$Co(CN)_5^{3-}$ [3] and Cr^{2+}.[16] Other evidence in favor of stabilization of α-bromoalkyl free radicals by cyclic bridging has come from studies on the photobromination of alkyl bromides[17,18] and from esr measurements on such radicals.[19] The slightly lower reactivity of $Co(CN)_5^{3-}$ toward $ICH_2CH_2CH_2Br$ than toward $ICH_2CH_2CH_2I$ is consistent with the expectation that such stabilization should be more effective for I than for Br. While considered less likely than the explanation just offered, an alternative possibility, namely that the enhanced reactivities of the dihalides result, in part at least, from an inductive effect transmitted through the carbon chain, cannot be ruled out.

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[17] W. Thaler, *J. Am. Chem. Soc.*, **85**, 2607 (1963).

[18] P. S. Skell, K. I. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

[19] P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

Transition Metal Polypyrazolylborates Containing Other Ligands

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Abstract: Tripyrazolylborate ions, $RB(pz)_3^-$, a new class of uninegative tridentate ligands of C_{3v} symmetry, react with group VIb hexacarbonyls yielding anions of structure $RB(pz)_3M(CO)_3^-$ isolable as tetraethylammonium salts. These anions react with allylic halides yielding directly the thermally very stable π-allyl compounds $RB(pz)_3M(CO)_2$-π-C_3H_5, including those with diverse substituents on carbon and boron. The carbonyl stretching frequencies in these compounds reflect the electron-releasing or -withdrawing nature of the substituents. Reaction with alkyl halides and with protonic acids yields the air-sensitive, seven-coordinate species $RB(pz)_3M(CO)_3R'$ and $RB(pz)_3M(CO)_3H$, respectively. The reaction of $B(pz)_4Mo(CO)_3^-$ with $C_7H_7BF_4$ leads to $B(pz)_4Mo(CO)_2$-π-C_7H_7 which, as well as substituted analogs, is also obtained by the reaction of $RB(pz)_3^-$ with $C_7H_7Mo(CO)_2I$. The compound $B(pz)_4Mo(CO)_2$-π-C_5H_5 results from the reaction of $B(pz)_4^-$ with $C_5H_5Mo(CO)_3Cl$. In $B(pz)_4Mo(CO)_2$-π-C_7H_7 and $B(pz)_4Mo(CO)_2$-π-C_5H_5, the $B(pz)_4^-$ ion seems to act as a bidentate ligand. $RB(pz)_3Mn(CO)_3$, $RB(pz)_3Pd$-π-C_3H_5, and $RB(pz)_3Rh(C_2H_4)_2$ have resulted from the nucleophilic reaction of $RB(pz)_3^-$ with the appropriate halogenated precursor. A number of these molecules are stereochemically nonrigid.

The recent discovery[1] of poly(1-pyrazolyl)borate anions, a novel class of chelating ligands, has opened up a new subarea of organometallic chemistry. Numerous four- and six-coordinate transition metal compounds, based on bis- and tris(pyrazolyl)borates, have been prepared.[2] The latter, of essentially D_{3d} symmetry, are exceedingly stable, many being more stable than their metallocene analogs.

The tris(1-pyrazolyl)borate ligand, a uninegative tridentate of C_{3v} (or local C_{3v}) symmetry, may be used to prepare sandwich-like compounds, where the transition metal is surrounded in essentially octahedral fashion by the termini of the two tridentate ligands. Moreover, it is possible to synthesize half-sandwiches[3] where three coordination sites on the metal are taken up by the $RB(pz)_3$ ligand (pz = 1-pyrazolyl group) and the remaining coordination sites by other groups. Since these other ligands may be varied in manifold ways, the scope of half-sandwich chemistry based on the $RB(pz)_3$ ligand ought to considerably exceed that of the corresponding full sandwiches—just as in the case of the C_5H_5 ligand or the more recently discovered carbollide[4] and related ions.[5-7] This is borne out by some recently reported preliminary results.[8] Several features of the $RB(pz)_3$ ligand make it very attractive. (1) The salts, *e.g.*, $KRB(pz)_3$, are easy to prepare and are indefinitely stable to storage in air; furthermore, the cation may be also varied, as needed, for solubility purposes. (2) When C-substituted pyrazoles are used to synthesize the tris(1-pyrazolyl)borate ligand, the C_{3v} symmetry is maintained,[9] and the substituted $RB(pz)_3$ ligand may thus be used to probe the symmetry of other groups bonded to the metal. (3) Up to ten substituents (including R) may be put on the $RB(pz)_3$ ligand enabling one to influence the environment of the transition metal electronically or sterically, yet maintain the basic chelate geometry intact. Such substitution was found to alter dramatically, for instance, the magnetic properties[10] of some transition metal poly(1-pyrazolyl)borates.

This paper reports the synthesis and properties of

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[1] S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

[2] S. Trofimenko, *ibid.*, **89**, 3170 (1967).

[3] The term sandwich has been traditionally used to denote transition metal compounds π-bonded to aromatic ligands. While $RB(pz)_3$ is not a π-bonding aromatic ligand, when one regards its chemistry, it is convenient to visualize $RB(pz)_3$ as replacing a C_6H_6 ligand in full or half-sandwiches. It is in this context that the term "sandwich" is used.

[4] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

[5] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

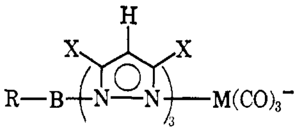
[6] W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 3342 (1967).

[7] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, **89**, 3342 (1967).

[8] S. Trofimenko, *ibid.*, **89**, 3904 (1967).

[9] S. Trofimenko, *ibid.*, **89**, 6288 (1967).

[10] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3158 (1967).

Table I. Compounds of Structure Et_4N^+ 

M	R	X	Mp, °C	% yield	— C, % — Calcd	Found	— H, % — Calcd	Found	— N, % — Calcd	Found	— O, % — Calcd	Found	Ir,[d] cm^{-1}
Cr	H	H	281–282 dec[c]	86	50.0	49.6	6.26	6.37	20.5	20.7			
Cr	pz[a]	H	294–296 dec	28[b]	50.6	50.1	5.87	5.84	23.1	23.1			1900, 1762
Cr	H	CH_3	341–342 dec	87	55.4	55.6	7.46	7.39	17.4	17.6			1891, 1748
Mo	H	H	283–285 dec	31[b]	45.8	45.3	5.74	5.82	18.7	18.7			1897, 1761
Mo	pz[a]	H	318–320 dec	31[b]	46.8	47.3	5.43	5.33	21.4	21.5	8.2	8.2	1898, 1765
Mo	H	CH_3	392–394 dec	73[b]	51.4	51.3	6.92	6.79	16.2	16.0	7.9	7.9	1891, 1751
W	H	H	301–302 dec	80	39.3	38.9	4.92	4.82	16.1	16.1			
W	pz[a]	H	325–327 dec	47[b]	40.8	40.8	4.73	4.32	18.6	18.6			1888, 1755
W	H	CH_3	380–385 dec	62[b]	44.8	44.8	6.04	6.24	14.1	14.1			1881, 1744

[a] pz = 1-pyrazolyl. [b] Yields of material recrystallized from acetonitrile with substantial solubility losses. [c] Crystals are thermochromic (yellow ⇌ orange). [d] In acetonitrile.

some transition metal compounds containing one tris(1-pyrazolyl)borate ligand along with other groups, particularly those involving an M–C bond.

