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TRIS(PYRAZOLYL)BORATO-RUTHENIUM CARBONYL COMPLEXES

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SUMMARY

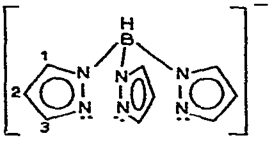
The reaction between $Ru_3(CO)_{12}$ and potassium tris(pyrazolyl)borate, $KHBpz_3$, gives a deep red solution from which the compounds $HBpz_3Ru(CO)_2X$ [X=Cl, Br, I] may be obtained on treatment with the appropriate halogen. The chemistry of some related compounds containing ruthenium or iron is briefly discussed.

The use of the tris(pyrazolyl)borate anion (I) to form complexes with a variety of transition metals has been described by Trofimenko[1], who has pointed out the analogy between (I) and the cyclopentadienide anion. This results from both ligands being uninegative tridentate donors, six electrons being derived from the three nitrogen atoms in (I), or the aromatic sextet in $[C_5H_5]^-$.

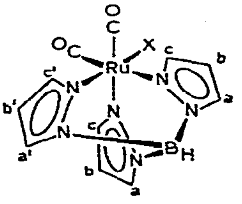
No complexes have been described containing both (I) and carbonyl ligands attached to a metal of the Fe-Ru-Os triad, in contrast with the extensive chemistry associated with the corresponding cyclopentadienyl complexes. Our preliminary experiments have shown that with a variety of iron compounds, such as $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe(CO)_4I_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, the major product even under the mildest conditions, isolated was the known $Fe(HBpz_3)_2$, the high reactivity and strong chelating power of (I) apparently being sufficient to displace all the carbonyl groups from the iron atom.

In contrast, the reaction between $Ru_3(CO)_{12}$ and the potassium derivative of (I) gave a deep red solution, which reacted with halogens to give moderate yields of the compounds $HBpz_3Ru(CO)_2X$ (X=Cl, Br, or I). These compounds formed white or yellow crystalline solids, which were soluble in the more polar solvents to give solutions which were stable in air. The complexes could not be sublimed below 125° (0.1 mm), but were sufficiently volatile in the mass spectrometer to give useful spectra.

The structures were elucidated readily by a consideration of their infrared and



(I)

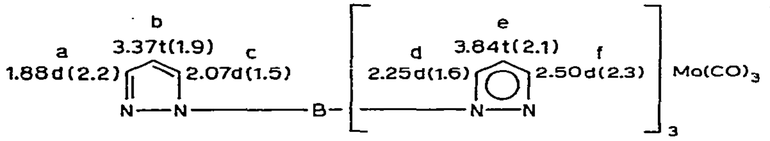


(II)

proton NMR spectra. The carbonyl regions of their infrared spectra each showed two strong ν(CO) bands, similar in appearance and position to those found in the related (π-C_5H_5)Ru$(CO)_2$X complexes, and suggesting the presence of two mutually *cis* carbonyl groups.

The proton NMR spectra showed two groups of three lines, each of equal intensity, with one group being twice the intensity of the second. These observations are readily explained on the basis of structure (II) for these complexes. In (II), two of the pyrazolyl groups are equivalent, whilst the third has a unique position. Furthermore, the two types of pyrazole ring will each contain three different protons, resulting from the differing environments of the two nitrogen atoms. Assuming a small or zero coupling between H(a) and H(c), the resulting first-order spectrum would consist of a two doublets [H(a) and H(c)] and a quartet [H(b)] (which might be observed as a triplet if $J_{23} \sim J_{34}$) for each type of pyrazolyl group.

The observed spectra of the three complexes are summarised in Table 1, and correspond closely to the predicted first-order spectra. However, no unambiguous assignment of the resonances for H(a) and H(c) can be made. Trofimenko[2] has made assignments in the spectrum of the anion $[Bpz_4Mo(CO)_3]^-$ as follows:



Chemical shifts (ppm), with coupling constants (Hz) in parentheses.

suggesting that the doublet with the smaller coupling constant is due to the proton nearest the boron atom. One of the arguments depends on the environments of H(c) and H(d) being more similar than those of the H(a) and H(f).

