Group IB Metal Chemistry. Part I. Preparation and Reactions of the Carbonyl(hydrotripyrazol-1-ylborato)copper(I) Complex

By **Michael I. Bruce** *† and **Andrew P. P. Ostazewski**, Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The reaction between copper(I) chloride and K[HB(pz)$_3$] (pz = pyrazol-1-yl) in the presence of CO affords white, crystalline $[\{HB(pz)_3\}Cu(CO)]$ (I) as an air- and heat-stable copper carbonyl complex. Reactions between (I) and ligands L [L = PPh_3, $PMePh_2$, $P(OMe)_3$, $P(OPh)_3$, $Ph_2PCH_2CH_2PPh_2$ (dppe), $AsPh_3$, $SbPh_3$, or Bu^tNC] afford the complexes $[\{HB(pz)_3\}CuL]$. On heating, (I) first decarbonylates to $[Cu_2\{HB(pz)_3\}_2]$ (II) which then disproportionates to copper metal and $Cu[HB(pz)_3]_2$.

CARBONYL chemistry of the Group IB elements has interested chemists for over 100 years, but no stable copper carbonyl complex has ever been reported; the subject has been reviewed recently.[1] Examples of solid complexes containing carbonyl groups are limited to some halides, which lose carbon monoxide at room temperature, and $[Cu(CF_3CO_2)(CO)]$, which loses carbon monoxide on prolonged pumping *in vacuo* and is extremely sensitive to oxygen.[2] Solution studies have indicated the existence of complexes such as [Cu(en)(CO)]Cl and $[(en)Cu(CO)_2Cu(en)]Cl_2$ (en = ethylenediamine),[3] $[CuCl(Me_2N{=}CH_2)(CO)]Br$,[4] and [(cp)Cu(CO)] (cp = π-cyclopentadienyl).[5] The latter complex co-distils with pentane *in vacuo*, and has not yet been obtained pure.

We reasoned that more stable copper carbonyl derivatives might be formed if the π-back-bonding component of the Cu–CO bond could be strengthened; any instability was evidently not the result of poor σ-acceptor properties of copper, since a multitude of tertiary phosphine and arsine complexes containing the element have been described. The π-back-bonding overlap could be improved if the electron density on copper could be increased, and the choice of an anionic donor ligand was dictated by its ability to form the required copper(I) derivative without the necessity for other ligands or counter-ions. Our experience with the poly(pyrazol-1-yl)borate ligands of Trofimenko,[6] coupled with the known stabilising effect of the hydrotripyrazol-1-ylborate ligand over similar complexes containing cyclopentadienyl groups, led us to examine the reaction between copper(I) derivatives and K[HB(pz)$_3$]. A preliminary account has appeared.[7]

RESULTS

The simple and quick reaction between copper(I) chloride and potassium hydrotripyrazol-1-ylborate in the presence of carbon monoxide in polar solvents such as acetone or tetrahydrofuran, afforded a colourless solution. Evaporation and extraction of the white residue with light petroleum gave a similar colourless solution, which readily crystallised. Although initially evaporated in a stream of carbon monoxide, we subsequently found that the complex is stable enough to survive evaporation by more usual methods, *e.g.* using a rotary evaporator.

The resulting white crystals were characterised as monomeric $[Cu\{HB(pz)_3\}(CO)]$ (I) by analysis, osmometric molecular-weight determination, and from its spectral properties. Thus the i.r. spectrum contained a sharp ν(CO) band at 2 083 cm^{-1}, and a ν(BH) band at 2 465 cm^{-1}; other bands characteristic of the pyrazol-1-ylborate ligand

---

† *Present address:* Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia.

[1] M. I. Bruce, *J. Organometallic Chem.*, 1972, **44**, 209.

[2] A. F. Scott, L. L. Wilkening, and B. Rubin, *Inorg. Chem.*, 1969, **8**, 2533.

[3] G. Rucci, C. Zanzottera, M. P. Lachi, and M. Camia, *Chem. Comm.*, 1971, 652.

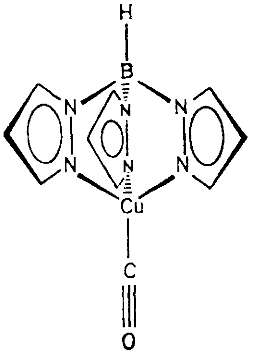
[4] R. Mason and A. Rucci, *Chem. Comm.*, 1971, 1132.