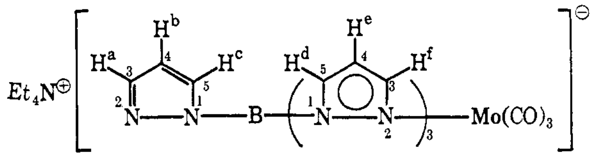
Results and Discussion

A. The $RB(pz)_3M(CO)_3^-$ Anions. Tris(1-pyrazolyl)borate salts (I) react, on heating in dimethyl sulfoxide or dimethylformamide, with group VIb hexacarbonyls to yield the tricarbonyl anions of structure II, isolable conveniently as tetraethylammonium salts (Table I), which are more stable toward oxidation than the alkali metal salts. The oxidative stability of the tetraethylammonium salts depends on the transition metal, decreasing in the order Mo > W > Cr (in agreement with the polarographic oxidation potentials), and the type of substitution on the ligand. For instance, carbonyl anions derived from $B(pz)_4^-$ are more stable than those derived from $HB(pz)_3^-$. On the other hand, the ligand $HB(3,5\text{-}Me_2pz)_3^-$ yields carbonyl anions of, essentially, indefinite stability in the solid state. This effect is probably steric as indicated by Stewart–Briegleb models which show severely restricted access to the transition metal as well as to boron. All these carbonyl anions exhibit two strong CO stretch bands in the infrared at lower frequencies than the $C_5H_5M(CO)_3^-$ salts[11] but very close to the values reported in the same solvent for the carbollide system,[4] $[B_9C_2H_{11}Mo(CO)_3]^{2-}$. The CO frequencies for a given ligand decrease in the order Cr > Mo > W. Methyl substitution on the ligand leads to a lowering of the frequency by about 10 cm^{-1}, which is consistent with the expected increase of the M–C bond order. Substitution at the boron (*i.e.*, $B(pz)_4$ *vs.* $HB(pz)_3$) has no noticeable effect.

The nmr spectra of compounds II are in good agreement with the proposed structure and indicate equivalence of the three coordinated pyrazolyl groups. The spectra also aided in assigning the 3- and 5-hydrogens in the ligand.

In analyzing nmr spectra of poly(pyrazolyl)borates, the doublets due to the 3- and 5-pyrazole hydrogens have often been difficult to assign. Even though their coupling constants were different (usually about 1.8 and 2.2 cps), thus making it possible to distinguish the two peaks, they could not be assigned unequivocally. A tentative assignment was made[2] by studying changes of the chemical shifts of a given $MB(pz)_4$ salt as a function of solvent and changes in the chemical shifts in a given solvent as a function of cation size. It was concluded that the doublet ($J = \sim 2.2$) most affected by changes in solvent and/or size of the cation is that due to the 3-H. Consequently, the doublet with $J = \sim 1.8$ was assigned to the 5-H which one would expect to be relatively unaffected by environmental changes at the periphery of the ion.

The nmr spectrum of $Et_4NB(pz)_4Mo(CO)_3$ corroborated this assignment. This spectrum consists of doublets at τ 1.88 (J = 2.2 cps), 2.07 (J = 1.5 cps),



2.25 (J = 1.6 cps), and 2.50 (J = 2.3 cps) and triplets at τ 3.37 (J = 1.9 cps) and 3.84 (J = 2.1 cps) in 1:1:3:3:1:3 ratio. The assignment of the τ 3.37 and 3.84 peaks to protons b and e, respectively, follows from their multiplicity and intensity. Again, it is apparent that the environments of the c and d hydrogens are much more similar than those of the a and f hydrogens. Consequently, the peaks with approximately identical coupling constants and similar chemical shifts would be due to protons c and d while those with widely different chemical shifts would be a and f. On this basis (plus intensity data) the τ 1.88, 2.07, 2.25, and 2.50 peaks are assigned to the a, c, d, and f hydrogens, respectively. This assignment agrees with the earlier studies. All the data indicate that the doublet with the *smaller* coupling constant is due to the 5-H (hydrogen nearest to boron).

B. The Reactions of the $RB(pz)_3M(CO)_3$ Anions. With Allylic Halides. The salts II react with allylic halides, in many cases even below room temperature, to yield the yellow π-allyl derivatives III, of extraordinary thermal, oxidative, and hydrolytic stability. One

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(11) This comparison is a rough one, since the infrared spectra of $C_5H_5M(CO)_3^-$ salts were measured in mineral oil mulls: R. B. King, *Inorg. Chem.*, 4, 1518 (1965). Moreover, the CO frequencies were cation dependent.

exception was the salt II derived from $HB(3,5\text{-}Me_2pz)^-$, which failed to react under comparable conditions with allyl bromide. It is noteworthy that while irradiation is necessary to obtain, *e.g.*, the analogous $C_5H_5Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ compound (which is not conveniently available by thermolysis of the σ-allyl precursor), the $RB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ compounds form spontaneously at low temperatures or are obtained on moderate heating of the components. A variety of derivatives of the general structure III has been prepared starting with the appropriately substituted pyrazolylborate and allylic halide components. Usually, best yields were obtained by the reaction of pure tetraethylammonium salts of II with allylic halides. However, isolation of the salts is not necessary; they may be prepared *in situ* and immediately treated with allylic halides. Reasonable yields of some substituted compounds of structure III can be obtained by running the three reactions $BH_4^- \rightarrow HB(pz')_3^- \rightarrow HB(pz')_3Mo(CO)_3^- \rightarrow HB(pz')_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ consecutively in the same reaction vessel. In general, the corresponding molybdenum and tungsten compounds are quite similar, except that the tungsten compounds are formed more slowly.

The behavior of chromium salts in the above reaction sequence was intriguing. It is noteworthy that, in contrast to abundant examples of $C_5H_5M(CO)_2\text{-}\pi\text{-}$allyl (or substituted π-allyl) compounds, where M = Mo or W, there are few unambiguous examples of the analogous chromium compounds.[12] When the ion $B(pz)_4Cr(CO)_3^-$ was treated with allyl bromide at room temperature, it reacted very rapidly, evolving 1 equiv of carbon monoxide. A red solid (rather than yellow as with Mo or W compounds) was obtained in 88% yield; analysis, infrared spectrum, and nmr spectrum[13] agreed with the $B(pz)_4Cr(CO)_2\text{-}\pi\text{-}C_3H_5$ structure. This red solid dissolves in halocarbons with decarbonylation to form an unidentified violet species, presumably containing Cr(III). On the other hand, its solutions in benzene are stable at or below room temperature; on heating to about 50° gas is evolved and a crystalline greenish precipitate is obtained. This material has a well-defined infrared spectrum containing carbonyl bands at 1900 (s) and 1760 (vs) cm^{-1} which might suggest the presence of $B(pz)_4Cr(CO)_3^-$ ion, but it has not been identified. On boiling in chloroform more gas is evolved and a yellow solid precipitates. This has been assigned the structure $[B(pz)_4]_2CrCl$ since it is water soluble and on treatment with hexafluorophosphate ion yields $[B(pz)_4]_2CrPF_6$, identical in all respects with authentic material obtained from $KB(pz)_4$ and Cr^{3+} ion and also isomorphous with $[B(pz)_4]_2FePF_6$ which was prepared from $B(pz)_4^-$ and Fe^{3+}. The exact course of these oxidative transformations has not been investigated.

The nmr spectra of compounds III (Table II) agree with the structures assigned; moreover, they indicate these compounds to be fluxional molecules.[13]

The infrared spectra of compounds III were also informative. First, in all cases there were only two CO bands (measured in cyclohexane at high resolution), in contrast to four[14] found in $C_5H_5Mo(CO)_2\text{-}\pi\text{-}C_3H_5$. Considering the likely explanation that this phenomenon[15,16] is due to presence of rotamers of the π-allyl group, the conclusion can be drawn that the π-allyl group in compounds III is stereochemically rigid on the nmr time scale,[17] which is unsurprising in view of the steric restrictiveness of the ligand and invariance of nmr signals of the π-allyl group in compounds III with changing temperature.

