

Tetraphenylborate Anion Oxidation by Acidic Co^{2+} Cations: Synthesis and Properties of Pyridine–Cobalt(I) Complexes

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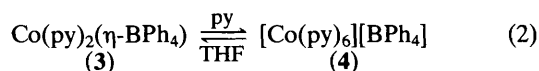
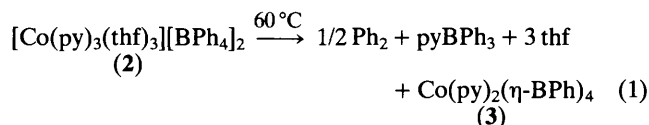
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The neutral cobalt(I) complex $\text{Co}(\text{py})_2(\eta\text{-BPh}_4)$ (py = pyridine) was obtained on removal of py and thf (thf = tetrahydrofuran) from $[\text{Co}(\text{py})_3(\text{thf})_3][\text{BPh}_4]_2$ and its crystal structure has been determined; in py as solvent, the former is converted into the ionic $[\text{Co}(\text{py})_6][\text{BPh}_4]$, which reduces CO_2 to CO and water to dihydrogen.

The disproportionation of $\text{Co}_2(\text{CO})_8$ (**1**) promoted by small amounts of bases yields acidic Co^{2+} cations, which oxidize $[\text{Co}(\text{CO})_4]^-$ anions and dihydrogen under unusually mild conditions, in the presence of CO .¹ We report now that acidic Co^{2+} cations, formed on removal of pyridine (py) and tetrahydrofuran (thf) from $[\text{Co}(\text{py})_3(\text{thf})_3][\text{BPh}_4]_2$,[†] (**2**) oxidize $[\text{BPh}_4]^-$ anions to biphenyl, with the formation of the new, red, $\text{Co}(\text{py})_2(\eta\text{-BPh}_4)$ (**3**)[‡] in good yields [equation (1)].[‡] Complex (**3**) was characterized by an X-ray crystal structure determination[§] (Figure 1). The structure consists of monomeric molecules in which the cobalt centre binds two pyridine groups and a phenyl ring of the $[\text{BPh}_4]^-$ anion in a fashion analogous to that in $\text{Co}(\text{PMe}_3)_2(\eta\text{-BPh}_4)$.³ However, the change from phosphine to pyridine as ligands leads to different magnetic properties; while $\text{Co}(\text{PMe}_3)_2(\eta\text{-BPh}_4)$ is diamagnetic, $\mu_{\text{eff.}} = 3.0 \mu_{\text{B}}$ at 298 K was determined for (**3**). Complex (**3**) is a non-conductor in thf and a conductor in py ,[¶]

in which the characteristic intense blue colour of polypyridine–cobalt(I) complexes⁴ was observed. The u.v.–visible spectrum of these solutions features a broad band at 780 nm (ϵ 4300 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and a much less intense maximum at 370 nm. The addition of bpy ($\text{bpy} = 2,2'$ -bipyridine) to (**3**) in py [molar ratio $\text{bpy}/(\text{3}) = 4$] reduces the wavelength of the 780 nm band to 630 nm, while an equally intense band at longer wavelength (1390 nm) appears, as a consequence of $[\text{Co}(\text{bpy})_3]^+$ complex formation.⁵ On adding diethyl ether to (**3**) in py (0.16 M) deep blue leaflets, identified as $[\text{Co}(\text{py})_6][\text{BPh}_4]^+$ (**4**), were obtained. On treating (**4**) with thf , py is released and (**3**) is re-formed according to the equilibrium (2).



Complex (**4**) is the first example of a cobalt(I) complex with a monodentate N-donor ligand. Attempts to prepare (**3**) or (**4**) on treating (**2**) with strong reducing agents were unsuccessful.

Owing to the interest in cobalt(I) polypyridine complexes as reducing agents,⁶ we tested properties of (**4**) for reduction of CO_2 and H_2O . A 0.08 M py solution of (**4**) was found to react instantaneously with CO_2 at room temperature and atmospheric pressure as shown by the change in colour from intense blue to brown-green. The i.r. spectrum of the solution in the CO stretching region features bands at 1942s, 1532m, and 1382m cm^{-1} , the first band being attributable to a carbonyl complex and the last two to bridging carbonate.⁷ On these

[†] Satisfactory analytical data were obtained for all new compounds.

[‡] Pyridine (0.31 mol) was added to a stirred aqueous solution of NaBPh_4 (1.5 l; 0.080 mol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.038 mol). The pink solid which was formed was filtered off, washed with water, dried *in vacuo* and redissolved in anhydrous pyridine (150 ml). The solvent was removed *in vacuo* and the residue treated with MeOH (150 ml). The $[\text{Co}(\text{py})_6][\text{BPh}_4]_2^{\ddagger}$ which was formed was warmed at 65°C *in vacuo* (12 h) yielding the violet $[\text{Co}(\text{py})_4][\text{BPh}_4]_2^{\ddagger}$ which was suspended and stirred (24 h) in thf (800 ml). Complex (**2**)[†] was formed as a pink microcrystalline solid and filtered off (40 g, 87% yield). Complex (**2**) (0.017 mol) was heated at 60°C *in vacuo* (24 h); biphenyl sublimed out and a brick-red solid was obtained, which was washed with thf (2×50 ml) and extracted under reduced pressure at 30°C with thf to yield (**3**) (5.1 g, 55% yield) as a microcrystalline red solid. A single crystal suitable for X-ray analysis was obtained by slow diffusion of Et_2O into a saturated thf solution of (**3**).