[5] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 5114.

[6] S. Tromfimenko, *Accounts Chem. Res.*, 1971, **4**, 17.

[7] M. I. Bruce and A. P. P. Ostazewski, *J.C.S. Chem. Comm.*, 1972, 1124.

were also present. The ^1H n.m.r. spectrum contained two bands at τ 2·30d (intensity 2) and 3·83t (intensity 1). Although three bands are normally expected for the three protons of the pz groups, we have observed other cases where the two ' outer ' protons (on carbons adjacent to N–B and N-metal, respectively) have the same or closely similar chemical shifts.



(I)

The mass spectrum did not contain a parent ion. Instead, decomposition occurred in the spectrometer to give a binuclear species, $[Cu_2\{HB(pz)_3\}_2]$ (II). This material was also formed by attempted sublimation of complex (I), as a white sublimate, or from the direct reaction between copper(I) halides and $K[HB(pz)_3]$. It was characterised by analysis, solution molecular weight, and by i.r. and mass spectrometry. The i.r. spectrum was virtually superimposable on that of complex (I), with the exception of the ν(CO) band; Raman spectra showed no intense bands which could be assigned to ν(CuCu). No ^1H n.m.r. spectrum could be obtained as the complex rapidly decomposed in those more polar solvents in which it was soluble. The mass spectrum contained a parent-ion cluster centred on *m/e* 553, and other prominent ions were formed by loss of pz groups. More or less intense ions were found in most spectra at *m/e* 489, and were assigned to the ion $[Cu\{HB(pz)_3\}_2]^+$.

If heating of complex (II) during sublimation was prolonged (*e.g.* 100°–0·1 mm for 30 min), the sublimate became blue and the pot residue reddish brown. Further examination of these products showed that thermal decomposition of complex (I) occurs in two stages: first, decarbonylation to complex (II), followed by disproportionation of this copper(I) complex to copper metal and the known copper(II) complex, $Cu[HB(pz)_3]_2$. The decarbonylation is at least partially reversible, passage of carbon monoxide into suspensions of complex (II) resulting in formation of solutions of (I). The solid carbonyl complex (I) is stable at room temperature for months in the solid state; on heating, decarbonylation occurs on melting at 165 °C. It is less stable in solution, especially in carbon disulphide and chlorinated solvents, solutions rapidly turning green.

$$2[Cu\{HB(pz)_3\}(CO)] \longrightarrow [Cu_2\{HB(pz)_3\}_2] + 2CO \quad (1)$$

$$[Cu_2\{HB(pz)_3\}_2] \longrightarrow Cu[HB(pz)_3]_2 + Cu \quad (2)$$

Other Reactions.—The formation and isolation of a stable copper carbonyl derivative has enabled us to examine reactions of the Cu–CO bond in some detail. Our initial experiments, reported below, were directed at the preparation of a variety of related complexes by displacement of the co-ordinated carbon monoxide by a range of donor ligands.

Reactions between complex (I) and monodentate phosphorus donor ligands gave the new complexes $[\{HB(pz)_3\}CuL]$ [L = PPh_3, $PMePh_2$, $P(OPh)_3$, or $P(OMe)_3$], with evolution of carbon monoxide. All the complexes contained the characteristic ν(BH) peak at *ca.* 2 450 cm^{-1} in their i.r. spectra; other bands were characteristic of the $HB(pz)_3$ and L groups. The ^1H n.m.r. spectrum of the $P(OMe)_3$ derivative contained the characteristic doublet at τ 6·26 (J_{PH} 13 Hz) of the co-ordinated phosphite ligand. The spectrum of the related $PMePh_2$ complex contained a doublet at τ 8·00 (J_{PH} 3 Hz). Using the bidentate ligand $Ph_2P(CH_2)_2PPh_2$ (dppe), a binuclear complex characterised as $[(dppe)\{Cu[HB(pz)_3]\}_2]$ was obtained, in which the ligand bridges two copper atoms. Evidently the donor power of the phosphorus atoms is not great enough to displace one of the pz nitrogen atoms from the copper co-ordination sphere.