The positions of carbonyl bands in the parent compounds $HB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ and $B(pz)_4Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ were essentially identical, at 1958 and 1874 cm^{-1}, and thus again lower by about 10 cm^{-1} than in the corresponding C_5H_5 analogs. However, substitution either on the $HB(pz)_3^-$ or the π-allyl ligand shifted these bands. By and large, the shifts were small and in the direction predicted by simple inductive effects. For instance, in the π-cyclopentenyl and π-cyclohexenyl compounds the ν_{CO} was lowered by 7 and 11 cm^{-1}, respectively (for the higher frequency band), but a boron-bonded butyl group caused a ν_{CO} lowering of only 3 cm^{-1}. On the other hand, an increase in the ν_{CO} by 3–5 cm^{-1} was observed when the 4 position in the $HB(pz)_3$ ligand was substituted with electron-withdrawing groups such as Cl, CN, or NO_2 and also in the compound $HB(pz)_3Mo(CO)_2\text{-}\pi\text{-}2\text{-}$phenylallyl. However, a bromine atom on the central carbon of the π-allyl groups increased ν_{CO} (12 cm^{-1}) more substantially. The tungsten compounds had lower ν_{CO} by about 10 cm^{-1}, as has been observed in the anions II.

C. With Alkyl Halides. The anions II reacted at slightly elevated temperatures and even at room temperature with lower alkyl halides to yield derivatives containing seven-coordinate molybdenum or tungsten with an alkyl–metal bond. These compounds, IV, are red, in contrast to the yellow π-allyl derivatives and the $C_5H_5M(CO)_3R$ analogs. They are diamagnetic and give high-resolution nmr spectra in excellent agreement with the proposed structure. For instance, in $HB(pz)_3Mo(CO)_3C_2H_5$ all the carbon-bonded hydrogens of the ligand were discernible as were the methylene and methyl peaks centered at τ 6.38 and 8.60, respectively. The 3-hydrogens of the ligand appeared in a 2:1 pattern indicating a stereochemically rigid structure, with the ethyl group being probably equidistant from two of the pyrazolyl groups. The nmr spectrum of the methyl analog was similar. The infrared spectra were fairly complex containing three strong carbonyl bands along with shoulders, the strong bands being at lower frequencies than those of $C_5H_5M(CO)_3R$ compounds.[18]

Less stable than the π-allyl compounds III, these alkyl derivatives decomposed on storage in several days but much more rapidly in solution.

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(12) E. O. Fischer, H. P. Kögler, and P. Kuzel, *Chem. Ber.*, **93**, 3006 (1960); E. O. Fischer and F. Ulm, *ibid.*, **94**, 2413 (1961); *Z. Naturforsch.*, **15b**, 59 (1960).

(13) The nmr spectrum was hazy and similar to those of the stereochemically nonrigid Mo and W compounds. The limiting high-temperature spectrum could not be obtained because the chromium compound was thermally unstable. On the other hand, the presence of the ligand and π- rather than σ-allyl group could be ascertained by integration. Stereochemical nonrigidity in $RB(pz)_3$ compounds will be the subject of a separate publication.

(14) R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

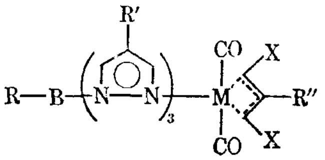
(15) A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

(16) J. W. Faller and M. J. Incorvia, *ibid.*, **7**, 840 (1968).

(17) The alternative explanation—rotation of the π-allyl group at a rate that is fast on the infrared time scale—can be safely disregarded.

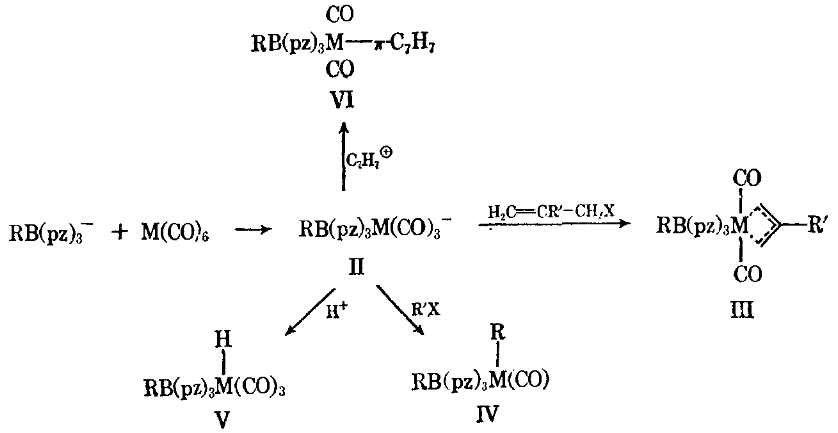
(18) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