In the present case, double irradiation experiments have been used to confirm the observed couplings. Thus, irradiation of the high-field multiplet results in collapse of the other three signals to four singlets, thereby establishing that each of the protons H(a), H(a′), H(c) and H(c′) is coupled only to H(b) or H(b′) and not to any other. Similarly irradiation of each of these other three resonances only altered the profile of the high-field signal.

However, our results do not allow an unambiguous assignment of H(a) and H(c). Using the values obtained by Trofimenko[2], who found that the proton nearest the transition metal resonates at higher field than that nearest the boron atom, we can assign the resonances at τ 2.02 and 2.37 to H(a) and H(a′), and those at τ 2.37 and 2.51 to H(c) and H(c′), respectively. The multiplet at τ 3.80 is due to H(b) and H(b′).

We also determined the proton NMR spectrum of $KHBpz_3$. The spectrum (in acetone-d_6) consists of three equal intensity signals at τ 2.52, (H_1), 2.67 (H_3), and 4.06 (H_2). Trofimenko[3] reports values of τ 2.43, 2.82, and 3.85 in D_2O. However, in contrast to this report, we find that each resonance is a quartet indicating a small cross-ring interaction, with coupling constants J_{13} 0.6, J_{12} 2.1, J_{23} 1.55 Hz.

The mass spectra of these complexes showed well-defined parent ion clusters, an accurate mass determination confirming the empirical formula in the case of the iodide. This was necessary since conventional analytical figures were reproducibly

TABLE 1

PROTON NMR DATA FOR TRIS(PYRAZOLYL)BORATE COMPOUNDS

Compound	Chemical shift (τ) and assignments		Coupling constants (Hz)
$KHBpz_3$[a]	2.52dd	H(a)	J_{ab}, 2.1; J_{ac}, 0.6;
	2.67dd	H(c)	J_{bc}, 1.55
	4.06dd	H(b)	
$HBpz_3Ru(CO)_2Cl$[b]	2.08d	H(a)	J_{ab}, 2.2; J_{bc}, 2.5;
	2.37t	H(a'), H(c)	$J_{a'b'}$, 2.0; $J_{b'c'}$, 2.3
	2.51d	H(c')	
	2.79q	H(b), H(b')	
$HBpz_3Ru(CO)_2Br$[b]	2.02d	H(a)	J_{ab}, 2.25; J_{bc}, 2.5;
	2.37t	H(a'), H(c)	$J_{a'b'}$, 2.0; $J_{b'c'}$, 2.3
	2.51d	H(c')	
	3.79q	H(b), H(b')	
$HBpz_3(CO)_2I$[b]	2.02d	H(a)	J_{ab}, 2.1; J_{bc}, 2.35;
	2.37t	H(a'), H(c)	$J_{a'b'}$, 3.25; $J_{b'c'}$, 2.1
	2.50d	H(c')	
	3.80q	H(b), H(b')	
$HBpz_3Ru(CO)_2azb$[a,c]	2.08d	H(a)	
	2.68d	H(c)	
	3.76t	H(b), H(b')	
$HBpz_3Ru(CO)azb$[a,c]	2.23d	H(a)	
	2.73d	H(c)	
	3.98t	H(b), H(b')	

[a] $(CD_3)_2CO$. [b] $CDCl_3$. [c] azb = *C,N*-di-*hapto*(phenylazo)phenyl. H(a') resonance not unambiguously identified (see ref. 4).

about 5 (carbon) and 1 (hydrogen) % high. This phenomenon has been observed previously with similar ruthenium complexes[4]. Other features of the mass spectra include stepwise loss of carbonyl groups, and elimination of halogen. The resulting $[HBpz_3Ru]^+$ ion then fragments by a complex series of CH, NH and BH eliminations, giving peak clusters separated by 11–15 mass units, which were not fully analysed.