[§] Crystal data: $\text{Co}(\text{py})_2(\eta\text{-BPh}_4)$, $M = 536$, triclinic, space group $P\bar{1}$, $a = 13.875(3)$, $b = 10.947(3)$, $c = 9.810(3)$ Å, $\alpha = 100.77(2)$, $\beta = 108.37(2)$, $\gamma = 85.76(2)^\circ$, $U = 1389.0$ Å³, $D_c = 1.280$ g cm^{-3} , $Z = 2$. Data were collected on a Philips PW1100 diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 1286 reflections [$I > 3\sigma(I)$] out of 4880 were used. The structure was solved by direct methods and refined by full-matrix least-squares using SHELX-76.² H atoms were included at calculated positions, with an overall isotropic thermal parameter which refined to 0.13 Å². Owing to the unfavourable observation to parameter ratio, the phenyl groups were constrained to perfect hexagons (C–C 1.395 Å), and refined as rigid groups; anisotropic thermal parameters were refined only for the cobalt atoms. The refinement converged to $R = 0.062$ (111 parameters); $R_w = 0.059$. The same agreement between F_o and F_c was observed by refining the structure without constraint to a perfect hexagon of the phenyl group linked to cobalt; the cobalt–carbon 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 No. 1.

[¶] $\Lambda_M = 29.4$ S $\text{mol}^{-1} \text{cm}^2$ for a 2×10^{-3} M solution. For comparison, a 2×10^{-3} M py solution of NaBPh_4 (298 K) showed Λ_M 35.5 S $\text{mol}^{-1} \text{cm}^2$.

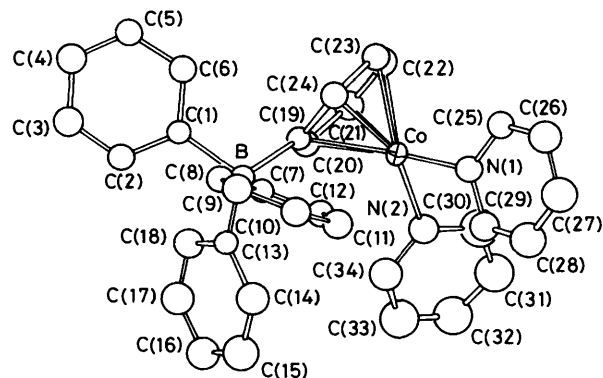


Figure 1. Structure of $\text{Co}(\text{py})_2(\eta\text{-BPh}_4)$ (**3**). Selected bond lengths (Å) and angles ($^\circ$): $\text{Co-N}(1)$ 2.081(8), $\text{Co-N}(2)$ 2.112(9), Co-C (average) 2.190(7), $\text{N}(1)\text{-Co-N}(2)$ 91.2(3).

grounds (4) appears to be a more versatile reagent in promoting CO₂ reduction than polypyridine-cobalt(I) complexes which were found to be active only in aqueous solution where hydrogen formation also occurs.⁶

In order to define better the nature of the carbonyl complex formed in the reaction of (4) with CO₂ and marked by the 1942 cm⁻¹ band, we treated (4) directly with CO in py, 0.5 mol of CO per g atom of cobalt being absorbed in a fast reaction; the i.r. spectrum of the solution showed the 1942 cm⁻¹ band as the only absorption in the CO stretching region. Changing to an Ar atmosphere did not affect the intensity of the band. On these grounds the reaction can be formulated as a CO-promoted disproportionation of (4) to Co^{II} and a monocarbonyl complex of Co⁰ also containing py ligands [equation (3)]. Reaction (3) is analogous to that of [Co(bpy)₃]⁺ with CO⁶ yielding [Co(bpy)₃]²⁺ and [Co(bpy)(CO)₂]₂. In the present case, however, the carbonyl complex formed is less stable and after several hours the 1897 cm⁻¹ band of [Co(CO)₄]⁻ replaces the 1942 cm⁻¹ band, while small amounts of metal separate from the solution.



The hard Lewis base H₂O also promotes the disproportionation of (4) to Co⁰ and Co^{II}; the addition of water (0.3 ml) to a py solution of (4) (0.064 M; 15 ml) caused rapid formation of cobalt metal, while the blue colour of the solution turned pink;

only traces of dihydrogen were formed during the reaction. However water reduction occurred to an appreciable extent when smaller amounts of water were used: 0.17 mol of dihydrogen per mol of (4) was formed in two hours at room temperature on adding equimolar amounts of water to a solution (0.064 M) of (4) in py.

The catalytic properties of (3) and (4) are being studied.

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