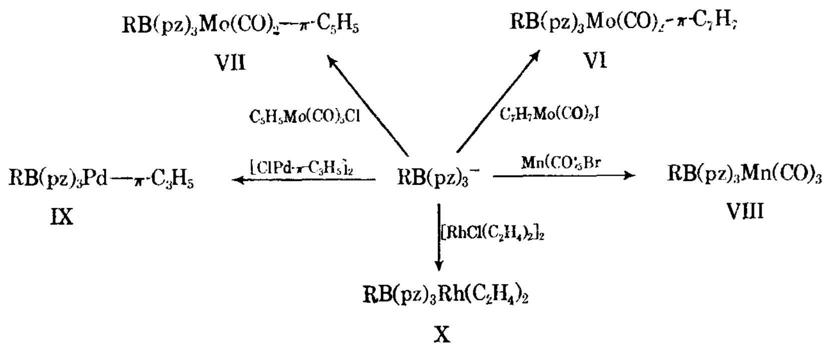
Table II. Compounds of Structure III,



M	R	R′	R″	X	Mp, °C	%	C, %		H, %		N, %		Z, %		Ir, cm^{-1}	Miscellany
						yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
Cr	pz[a]	H	H	H	~120 dec	88	47.7	47.8	3.97	4.01	26.1	26.2				The only red compound in this table; all others are yellow
Mo	H	H	H	H	250–252 dec	64	41.4	41.1	3.70	3.82	20.7	20.6			1958, 1874[b]	B^{11} nmr: d (J = 116 cps) + 22.5 ppm[e]
Mo	H	H	CH_3	H	245–246 dec	65	42.8	42.3	4.05	4.41	20.0	19.9			1958, 1874[b]	
Mo	H	H	C_6H_5	H	214–215	54	49.8	49.7	3.95	3.67	17.4	17.6	O, 6.6	O, 6.6	1960, 1881[b]	B^{11} nmr: d (J = 112 cps) + 22.3 ppm[e]
Mo	H	H	H	X,X = $(-CH_2-)_2$	304–305 dec	11	45.7	45.6	4.27	4.35	18.8	18.8			1947, 1867[b]	
Mo	H	Cl	H	H	253–254 dec	67[d]	33.0	33.2	2.35	2.22	16.4	16.4	Cl, 20.9	Cl, 21.0	1964, 1882[b]	Uv:[b] 382 mμ (ε 1440), 228 mμ (ε 24,200)
Mo	H	CN	H	H	Gradually darkens from ~280°	13[d]	42.4	42.1	2.50	2.48	26.2	26.0			1961, 1874[c]	Uv:[c] 380 mμ (ε 1500)
Mo	H	NO_2	H	H	Darkens from ~240°, explodes ~265°	12[d]	31.1	31.0	2.22	2.56	23.3	23.1	O, 24.6	O, 23.7	1964, 1878[c]	Uv:[c] sh 380 mμ (ε 2600), 265 mμ (ε 38,500)
Mo	Bu	H	H	H	206–207	70	46.8	46.6	4.98	5.25	18.2	18.3			1955, 1872[b]	
Mo	pz[a]	H	H	H	253–255 dec	85	43.3	43.4	3.67	3.62	23.7	23.8	Mo, 20.3 Mol wt, 472	Mo, 20.2 Mol wt, 474[f]	1958, 1875[b]	
Mo	pz[a]	H	CH_3	H	218–219	91	44.5	44.3	3.91	4.13	23.1	23.1			1958, 1875[b]	
Mo	pz[a]	H	Br	H	195–198 dec	64	37.0	37.1	2.91	2.99	20.3	20.3	Br, 14.5	Br, 14.6	1970, 1890[b]	
Mo	pz	H	C_6H_5	H	219–220	73	50.3	50.3	3.83	3.78	20.4	20.7				
Mo	pz[a]	H	H	X,X = $(-CH_2-)_2$	245–250 dec	74	45.8	46.1	3.81	3.82	22.5	22.5			1951, 1873[b]	
Mo	pz[a]	H	H	X,X = $(-CH_2-)_3$	265–270 dec	35	46.9	47.0	4.11	4.09	21.9	21.7			1946, 1867[b]	
W	H	H	H	H	275–276 dec	58	34.0	33.5	3.01	2.77	17.0	17.1			1949, 1862[b]	B^{11} nmr: d (J = 113 cps) +22.4 ppm[e]
W	H	H	CH_3	H	268–270 dec	72	35.4	35.5	3.34	3.49	16.5	16.5			1950, 1861[b]	
W	pz[a]	H	H	H	259–260	79	36.4	36.2	3.04	2.98	20.0	20.0			1949, 1862[b]	
W	pz[a]	H	CH_3	H	227–228	49	37.6	37.3	3.31	3.54	19.5	19.4			1951, 186[b]	

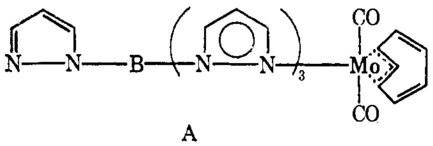
[a] pz = 1-pyrazolyl. [b] In cyclohexane. [c] In methylene chloride. [d] Prepared by method B. [e] Referred to external trimethyl borate. [f] By osmometry in chloroform.



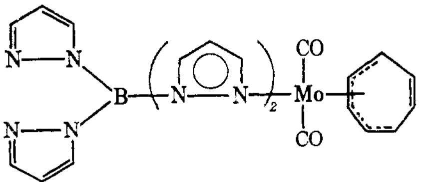


D. With Acids. Acidification of the salts III yielded readily the free acids V as yellow solids soluble in polar organic solvents and alkali but insoluble in water. The M–H resonance for $HB(pz)_3M(CO)_3H$ appeared at τ 13.3 for Mo and τ 12.5 for W, and for $HB(3,5\text{-}Me_2pz)_3M(CO)_3H$ at τ 13.5 for Mo and τ 12.4 for W; thus it was at lower field than in the corresponding $C_5H_5M(CO)_3H$ compounds.[17] These acids were air sensitive and slowly decomposed on storage. Of the two, the Mo compound was significantly less stable, particularly in solution. It should be noted that the dimeric species, analogous to $[C_5H_5Mo(CO)_3]_2$ (which forms very readily and is often the only isolable product in the C_5H_5 system), was not observed.

E. The Compounds $RB(pz)_3M(CO)_2C_7H_7$ and $RB(pz)_3M(CO)_2C_5H_5$. The reaction of $KB(pz)_4Mo(CO)_2$ with $C_7H_7BF_4$ gave VI, a red solid, mp 224–225° dec, of the composition $B(pz)_4Mo(CO)_2C_7H_7$, which was quite stable toward air and moisture. The same compound was also obtained by the reaction of $KB(pz)_4$ with $C_7H_7Mo(CO)_2I$, as were the analogous derivatives $HB(pz)_3Mo(CO)_2C_7H_7$ and $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2C_7H_7$ by the reaction of $C_7H_7Mo(CO)_2I$ with the appropriate poly(pyrazolyl)borate ions. All these compounds presented the same structural problem as that encountered in $C_5H_5Mo(CO)_2C_7H_7$[19,20] namely, that utilization of all electrons available from the ligands would yield a formally eight-coordinate molybdenum with a noninert gas configuration (20 electrons). While eight-coordination in some molybdenum compounds has been established,[21] it is by no means common; it is confined to small ligands and would be unlikely with ligands as bulky as $B(pz)_4$ and C_7H_7. Moreover, no reason can be envisaged for a 20-electron configuration. Assuming, then, an inert-gas configuration and a formal seven-coordination[22] for $B(pz)_4Mo(CO)_2C_7H_7$, two structures can be arrived at satisfying these conditions: structure A contains a normal, tridentate $B(pz)_4$ ligand and an allylic $\pi\text{-}C_7H_7$ ligand, while B has a bidentate $B(pz)_4$ group and a probably nonplanar $\pi\text{-}C_7H_7$ ring containing an uncomplexed double bond. A structure with a planar $\pi\text{-}C_7H_7$ ring and a monodentate $B(pz)_4$ ligand is considered unlikely.



A

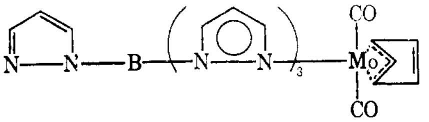


B

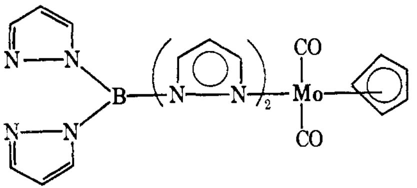
The nmr spectrum shows three types of pyrazolyl groups in 2:1:1 ratio along with a sharp cycloheptatrienyl spike at τ 4.76 and thus is equivocal since it can be reconciled with either structure A or B. In A the normal disposition of the two carbonyl groups and the C_7H_7 ligand with regard to the tridentate $B(pz)_4$ ligand of local C_{3v} symmetry would make two of the coordinating pyrazolyl groups identical and different from the third.[23] At the same time the fluxional nature of the allylic $\pi\text{-}C_7H_7$ ring would make all its protons identical on the nmr time scale. In structure B the bidentate $B(pz)_4$ ligand, being puckered, would possess a pseudoaxial and a pseudoequatorial pyrazolyl group (the uncoordinated ones), each in a different magnetic environment, and all the hydrogens in the presumably fluxional C_7H_7 ligand would be identical.

Of the two structures, however, B is favored for compound VI on the basis of the following considerations. (1) Of the two structures, B involves, according to molecular models, less steric hindrance. In particular, the fact that $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2C_7H_7$ is formed and possesses properties very similar to those of $B(pz)_4Mo(CO)_2C_7H_7$ speaks very strongly against structure A since the $HB(3,5\text{-}Me_2pz)_3$ ligand, when tridentate in $HB(3,5\text{-}Me_2pz)Mo(CO)_3^-$, cannot even accommodate an unsubstituted π-allyl group. (2) The high-resolution infrared spectrum has only two CO peaks (in cyclohexane) in contrast[24] to $C_5H_5Mo(CO)_2C_7H_7$.