Similar reactions occurred with other Group V atom-donor ligands, and the complexes $[\{HB(pz)_3\}Cu(EPh_3)]$ (E = As or Sb) are illustrative. These were characterised in the usual manner, and both contained bands at *ca.* 2 450 cm^{-1} in their i.r. spectra. As with the phosphine and phosphite complexes, the mass spectra only contained ions derived from the dimeric complex (II) above, together with those from the free ligand, probably as a result of thermal decomposition in the mass spectrometer source. Using t-butyl isocyanide, a high yield of the complex $[\{HB(pz)_3\}Cu(CNBu^t)]$ was obtained, as a white crystalline solid. The i.r. spectrum contained bands at 2 480 [ν(BH)] and 2 155 cm^{-1} [ν(CN)], while the ^1H n.m.r. spectrum contained a sharp singlet at τ 8·40 (CMe_3).

In all cases studied, the characteristic resonances of the pz groups were also present in the ^1H n.m.r. spectra, although sometimes resonances arising from the ligand L overlapped one or other of the signals.

Attempts to obtain the dicarbonyl $[\{H_2B(pz)_2\}Cu(CO)_2]$ afforded only the complex $[Cu_2\{H_2B(pz)_2\}_2]$.

DISCUSSION

The use of the hydrotripyrazol-1-ylborate anion as a ligand on copper(I) has permitted isolation of a stable copper carbonyl derivative. Values of ν(CO) bands for this and related complexes, *e.g.* (I) 2 083, $[\{HB(Me_2pz)_3\}Cu(CO)]$ (Me_2pz = 3,5-dimethylpyrazol-1-yl) 2 066, [(cp)Cu(CO)] 2 093, $[Cu(CF_3CO_2)(CO)]$ 2 155, and free CO 2 143 cm^{-1}, have confirmed the suggestion that increasing back-bonding in the Cu–CO bond [as shown by a decrease in ν(CO) frequency] does indeed increase the stability of these derivatives (in the sense that they can be isolated and studied). The use of hydrotris(3,5-dimethylpyrazol-1-yl)borate, for example, led to a dramatic decrease in the ν(CO) frequency, as expected for a stronger σ-donor ligand. Compared to the cp complex, which has ν(CO) at 2 093 cm^{-1}, the lowering of *ca.* 10 cm^{-1} found for complex (I) parallels a considerable increase in thermal stability found in the latter complex.

The carbonyl group is displaced readily, however, by donor ligands such as tertiary phosphines, arsines, stibines, phosphites and isocyanides. These reactions parallel those of the cp carbonyl complex, complexes $[(cp)CuL]$ ($L = PBu^n_3$ or CNC_6H_4OMe-*p*) being isolated.[5] Analogies between the reactions of complex (I) and those of $[(cp)Cu(CO)]$, together with the physical properties of the derived complexes, suggest that the two carbonyl complexes have similar structures. The molecular structures of the complexes $[(cp)CuL]$ ($L = PEt_3$ or PPh_3) have been reported,[8] and the proposed similarity of the $HB(pz)_3$ ligand to cp has been confirmed by other structural studies,[9] so that it is probable that complex (I) has the structure indicated.

TABLE 1

Analytical data

		Found (calc.) (%)		
Complex	M.p.(*t*/°C)	C	H	N
$[\{HB(pz)_3\}Cu(CO)]$ [a]	d. 165—167	39·7 (39·4)	3·6 (3·3)	27·4 (27·55)
$[\{HB(pz)_3\}Cu(PPh_3)]$	d. 200—202	59·1 (60·2)	4·5 (4·65)	
$[\{HB(pz)_3\}Cu(PMePh_2)]$	170—172	56·05 (55·45)	5·1 (4·85)	17·2 (17·65)
$[\{HB(pz)_3\}Cu\{P(OPh)_3\}]$	124—126	55·6 (55·3)	4·75 (4·25)	14·4 (14·3)
$[\{HB(pz)_3\}Cu\{P(OMe)_3\}]$ [b]	190—193	35·5 (36·0)	4·55 (4·75)	20·85 (21·0)
$[\{[HB(pz)_3]Cu\}_2(dppe)]$ [c]	d. 160	56·35 (55·7)	4·85 (4·65)	16·8 (17·7)
$[\{HB(pz)_3\}Cu(AsPh_3)]$	280—282	55·85 (55·65)	4·3 (4·3)	15·05 (14·45)
$[\{HB(pz)_3\}Cu(SbPh_3)]$	105—107	51·35 (51·5)	4·15 (4·0)	12·65 (13·35)
$[\{HB(pz)_3\}Cu(CNBu^t)]$	156—158	46·5 (46·8)	5·15 (5·3)	27·1 (27·3)
$[Cu_2\{HB(pz)_3\}_2]$ [d]	d. 182—184	38·95 (39·05)	3·8 (3·6)	30·0 (30·4)
$[\{HB(Me_2pz)_3\}Cu(CO)]$	d. 185—187	50·4 (49·5)	5·4 (5·65)	
$[Cu_2\{H_2B(pz)_2\}_2]$	d. 145—147	33·6 (34·3)	3·6 (3·1)	26·0 (26·65)