We were unable to isolate any derivatives containing $HBpz_3Ru(CO)_2$ groups by subsequent reactions of any of the halides with methyllithium, methylmagnesium iodide, pentafluorophenyllithium, lithium aluminium hydride, tin(II) chloride, or similar reagents. From these reactions, either the starting halide, or decomposition products, including pyrazole, were the only products which were identified. We are unable to explain this apparent lack of reactivity, unless it is a result of the strengthening of the Ru–X bond, resulting from the reduced π-acceptor power of the ligand compared to that of the cyclopentadienyl group. This is also expected to be manifested in a corresponding change in the ν(CO) frequencies. The chlorides have ν(CO) bands at 2056, 2008 (π-C_5H_5) and 2071, 2011 (I) cm^{-1}. This is in the opposite sense to that anticipated, so that this simple explanation is not sufficient to explain the relative reactivities.

Because of the inertness of (II) towards nucleophilic reagents, the crystal and molecular structures of the iodide have been determined[5]. However, no unusual features were found to explain the differences in reactivity of the two series of compounds.

The reaction between $Fe(CO)_5$ and (I), followed by addition of methyl iodide, gave a small amount of a volatile orange-yellow compound, which appears to be $HBpz_3Fe(CO)_2Me$. However, although this material analysed correctly, the infrared spectrum shows four $\nu(CO)$ bands, in two pairs, the relative intensities of which change on keeping the solid complex for a time. The mass spectrum of this material is dominated by the ions which are present in the spectrum of $Fe(HBpz_3)_2$, but in addition, peaks at *m/e* 311 and 283 may be assigned to $[P-CO]^+$ and $[P-2CO]^+$, respectively, from the methyl compound. We are not able to account for the four $\nu(CO)$ bands at present.

A similar complex can be isolated directly from the reaction between $KHBpz_3$ and $Fe(CO)_4I_2$. This material also shows four $\nu(CO)$ bands, the lowest energy absorption being broadened. The mass spectrum again resembles that of $Fe(HBpz_3)_2$, but contains no other peaks. The small amount obtained precluded a detailed investigation, but this may be the hydride, $HBPz_3Fe(CO)_2H$.

EXPERIMENTAL

Spectroscopic measurements were made with Perkin–Elmer 257 (infrared), Varian HA 100 (proton NMR) or GEC-AEI MS 902 (mass) instruments. Solvents were dried and distilled before use, and all reactions were carried out in a nitrogen atmosphere. Potassium bis- and tris(pyrazolyl)borates were prepared by heating pyrazole with potassium tetrahydroborate until the theoretical amount of hydrogen had been evolved[3]. The synthesis of the thallium derivatives has been described recently[4].

Reactions of $Ru_3(CO)_{12}$ with $KHBpz_3$

(*a*). A mixture of $Ru(CO)_{12}$ (500 mg, 0.78 mmole) and $KHBpz_3$ (675 mg, 2.69 mmoles) in tetrahydrofuran (25 ml) was refluxed for 30 min to give a dark red solution. After cooling, addition of iodine (700 mg, 2.76 mmoles) gave a flocculent white precipitate. Refluxing the mixture for 30 min, followed by filtration and evaporation of the pale orange filtrate, gave a red oil, which was recrystallised from methanol to give bright yellow crystals of dicarbonyltris(pyrazolyl)boratoruthenium iodide (650 mg, 49%), m.p. 243°. [Found: C, 31.1; H, 2.9; B, 2.15; mol.wt., 497. $C_{11}H_{10}BIN_6O_2Ru$ calcd.: C, 26.6; H, 2.05; B, 2.18%; mol.wt., 497 (see text).].

Parent ion cluster, observed (calculated) values: *m/e* 494.9074 (494.9062), 495.9054 (495.9045), 496.9067 (496.9059), 497.9038 (497.9046). Infrared: $\nu(BH)$ 2530w; $\nu(CO)$ 2061s, 2003s; other bands at 1500w, 1320m, 1220s, 1120s, 1080w, 1055s, 990w, 800w, 780s, 720s cm^{-1}.