A compound analogous to those above, $B(pz)_4Mo(CO)_2C_5H_5$ (VII), was synthesized by the reaction of $KB(pz)_4$ with $C_5H_5Mo(CO)_3Cl$. Here, too, similar considerations apply with regard to the structure, and of the two *a priori* possible structures with an inert-gas configuration, C and D, the latter is favored based on considerations similar to those above. First, there is no unequivocal precedent for an allylic $\pi\text{-}C_5H_5$.[25] The sharp C_5H_5 spike occurs at τ 4.72, a normal position for a $\pi\text{-}C_5H_5$ ring. The steric argument is valid here as in the $\pi\text{-}C_7H_7$ analog. While the summation of these



C



D

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[19] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[20] R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[21] *E.g.*, in $[Mo(CN)_8]^{4-}$: J. L. Hoard and H. H. Nordsieck, *ibid.*, **61**, 2853 (1939); in $[MoF_8]^{2-}$: B. Cox, D. W. A. Shap, and A. G. Sharpe, *J. Chem. Soc.*, 1242 (1956); G. B. Hargreaves and R. D. Peacock, *ibid.*, 4390 (1958).

[22] This presupposes $\pi\text{-}C_7H_7$ to be three-coordinate and allylic $\pi\text{-}C_7H_7$ two-coordinate, although the bidendate nature of an allyl group is to some extent a formalism.

[23] The bulk of the C_7H_7 ligand would preclude equalization of pyrazolyl groups *via* a rotation process which does take place with simple allyls, *e.g.*, $B(pz)_4Mo(CO)_2\text{-}\pi\text{-}C_3H_5$.

[24] This argument, *per se*, is not compelling since, even if structure A were assumed, only one rotamer would probably be capable of existence for steric reasons.

[25] The compounds $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$ have been postulated to involve a dynamic π-allyl C_5H_5 ligand (R. B. King, *Inorg. Chem.*, **7**, 90 (1968)), but the evidence, as yet, has not been conclusive.

arguments appears persuasive and while low-temperature nmr studies will shed additional light on this problem, the last doubts as to the actual structures would have to be resolved by an X-ray crystallographic determination.

F. Other Transition Metal Derivatives. Apart from the wealth of chemistry arising from the reactions of the $RB(pz)_3M(CO)_3^-$ anions, other transition metal derivatives are accessible by simple metathetical reactions. All of these derivatives are stable and can be handled and stored in air. They are diamagnetic and give rise to sharp and well-resolved nmr spectra.

The reaction of $RB(pz)_3^-$ with $Mn(CO)_5Br$ proceeded readily to yield the colorless, sublimable, and thermally quite stable $RB(pz)_3Mn(CO)_3$ compounds VIII. Surprisingly, $B(pz)_4Mn(CO)_3$ was also obtained from the reaction of $B(pz)_4Mo(CO)_3^-$ with $BrMn(CO)_5$. The nmr spectra of these compounds were temperature independent in the +60 to −40° range and indicated spectroscopic identity of the three coordinated pyrazolyl groups. For instance, in $B(pz)_4Mn(CO)_3$ they could be clearly distinguished from the fourth, uncoordinated pyrazolyl group. The infrared spectra were characterized by two strong and sharp carbonyl bands at 2041 and 1941 cm^{-1} in the case of $HB(pz)_3Mn(CO)_3$ and $B(pz)_4Mn(CO)_3$, but at 2032 and 1928 cm^{-1} for $HB(3,5\text{-}Me_2pz)_3Mn(CO)_3$. Again these bands display the same shift toward lower frequency,[26] compared with $C_5H_5Mn(CO)_3$, as that observed in $RB(pz)_3M(CO)_2\text{-}\pi\text{-}C_3H_5$, the implication being that the $RB(pz)_3^-$ group is a better electron donor than $C_5H_5^-$.

The reaction of $KRB(pz)_3$ with π-allylpalladium chloride dimer led to compounds of structure IX, $RB(pz)_3Pd\text{-}\pi\text{-}C_3H_5$, which, unlike the red $C_5H_5Pd\text{-}\pi\text{-}C_3H_5$, are colorless. The compound $B(pz)_4Pd\text{-}\pi\text{-}C_3H_5$ melted cleanly at 246–248°, but $HB(pz)_3Pd\text{-}\pi\text{-}C_3H_5$ decomposed at 150–151° with deposition of metallic palladium. The nmr spectra of both compounds indicated the normal type of π-allyl group with the π-allyl protons in the usual range.

On the other hand, in each compound only one type of pyrazolyl group was discernible. This implies an exchange process since if palladium were four-coordinate, as it usually is, in the absence of intramolecular exchange two pyrazolyl groups should be identical (coordinated); the other one (or two) in a different magnetic environment should display different chemical shifts.

The compound $HB(pz)_3Rh(C_2H_4)_2$, X, a yellow, air-stable solid, was obtained by the reaction of $KHB(pz)_3$ with $[Rh(C_2H_4)_2Cl]_2$. In the nmr spectrum, all eight ethylene hydrogens appeared at room temperature as a single peak at τ 7.46 showing Rh^{103} splitting of about 1.7 cps. The three pyrazolyl groups were spectroscopically identical. This is consistent with a stereochemically nonrigid molecule involving an intramolecular exchange process whereby the environments of all the ethylenic hydrogens and of all pyrazolyl groups become averaged. In this regard, $HB(pz)_3Rh(C_2H_4)_2$ resembled $acacRh(C_2H_4)_2$ rather than $C_5H_5Rh(C_2H_4)_2$, as in the latter compound the room-temperature spectrum shows two types of ethylenic hydrogens having quite different chemical shifts, while the former has one sharp peak for all eight ethylenic hydrogens.[27] It is surprising, however, that the nmr spectrum of $HB(pz)_3Rh(C_2H_4)_2$ remains virtually unchanged down to −60°, since one would expect a higher barrier to rotation in $HB(pz)_3Rh(C_2H_4)_2$ than that in the C_5H_5 or acac[28] analog.

Conclusion

The examples cited above indicate the $RB(pz)_3^-$ ion to be a most versatile ligand. The properties of its half-sandwich compounds are dominated by the relatively high electron supply to the metal (as compared with the C_5H_5 ligand) and the steric protection accorded the metal by the 3-hydrogens or methyl groups. This effect leads to enhanced stability of the complexes; on the other hand, the steric restraints imposed by the ligand preclude the formation of some complexes accessible with the C_5H_5 ligand, the steric demands of which are low. In this regard the $RB(pz)_3^-$ and $C_5H_5^-$ ligands complement each other. Further studies in this area will be reported shortly.

Experimental Section

Nmr spectra were measured on a Varian A-60 instrument using chloroform-*d* as solvent and tetramethylsilane as external standard. The infrared spectra were measured on a Perkin-Elmer 221 instrument with grating optics and the carbonyl peak positions were read off directly from the counter for an accuracy of ±1 cm^{-1}.

Materials. The simple allylic halides are commercially available and were used without further purification. 3-Bromocyclopentene was prepared by allylic bromination of cyclopentene.[29] The various $RB(pz)_3^-$ salts were synthesized by published methods.[2,8]

Synthesis of Compounds of Structure II. Compounds of structure II (M = Cr, Mo, or W) were prepared by the general method exemplified below for a specific compound (R = pz; X = H; M = Mo). The properties of these salts are summarized in Table I.

