalytic cyclotrimerisation of alkynes under such mild conditions.<sup>3</sup>

However, no free hexaphenylbenzene was formed when a 0.03 M solution of (1) in pyridine was reacted with diphenylacetylene: a fast irreversible disproportionation occurs at



Figure 1. Molecular structure of (2). Some selected bond lengths (Å) and angles (°): C(55)-C(56) 1.278(10),  $Co-C(C_6Ph_6)$  2.129(6)--2.149(6), Co-C(56) 1.912(8), Co-C(55) 1.888(8), C(43)-C(55)-C(56) 145.0(7), C(49)-C(56)-C(55) 138.4(8).



**Figure 2.** X-band e.s.r. spectrum of (2) in toluene solution at 290 K. [(2)] =  $2.25 \times 10^{-3}$  M. DPPH = 2,2-di(4-t-octylphenyl)-l-picryl-hydrazyl.

room temperature as shown by the colour change from deep blue to dark red. Two moles of  $Ph_2C_2$  per mole of (1) are required to complete the reaction, while a larger excess remained unreacted. At the end of the reaction, evaporation of the solution to dryness and extraction of the residue with  $Et_2O$  gave the dark red organometallic derivative ( $\eta^6$ - $C_6Ph_6)Co(\eta^2$ - $C_2Ph_2$ )† (2) and an insoluble pink residue of  $[Co(py)_6][BPh_4]_2$ , according to the stoicheiometry of equation (1).

$$2 [\operatorname{Co}(\mathrm{py})_6]^+ + 4 \operatorname{Ph}_2 \operatorname{C}_2 \xrightarrow{\mathrm{py}} [\operatorname{Co}(\mathrm{py})_6]^{2+} + (\eta^6 \cdot \operatorname{C}_6 \operatorname{Ph}_6) \operatorname{Co}(\eta^2 \cdot \operatorname{C}_2 \operatorname{Ph}_2)$$
(1)  
(2)

Compound (2) exhibits an unusually low magnetic moment ( $\mu_{eff} = 1.34 \ \mu_B$  at 298 K) in the solid state, it can be recrystallised from hot toluene and it is slowly oxidised by air.

Compound (2) was structurally characterised‡ (Figure 1). A cobalt atom is bonded between a hexaphenylbenzene ring and a diphenylacetylene group. The centroid of the  $C_6Ph_6$  ring, the cobalt atom, and the centre of the C=C bond are almost aligned [177.1(3)°]. The Co-C(55) and Co-C(56) distances and the C(43)-C(55)-C(56), C(49)-C(56)-C(55) angles, suggest that co-ordinated diphenylacetylene acts as a four-electron donor.<sup>2</sup> Figure 2 shows the X-band e.s.r. spectrum of (2) in toluene at room temperature. The spectrum exhibits a well resolved hyperfine structure, centred at  $g_{iso} = 2.092$ , and is characterised by an eight-line absorption pattern. The line-shape of Figure 2 is classically isotropic, and can be suitably interpreted in terms of a paramagnetic metal-centred system in which a single unpaired electron strongly interacts with a magnetically active cobalt nucleus.

No reaction occurs between (2) and but-2-yne or hex-l-yne in pyridine; however, the hexaphenylbenzene ligand is easily displaced by CO. A solution of (2) in tetrahydrofuran reacts with CO at room temperature and atmospheric pressure;  $C_6Ph_6$  is formed as a colourless precipitate. At the end of the reaction, in the CO stretching region, the solution shows only absorptions due to  $(CO)_6Co_2(C_2Ph_2)$ ,<sup>5</sup> while quantitative recovering of the precipitate together with gas volumetric measurements indicate the stoicheiometry of equation (2).

$$2 (\eta^{6} - C_{6} Ph_{6}) Co(\eta^{2} - C_{2} Ph_{2}) + 6 CO \rightarrow$$
(2)  

$$2C_{6} Ph_{6} + C_{2} Ph_{2} + (CO)_{6} Co_{2}(C_{2} Ph_{2}) \qquad (2)$$

A compound similar to (2), namely  $(\eta^{6}-C_{6}H_{6})$ Co- $(\eta^{2}-C_{2}Me_{2})$ , has been recently obtained, and structurally characterised, on reacting benzene/cobalt cocondensate and but-2-yne.<sup>6</sup> The low energy path of formation of an al-kyne(arene) cobalt complex reported in the present paper, is an interesting finding, especially in connection with the cobalt catalysed cyclotrimerisation of alkynes.

In conclusion, the reactions of (1) in pyridine with alkynes

<sup>†</sup> Satisfactory analytical data were obtained.

 $<sup>\</sup>ddagger$  Crystal data: (2) C<sub>56</sub>H<sub>40</sub>Co, triclinic, space group  $\overline{P1}$ , a = 16.996(3), b = 12.337(2), c = 11.413(3) Å, α = 115.46(2)°, β = 90.79(2)°, γ = 101.39(2)°, U = 2102.9 Å<sup>3</sup>, D<sub>c</sub> = 1.216 g cm<sup>-3</sup>, Z = 2. Data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å). A total of 2219 reflections  $[I>3\sigma(I)]$  out of 7277 were used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with SHELX-76.4 The contribution of H atoms at the calculated positions was included, with an overall isotropic parameter which refined to 0.13 Å<sup>2</sup>. The nine phenyl rings present in the molecule were constrained to perfect hexagons, with C-C bond lengths of 1.395 Å, and refined as rigid groups; anisotropic thermal parameters were refined only for the Co atoms. The refinement converged to an R value 0.075 (127 parameters);  $R_w = 0.076$ . The same agreement between  $F_0$  and  $F_c$  was observed by refining the structure without constraint to a perfect hexagon of the phenyl ring linked to cobalt; the Co-C distances remained equal within one standard deviation, and the ring planar, with C-C distances consistent with those expected for a phenyl ring. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

indicate the lability of py ligands, thus making (1) a promising candidate for other catalytic processes. On the other hand, (1) may perform as a versatile intermediate to  $Co^0$  complexes when suitable ligands for such reduced species are added or formed *in situ* (equation 1). The thermodynamic driving force for the attainment of high energy  $Co^0$  complexes presumably is the simultaneous formation of the stable complex cation  $[Co(py)_6]^{2+}$  by disproportionation.

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407