A Stable Copper Carbonyl Complex

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Summary The preparation and properties of the first air- and heat-stable copper carbonyl complex, $[HB(pz)_3]Cu(CO)$, are described.

ADDITION of copper(I) chloride to a solution of $K[HB(pz)_3]$ (pz = pyrazolyl, $C_3H_3N_2$), while passing a stream of carbon monoxide through the suspension, affords the highly crystalline, white, $[HB(pz)_3]Cu(CO)$, (I).† This compound is stable in air for weeks, and resists heating to over 100°, and thus contrasts with the labile cyclopentadienyl complex $(\pi\text{-}C_5H_5)Cu(CO)$ (II).[1,2] Similar increases in stability on replacement of $\pi\text{-}C_5H_5$ by $HB(pz)_3$ have been reported before with some molybdenum carbonyl complexes.[3]

Complex (I) is very soluble in light petroleum, such solutions showing the characteristic ν(BH) of the ligand at 2465 cm^{-1}, together with a single sharp ν(CO) at 2083 cm^{-1} [*cf.* ν(CO) in (II) at 2093 cm^{-1}].[2] On heating to 165°, complex (I) decarbonylates to form $Cu_2[HB(pz)_3]_2$, also formed by the direct reaction between $K[HB(pz)_3]$ and copper(I) halides in the absence of carbon monoxide. This complex is dimeric both in solution and in the gaseous state, the mass spectrum exhibiting a strong parent ion cluster centred on *m/e* 553.

Complex (I) reacts with many ligands, L, [*e.g.*, L = PR_3, $P(OR)_3$, AsR_3, SbR_3, RNC, acetylenes, olefins, etc.] to give $[HB(pz)_3]CuL$ with simultaneous evolution of carbon monoxide. As expected, the phosphite and isocyanide derivatives are both considerably more stable thermally than their cyclopentadienyl analogues.[2,4] Passage of carbon monoxide into a suspension of the dimer in light petroleum results in a slow reaction to give the carbonyl (I); selected ligands have also been found to react similarly.

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† All new compounds have been characterised by satisfactory analyses.

Although similarities between the $[HB(pz)_3]^-$ and the $C_5H_5^-$ ligands have been emphasised in the past, we feel that the stability of complex (I) results primarily from strengthening of the Cu–CO bond by back-bonding from an electron-rich copper atom resulting from the strong σ-donor character of the pyrazolylborate ligand. With the hydrotris(3,5-dimethylpyrazolyl)borate complex, dec. 186°, ν(CO) occurs at 2066 cm^{-1}, as expected for an even stronger electron donor. In the light of these results, $(\pi\text{-}C_5Me_5)$Cu(CO) also can be expected to be more stable than the unsubstituted cyclopentadienyl derivative.

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