A mixture of 128 g of $KB(pz)_4$ and 110 g of $Mo(CO)_6$ (both 0.4 mole) in 600 ml of dimethylformamide was stirred and heated at about 100° until about 30 l. of carbon monoxide was evolved. The solution was concentrated at 70° (2 mm) to about half the original volume and was poured with stirring into excess 1 *M* aqueous Et_4NCl solution. The resulting yellow precipitate was filtered, washed with water, and then, still moist, recrystallized from 2:1 acetonitrile–water to give 166 g (70.7%) of recrystallized material plus an additional 10 g (4.3%) of less pure product.

While recrystallization yields a somewhat more stable material, it is usually not necessary, and the thoroughly washed and dried tetraethylammonium salts may be used directly for further syntheses.

The solubilities of this salt at room temperature per 100 ml of solvent are as follows: 1,2-dimethoxyethane, 0.9 g; tetrahydrofuran, 1.2 g; acetonitrile, 4.1 g; dimethylformamide, 14 g.

The tetraethylammonium salts of the above anions were oxidized in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte. All three compounds exhibited two well-defined oxidation waves with the following $E_{1/2}$ values: Cr, −0.42 and +0.32; Mo, −0.20 and +0.45; and W, −0.30 and +0.42.

Synthesis of Compounds of Structure III. Compounds of structure III (M = Mo, W) were synthesized by the following two general methods illustrated by specific examples. Their properties are summarized in Table II.

Method A. π-2-Methylallyltetrakis(1-pyrazolyl)boratodicarbonylmolybdenum. To 0.1 mole of $KB(pz)_4Mo(CO)_3$, prepared *in situ* in 250 ml of dimethylformamide, was added at 50–60° 15 g (50% excess) of methallyl chloride. After gas evolution ceased,

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(26) Values of 2035 and 1953 cm^{-1} (in cyclohexane) have been reported: R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960); in a KBr pellet they are 2023 and 1939 cm^{-1} (R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 113.

(27) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(28) acac = anion derived from 2,4-pentanedione.

(29) K. Kochlaefl, V. Bazant, and F. Sorm, *Chem. Listy*, **49**, 519 (1955).

the yellow solution was poured into 1.5 l. of cold water. The product was extracted with methylene chloride, and the extracts were rapidly chromatographed on alumina, packing and eluting with methylene chloride. The yellow fraction was evaporated to dryness, and the residue was recrystallized from toluene–heptane to give 38 g (78%) of yellow crystals, mp 218–219°. The filtrate was rechromatographed, and the residue from stripping of the yellow band was recrystallized as above to yield an additional 6.2 g (13%) of the same material for a total yield of 91%.

Method B. **π-Allylhydrotris(4-chloro-1-pyrazolyl)boratodicarbonylmolybdenum.** A mixture of 5.4 g (0.1 mole) of potassium borohydride and 33 g (0.3 mole) of 4-chloropyrazole in 250 ml of dimethylacetamide was stirred and refluxed, the emanating gases being led through a −80° trap to a wet-test meter. The solution was cooled when about 7.3 l. of gas had been evolved, and 26.4 g (0.1 mole) of molybdenum hexacarbonyl was added. Heating was resumed, and when another 7.5 l. of gas had evolved, the solution was cooled again, and 15 ml (large excess) of allyl bromide was added dropwise at room temperature through a dropping funnel equipped with a pressure equalizer. The solution was heated until about 2.5 l. of gas was evolved. The solution was then cooled and poured, with stirring, into 600 ml of ice-water. The yellow product, which separated better upon addition of saturated sodium chloride solution, was filtered. It was purified by chromatography on acid-washed alumina with methylene chloride as eluent. The yellow band was collected and the solvent was distilled off. The yellow residue was stirred with methanol, filtered, and dried. The product, obtained in 34 g (67%) yield, was purified further by recrystallization from chlorobenzene; mp 253–254° dec.

π-Allyltetrakis(1-pyrazolyl)boratedicarbonylchromium and Its Reactions. 1. Synthesis. The salt $Et_4NB(pz)_4Cr(CO)_3$ was freshly prepared from 0.1 *M* amounts of $KB(pz)_4$ and $Cr(CO)_6$. It was washed well with water and then, still moist, transferred to a 1-l. flask and dissolved in 400 ml of acetonitrile. The yellow solution was cooled to 17° and 24 g (0.2 mole) of allyl bromide was added. Carbon monoxide was evolved rapidly, and the solution turned dark red as solid started precipitating. When gas evolution stopped (after 2.4 l. or 0.1 mole was evolved), the red slurry was filtered. The dark-red crystals were washed with acetonitrile and air-dried to give 37.4 g (87.5%) of product. It loses its red color and sinters at about 120°; more pronounced decomposition is observed at 240–260°. It was purified by solution in benzene at room temperature, filtration, and concentration of the solution on a Rinco evaporator.

Anal. Calcd for $C_{17}H_{17}BCrN_8O_2$: C, 47.7; H, 3.97; N, 26.1. Found: C, 47.8; H, 4.01; N, 26.2.

The infrared spectrum had two sharp carbonyl peaks at 1925 and 1845 cm^{-1}.

The nmr spectrum was taken in benzene-d_6 since the compound reacted rapidly with chloroform at room temperature. It was hazy and similar to the "dynamic" spectra of $B(pz)_4Mo(CO)_2$-π-C_3H_5, with the pyrazole 4-hydrogens clearly discernible as two peaks at τ 3.82 and 4.25 in a 1:3 ratio, the rest being rather broad and hazy in the τ 1.5–3.0 range. The π-allyl hydrogens could be discerned only by integration and were at τ 5.7 and 8.4.

2. Pyrolysis. Ten grams (0.023 mole) of $B(pz)_4Cr(CO)_2$-π-C_3H_5 was dissolved in 500 ml of benzene, and the solution was filtered. The red solution was heated slowly to reflux. Gas was evolved briskly; its evolution stopped after about 1.0 l. The reaction mixture was yellowish green and contained solid. It was concentrated to 200 ml, cooled, and filtered. The solid was washed with benzene and dried to give 4.2 g as yellowish green crystals.

Anal. Found: C, 48.1, 47.9; H, 3.99, 3.83; N, 30.3, 29.9; Cr, 9.32, 9.43; B, 1.04, 1.14.

This analysis fits no simple structure. The infrared spectrum is well defined and has two sharp carbonyl bands at 1900 (m) and at 1760 cm^{-1} (vs).

Evaporation of the filtrate yielded 4.0 g of brown solid, the infrared spectrum of which was devoid of carbonyl bands.

Bis[tetrakis(1-pyrazolyl)borate]chromium(III) Hexafluorophosphate. 1. Five grams of the yellow-green crystals from the preceding experiment was dissolved in 200 ml of chloroform at room temperature, the solution was filtered, and the greenish yellow filtrate was boiled with stirring for 15 min and cooled. A greenish yellow solid separated and was washed with chloroform. It was obtained in 4.5 g yield as paramagnetic, water-soluble crystals with a strong and broad band at about 750 cm^{-1} in the infrared spectrum. The material was dissolved in water, and aqueous NH_4PF_6 solution was added. A yellow precipitate separated which was filtered and purified by recrystallization from 4:1 water–acetonitrile. The product was obtained as yellow needles, mp 358–359° dec.

Anal. Calcd for $C_{24}H_{24}BCrF_6PN_{16}$: C, 38.2; H, 3.18; Cr, 6.89; F, 15.1; N, 29.7. Found: C, 38.6; H, 3.67; Cr, 6.95; F, 14.7; N, 29.8.