(*b*). In a similar reaction to (*a*), the initial solution obtained from the reaction between $Ru_3(CO)_{12}$ and $KHBpz_3$ was treated with bromine (430 mg, 2.7 mmoles). A similar work-up procedure, followed by recrystallisation from methanol, gave pale yellow microcrystalline dicarbonyltris(pyrazolyl)boratoruthenium bromide (700 mg, 58%), m.p. 256°. (Found: C, 29.6; H, 2.25; Br, 17.75; mol.wt., 450. $C_{11}H_{10}BBrN_6O_2Ru$ calcd.: C, 29.4; H, 2.25; Br, 17.75%; mol.wt., 450.) Infrared: $\nu(BH)$ 2540w; $\nu(CO)$ 2068s, 2011s; other bands at 1500w, 1320m, 1220s, 1080w, 1055s, 995w, 800w, 780s, 735sh, 720s cm^{-1}.

Reaction between $[Ru(CO)_3Cl]_2$ *and* $TlHBpz_3$

A mixture of $[Ru(CO)_3Cl_2]_2$ (500 mg, 1.95 mmoles) and $TlHBpz_3$ (812 mg, 1.95 mmoles) in tetrahydrofuran (25 ml) was refluxed for 30 min. A flocculent white precipitate was filtered off, and the pale purple filtrate was concentrated to an oil under reduced pressure. Sublimation (125°/0.1 mm) gave a lilac sublimate, leaving a white residue, which was recrystallised from methanol to give white dicarbonyltris(pyrazolyl)boratoruthenium chloride (230 mg, 29%), m.p. 261–262°. (Found: C, 32.85; H, 2.8; B, 3.25; Cl, 8.9; mol.wt., 406. $C_{11}H_{10}BClN_6O_2Ru$ calcd.: C, 32.6; H, 2.5; B, 2.65; Cl, 8.85%; mol.wt., 406.) Infrared: ν(BH) 2520w; ν(CO) 2071s, 2011s; other bands at 1500w, 1320m, 1220s, 1120s, 1075w, 1055s, 990w, 800w, 785s, 765sh, 735sh, 720s cm^{-1}.

Reactions with iron carbonyl complexes

(*i*). Pentacarbonyliron (800 mg, 4 mmoles) was added rapidly to a solution of $KHBpz_3$ (1.0 g, 4 mmoles) in THF (25 ml), and the mixture was gently refluxed. The colour gradually changed from yellow, through orange, to dark red. Subsequent treatment with methyl iodide (600 mg, 4 mmoles), refluxing for 1 h, and removal of solvent gave a red solid. Chromatography on Florisil gave lilac $Fe(HBpz_3)_2$ (200 mg, 20%) (eluted with light petroleum/benzene mixtures), m.p. 269–272° (lit.[3] 265–269°). (Found: C, 45.05; H, 4.3; N, 34.6. $C_{18}H_{20}B_2FeN_{12}$ calcd.: C, 44.8; H, 4.2; N, 34.85%.) The mass spectrum showed ions at *m/e* 482 $[P]^+$, 415 $[P-pz]^+$; 337 $[P-HBpz_2]^+$; 270 $[FeHBpz_3]^+$; 203 $[FeHBpz_2]^+$. Benzene eluted a brown oil, which was sublimed (110–120°/0.1 mm) to give yellow-orange $HBpz_3Fe(CO)_2CH_3$. (Found: C, 42.4; H, 4.2; N, 25.1. $C_{12}H_{13}BFeN_6O_2$ calcd.: C, 42.4; H, 3.8; N, 24.3%.) The mass spectrum showed strong ions at *m/e* 482, 415, 337, 270, and 203 (see above), together with peaks at *m/e* 311 $[P-CO]^+$ and 283 $[P-2CO]^+$. Infrared spectrum: 2021vs, 2013vs, 1980vs, 1962vs, [ν(CO)]; 2510 [ν(BH)]; other bands at 1397w, 1309w, 1210s, 1110s, 1042br, 798w, 757s, 751m, 728w, 721s, 667s cm^{-1}.

(*ii*). A similar reaction between $Fe(CO)_4I_2$ (1.7 g, 4 mmoles) and $KHBpz_3$ (1 g, 4 mmoles) in THF (10 ml) gave a small amount of a brown volatile solid, with ν(CO) 2026vs, 2016vs, 1984vs, 1960br cm^{-1}, which may be the hydride, $HBpz_3Fe(CO)_2H$. The mass spectrum was similar to that of $Fe(HBpz_3)_2$.

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