pz = Pyrazol-1-yl, Me_2pz = 3,5-dimethylpyrazol-1-yl, and dppe = bis(diphenyphosphino)ethane.

[a] Cu, 21·2 (20·85); O, 4·0 (5·25)%. [b] P, 7·7 (7·75)%. [c] Cu, 13·2 (13·35); P, 6·3 (6·5)%. [d] Cu, 22·75 (22·95); O, 0·3 (0·0)%; *M*, 524 (553) (chloroform); *M*, 552·072, 553·073, 554·072 (552·071, 553·073, 554·075) (mass spectrometry).

The nature of complex (II) is not so clear, since we were unable to obtain a satisfactory ^1H n.m.r. spectrum, or suitable crystals for an *X*-ray study. The ready regeneration of (I) from (II) and carbon monoxide, however, suggests that similar structures hold for both complexes: polymerisation of the $[HB(pz)_3]Cu$ unit may occur by the formation of $B\text{-}H\cdots Cu$ bridges, as found in the complexes $[(Ph_3P)_2Cu(BH_4)]$ [10] and $[(Ph_3P)_2Cu(B_3H_8)]$.[11] In solution, and in the vapour state, complex (II) exists as dimeric species.

EXPERIMENTAL

The salts $K[HB(pz)_3]$ and $K[HB(Me_2pz)_3]$ were made from the pyrazole and potassium tetrahydroborate.[12] Analytical data and m.p.s appear in Table 1, and some i.r. and ^1H n.m.r. data are collected in Table 2.

Preparation and Reactions of Carbonyl(hydrotripyrazol-1-ylborato)copper(I), (I).—Potassium hydrotripyrazol-1-ylborate (251 mg, 1·0 mmol) was added to a suspension of copper(I) chloride (100 mg, 1·0 mmol) in CO-saturated acetone (10 cm³) at 0 °C. Carbon monoxide was passed through the suspension for 30 min. After filtration, the colourless solution was evaporated, and the residue recrystallised from light petroleum to give white crystals of the *complex* (192 mg, 63%).

A sample of the complex (100 mg) was heated (0·1 mm, bath temperature 100 °C) for 30 min. The white *residue* (91 mg, 99%) showed no ν(CO) band, and was pure $[Cu_2\{HB(pz)_3\}_2]$, (II).

Reactions with various ligands. Typically, the complex $[\{HB(pz)_3\}Cu(CO)]$ (50 mg, 0·16 mmol) was added to triphenylphosphine (39 mg, 0·16 mmol) in benzene (20 cm³). The solid complex dissolved with effervescence; evaporation of the solvent and recrystallisation (light petroleum) afforded white *crystals* of $[\{HB(pz)_3\}Cu(PPh_3)]$ (64 mg, 80%). In a similar fashion were prepared: $[\{HB(pz)_3\}Cu(PMePh_2)]$ (89%); $[\{HB(pz)_3\}Cu\{P(OMe)_3\}]$ (83%); $[\{HB(pz)_3\}Cu\{P(OPh)_3\}]$ (91%); $[\{[HB(pz)_3]Cu\}_2(dppe)]$ (80%); $[\{HB(pz)_3\}Cu(AsPh_3)]$ (91%); $[\{HB(pz)_3\}Cu(SbPh_3)]$ (88%); and $[\{HB(pz)_3\}Cu(CNBu^t)]$ (85%).