2. A mixture of 35 g (0.1 mole) of $KB(pz)_4$, 7.9 g (0.05 mole) of $CrCl_3$, and a pinch of zinc dust in 300 ml of DMF was stirred and refluxed for 6 hr. The brown suspension was poured into 1.5 l. of water and the mixture was filtered. To the orange filtrate 50 ml of 25% NH_4PF_6 solution was added, and the resulting precipitate was extracted with methylene chloride. The extracts were stripped to dryness and the residue was chromatographed on alumina, the yellow-orange band being collected. This fraction was stripped and the residue was stirred with 200 ml of methanol and filtered, yielding 6.2 g (16%) of a yellow solid identical in all respects with the product of mp 358–359° from the preceding experiment.

Bis(tetrapyrazol-1-ylborate)iron(III) Nitrate and Hexafluorophosphate. To a solution of 20.2 g (0.05 mole) of hydrated ferric nitrate in 400 ml of distilled water was added a concentrated aqueous solution of 32 g (0.1 mole) of $KB(pz)_4$. The resulting red slurry was digested for 20 min at 80–90°, then cooled and filtered. The solid was recrystallized from 900 ml of boiling water to yield 6.2 g (18%) of the nitrate which darkens at about 200° and decomposes at 300–305°.

To the filtrate was added excess ammonium hexafluorophosphate which precipitated a bright red solid. It was filtered, dried, and purified by dissolving it in methylene chloride and pouring the solution into carbon tetrachloride. The yield of the hexafluorophosphate was 13.9 g (37%). This compound decomposes sharply at 287–288°.

Anal. (Nitrate) Calcd for $C_{24}H_{20}B_2FeN_{17}O_3$: C, 42.6; H, 3.55; Fe, 8.28; N, 35.2. Calcd for $C_{24}H_{22}B_2FeN_{17}O_4$ (monohydrate): C, 41.5; H, 3.75; Fe, 8.05; N, 34.3. Found: C, 41.3; H, 3.86; Fe, 7.96; N, 35.3.

Anal. Calcd (hexafluorophosphate) for $C_{24}H_{24}B_2F_6FePN_{16}$: C, 37.9; H, 3.17; N, 29.5. Found: C, 37.6; H, 3.38; N, 29.3.

The infrared spectrum of the hexafluorophosphate was identical with that of the corresponding Cr(III) compound.

Hydrotris(1-pyrazolyl)boratoethylmolybdenum. To a solution of 0.2 mole of $KHB(pz)_3Mo(CO)_3$ prepared *in situ* in 500 ml of DMF was added 0.3 mole of ethyl iodide. The solution was maintained at 70° for 3 hr and then poured into 1400 ml of ice-water containing 100 ml of saturated NaCl solution. The red-brown precipitate was filtered and washed with large amounts of water and a few small portions of methanol. The yield of dried solid was 25.4 g (30%). It was purified by being dissolved in a minimum amount of methylene chloride and chromatographed *very rapidly* on a short alumina column applying nitrogen pressure so as to complete this "flash chromatography" in less than 1 min since on slower chromatography most of the material was destroyed. The orange eluate was stripped and stirred with hexane, and the mixture was filtered to give an orange-red solid, darkening gradually from ~120°.

Anal. Calcd for $C_{14}H_{15}BMoN_6O_3$: C, 39.8; H, 3.55; N, 19.9. Found: C, 39.9; H, 3.57; N, 19.9. Nmr (τ values): d 2.30, d 2.40, d 2.58, t 3.68, quadruplet 6.38, and t 8.60 in 3:1:2:3:2:3 ratio. B^{11} nmr: doublet (J = 105 cps) at +21.7 ppm from B-$(OMe)_3$. Ir (Nujol mull): CO at 1980, 1960, 1850, 1835 sh, and 1816 sh cm^{-1}.

The methyl compound, prepared similarly, was obtained as a red solid. It was less stable than the ethyl compound.

Anal. Calcd for $C_{13}H_{13}BMoN_6O_3$: C, 38.1; H, 3.18; N, 20.6. Found: C, 37.4; H, 2.99; N, 20.7. Nmr (τ values): d 2.30, d 2.40, d 2.57, t 3.84, and s 6.85 in 3:1:2:3:3 ratio. Ir (Nujol mull): CO at 1985, 1970 sh, 1948 sh, 1848, 1830, and 1800 sh cm^{-1}.

Free Acids Derived from Anions II. The free acids V were prepared by diluting a freshly prepared solution of $KRB(pz)_3M(CO)_3$ with 4–5 vol of water and acidifying with acetic or hydrochloric acid. The free acids precipitate as pale yellow air-sensitive solids which can be reconverted by bases to the original anions. The acids $HB(pz)_3M(CO)_3H$ (M = Mo, W) can be sublimed with little decomposition at 200° (1 mm), while the acids $HB(3,5\text{-}Me_2pz)_3M(CO)_3H$ (M = Mo, W), although more stable to air, decompose extensively on attempted sublimation. Within each pair the tungsten compound is more stable. The nmr spectrum (in CH_2Cl_2) of each shows a M–H bond which appears at τ 13.3 [$HB(pz)_3Mo(CO)_3H$], 12.5 [$HB(pz)_3W(CO)_3H$], 13.5 [$HB(3,5\text{-}Me_2pz)_3Mo(CO)_3H$], or 12.4 [$HB(3,5\text{-}Me_2pz)_3W(CO)_3$]. The infrared spectrum of $HB(pz)_3Mo(CO)_3H$ (in Nujol mull) is characterized by CO peaks at 2000 (s), 1905 (vs), and 1880 (vs) cm^{-1}, along with shoulders on the low-frequency side; that of $HB(pz)_3W(CO)_3H$ is similar but shifted by about 10 cm^{-1} to lower frequencies.

Tetrakis(1-pyrazolyl)boratecycloheptatrienylmolybdenum Dicarbonyl (VI). Method A. To a mixture of 8.9 g (0.05 mole) of tropylium fluoroborate[30] and 14.5 g (0.05 mole) of $Et_4NB(pz)_4Mo(CO)_3$ in a 200-ml round-bottom flask connected to a gas meter, comprising a closed system, was added 100 ml of DMF. The mixture was stirred as gas evolution proceeded rapidly until 0.7 l. was evolved. The reaction mixture was poured into 400 ml of ice–water and the product was filtered. It was taken up in methylene chloride and purified by chromatography on alumina, the orange-yellow band being collected. Evaporation of this fraction gave a residue, which was stirred with methanol. The mixture was filtered yielding, after washing with methanol and drying, 6.1 g (23%) of red solid. It was recrystallized from toluene; mp 224–225° dec.

Anal. Calcd for $C_{21}H_{19}BMoN_8O_2$: C, 48.3; H, 3.64; N, 21.5; O, 6.1; mol wt, 522. Found: C, 48.3; H, 3.41; N, 21.4; O, 6.2; mol wt (osmometric in chloroform), 518. Ir (cyclohexane): 1954 and 1884 cm^{-1}. Uv (cyclohexane): λ_{max} 385 mμ (ϵ 2040), 318 mμ (ϵ 15,200). Nmr ($CDCl_3$) (τ values): d (J = 2.3 cps) 1.75, d (J = 1.7) 1.94, d (J = 1.8) 2.02, d (unresolved) 2.18, d (J = 2.3) 2.91, t (J = 1.9) 3.52, t (J = 22) 3.91 (separation of another triplet at higher field noted), and s 4.76 in 1:1:2:2:2:1:3:7 ratio. The C_7H_7 peak appears at τ 4.97 in CS_2.

Method B. To a freshly prepared solution of 13.7 g (0.05 mole) of cycloheptatrienylmolybdenum dicarbonyl iodide[31] in 125 ml of DMF was added 19.2 g (0.06 mole) of $KB(pz)_4$. The mixture was stirred and heated intermittently with a 50° water bath. Soon the color of the solution changed from dark green to deep red. After 30 min the solution was poured into 500 ml of ice–water and the precipitated product was filtered and purified by chromatography. It was identical in all respects with the material from the preceding experiment and was obtained in 19.8 g (76%) yield.