TABLE 2

I.r. and ^1H n.m.r. data

	I.r. bands (cm⁻¹) [a]		^1H N.m.r.	
Complex	ν(BH)	Other	Pyrazolyl protons	Other
$[\{HB(pz)_3\}Cu(CO)]$	2 465m	ν(CO), 2 083s	2·30d, 3·83t	
$[\{HB(pz)_3\}Cu(PPh_3)]$	2 475m		2·38d, 2·85d, 3·95t	2·4—2·6m (P*Ph*)
$[\{HB(pz)_3\}Cu(PMePh_2)]$	2 460m		2·38d, 2·70d, 3·94t	2·28 (P*Ph*), 8·00d (P*Me*) J_{PMe} 4
$[\{HB(pz)_3\}Cu\{P(OPh)_3\}]$	2 450m			
$[\{HB(pz)_3\}Cu\{P(OMe)_3\}]$	2 460m		2·38d, 2·46d, 3·90t	6·26d (O*Me*), J_{PMe} 13
$[\{[HB(pz)_3]Cu\}_2(dppe)]$	2 440m			
$[\{HB(pz)_3\}Cu(AsPh_3)]$	2 450m		2·34d, 2·76d, 3·94t	2·6m (As*Ph*)
$[\{HB(pz)_3\}Cu(SbPh_3)]$	2 440m			
$[\{HB(pz)_3\}Cu(CNBu^t)]$	2 480m	ν(NC), 2 155s	2·62d, 2·69d, 4·06t	8·40s (CMe_3)
$[Cu_2\{HB(pz)_3\}_2]$	2 460s			
$[\{HB(Me_2pz)_3\}Cu(CO)]$ [b]	2 500m	ν(CO), 2 066s		

[a] Spectra also contained bands due to the $HB(pz)_3$ ligand at 1 490s, 1 400s, 1 300s, 1 200s, 1 110s, 1040s, 1 030s, 950m, 740s, 705m, and 660m cm⁻¹. [b] Me_2pz = 3,5-Dimethylpyrazol-1-yl.

---

[8] For $L = PEt_3$ see L. T. J. Delbaere, D. W. McBride, and R. B. Ferguson, *Acta Cryst.*, 1970, **B26**, 515; for $L = PPh_3$ see F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, 1970, **92**, 2353.

[9] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

[10] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.

[11] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8**, 2755.

[12] S. Trofimenko, *J. Amer. Chem. Soc.*, 1967, **89**, 3170.

Preparation of Carbonyl[hydrotris(3,5-*dimethylpyrazol*-1-*yl)borato]copper*(I).—A suspension of copper(I) chloride (100 mg, 1 mmol) in CO-saturated acetone at 0 °C was treated with K[HB(Me_2pz)$_3$] (335 mg, 1 mmol), and CO was passed into the mixture for 30 min. After filtration and evaporation, recrystallisation from light petroleum afforded the white *complex* (121 mg, 32%). A similar reaction using K[H_2B(pz)$_2$] (186 mg, 0·1 mmol) and copper(I) chloride (100 mg, 0·1 mmol) afforded a white solid, identified as [Cu_2{H_2B(pz)$_2$}$_2$].

Preparation and Reactions of Bis[hydrotripyrazol-1-*yl-boratocopper*(I)].—An aqueous solution of K[HB(pz)$_3$] (251 mg, 1 mmol) was added to copper(I) chloride (100 mg, 1 mmol) dissolved in concentrated KI solution. A white precipitate separated immediately, and was filtered off, washed with methanol and diethyl ether, to give the pure *product* (380 mg, 70%) identical with that obtained by thermal decomposition of complex (I).

On heating the product to 180 °C (0·1 mm), a blue material sublimed, while a red residue of copper metal remained in the flask. The blue sublimate was identified as Cu[HB(pz)$_3$]$_2$ by comparison with an authentic sample, prepared as described by Trofimenko.[12]

Passage of CO into a suspension of [Cu_2{HB(pz)$_3$}$_2$] in light petroleum resulted in slow dissolution of the white solid. After filtration, the solution afforded white [{HB(pz)$_3$}Cu(CO)] on evaporation. Addition of [Cu_2{HB(pz)$_3$}$_2$] (100 mg, 0·18 mmol) to a solution of PPh_3 (47 mg, 0·18 mmol) in benzene gave a green colouration. Evaporation and recrystallisation afforded [{HB(pz)$_3$}Cu(PPh_3)] (111 mg, 62%). A similar reaction to that with PPh_3, using [Cu_2{HB(pz)$_3$}$_2$] (276 mg, 0·5 mmol) and Bu^tNC (83 mg, 1 mmol), afforded the complex [{HB(pz)$_3$}Cu($CNBu^t$)] (118 mg, 66%).

[3/1036 *Received*, 21*st May*, 1973]