Hydrotris(1-pyrazolyl)boratocycloheptatrienylmolybdenum Dicarbonyl. This compound was synthesized as above, substituting an equivalent amount of $KHB(pz)_3$ for $KB(pz)_4$. It was obtained in 15.4 g (67%) yield. This compound is sparingly soluble in most solvents, and the analytical sample was purified by recrystallization from DMF and then from toluene; mp 255–256° dec.

Anal. Calcd for $C_{18}H_{17}BMoN_6O_2$: C, 47.4; H, 3.73; N, 18.4. Found: C, 47.1; H, 3.93; N, 18.4. Nmr (τ values): d 1.87, d, 1.96, d 2.36, d 2.52, t 3.73, t 3.88, and s 4.66 in 1:2:2:1:2:1:7 ratio. Ir (cyclohexane): 1953 and 1872 cm^{-1}. Uv: 385 mμ (ϵ 2000), 317 mμ (ϵ 14,900).

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratecycloheptatrienylmolybdenum Dicarbonyl. This compound was prepared as in the preceding experiment, substituting $KHB(3,5\text{-}Me_2pz)_3$ for $KHB(pz)_3$ and was obtained, after purification by chromatography, in 48% yield. It was recrystallized from toluene; mp 210–212° dec.

Anal. Calcd for $C_{24}H_{29}BMoN_6O_2$: C, 53.3; H, 5.37; N, 15.6. Found: C, 52.9; H, 5.02; N, 15.6.

The nmr spectrum consisted of sharp singlets at τ 4.15, 4.42, 4.74, 7.38, 7.63, and 7.91 in 2:1:7:9:6:3 ratio, assigned to the 4-H of two coordinated pyrazole groups, 4-H of the uncoordinated pyrazole group, cycloheptatrienylium hydrogens, 5-methyls, 3-methyls of coordinated pyrazole group, and 3-methyl of uncoordinated pyrazole groups, respectively.

Ir (cyclohexane): 1939 and 1864 cm^{-1}. Uv: 387 mμ (ϵ 1820) and 318 mμ (ϵ 15,800).

Tetrakis(1-pyrazolyl)boratecyclopentadienylmolybdenum Dicarbonyl. A mixture of 6.5 g (0.02 mole) of $KB(pz)_4$ and 5.5 g of $C_5H_5Mo(CO)_3Cl$[16] (0.02 mole) in 40 ml of dimethylformamide was stirred and heated to 120°. Gas evolution proceeded briskly and stopped after 0.5 l. (0.02 mole) was evolved. The red solution was cooled and poured into ice–water, and the product was filtered. It was purified by chromatography on acid-washed alumina and was eluted with methylene chloride as an orange-red band. Evaporation of the solvent yielded 4.2 g (44%) of a brick-red solid which was recrystallized from toluene; mp 223–225°.

Anal. Calcd for $C_{19}H_{17}BMoN_8O_2$: C, 45.9; H, 3.43; N, 22.6. Found: C, 46.2; H, 3.68; N, 22.6. Ir (cyclohexane): 1968 and 1880 cm^{-1}. Nmr (τ values): d (J = 1.9 cps) 2.20, d (J = 1.5) 2.33, d (J = 1.5) 2.38, d (J = 2.4) 2.83, d (J = 2.2) 3.37, d (J = 2.2) 3.53, t (J = 1.9) 3.75, and t (J = 1.9) 3.85. Uv (CH_2Cl_2): 4.98 mμ (ϵ 366) and 390 mμ (ϵ 955).

π-Allylhydrotris(1-pyrazolyl)boratepalladium. A mixture of 2.25 g (0.0062 mole) of π-allylpalladium chloride dimer and 5 g of $KHB(pz)_3$ (0.02 mole) in 30 ml of methylene chloride was stirred at room temperature. Within a few minutes the yellow color had disappeared. The mixture was shaken with 50 ml of water and the layers were separated. The organic layer was dried and filtered, and the solvent was evaporated yielding 1.6 g (89%) of off-white solid which was purified by chromatography on alumina and then by recrystallization from methanol; melting point, darkens from ~130° and decomposes with deposition of metallic palladium at 150–151°.

Anal. Calcd for $C_{12}H_{15}BN_6Pd$: C, 40.0; H, 4.17; N, 23.3. Found: C, 40.2; H, 4.20; N, 23.5. Nmr: two overlapping doublets centered at τ 2.47, t (J = 2.1 cps) 3.80, m 4.5, d (J = 7.0) 6.18, and d (J = 12.0) 7.06 in 6:3:1:2:2 ratio.

π-Allyltetrakis(1-pyrazolyl)boratepalladium. This compound was obtained quantitatively by the above method as a white solid. It was purified by recrystallization from acetone with large solubility losses, mp 246–248°.

Anal. Calcd for $C_{15}H_{17}BN_8Pd$: C, 42.3; H, 3.99; N, 26.3. Found: C, 42.3; H, 3.96; N, 26.4. Nmr (τ values): d (J = 1.6 cps) 2.34, d (J = 2.5) 2.93, t (J = 2.1) 3.73, m 4.72, d (J = 6.9) 6.15, and d (J = 12.1) 7.12 in 4:4:4:1:2:2 ratio.

Hydrotris(1-pyrazolyl)boratemanganese Tricarbonyl. A mixture of 5.5 g (0.02 mole) of $Mn(CO)_5Br$ and 5.3 g (0.022 mole) of $KHB(pz)_3$ in 150 ml of DMF was stirred and warmed until 1 l. of gas was evolved. The orange solution was cooled and poured into 700 ml of ice–water. The product was extracted with methylene chloride. The extracts were evaporated and the residue was purified by chromatography on alumina. The product was purified further by a second chromatography and was obtained in 4.0 g (57%) yield as a white solid, mp 206–208°.

Anal. Calcd for $C_{12}H_{10}BMnN_6O_3$: C, 40.8; H, 2.84; N, 23.9. Found: C, 40.6; H, 2.97; N, 24.0.

Nmr (τ values): d (J = 1.9 cps) 2.13, d (J = 2.1) 2.31, and t (J = 2.0) 3.75 in 1:1:1 ratio. Ir (cyclohexane): 2041 and 1941 cm^{-1}.

Tetrakis(1-pyrazolyl)boratemanganese Tricarbonyl. This compound was synthesized by the above method in 85% yield and was purified by chromatography; mp 213–215°.

Anal. Calcd for $C_{15}H_{12}BMn_8O_3$: C, 43.0; H, 2.87; Mn, 13.2; N, 26.8. Found: C, 42.8; H, 3.10; Mn, 13.4; N, 27.0. Nmr (τ values): unresolved multiplet 2.10, d 2.27, t 3.41, and t 3.80 in 5:3:1:3 ratio. Ir (cyclohexane): 2042 and 1941 cm^{-1}.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratemanganese Tricarbonyl. This compound was prepared by the above method in 92% yield and was purified by chromatography. It darkens from ~280° and decomposes at 365–366°.

Anal. Calcd for $C_{18}H_{22}BMnN_6O_3$: C, 49.5; H, 5.05; N, 19.3; Mn, 12.6. Found: C, 49.8; H, 5.29; N, 19.3; Mn, 12.7. Nmr ($CDCl_3$): singlets at τ 4.52, 7.81, and 7.99 in 1:3:3 ratio. Ir (cyclohexane): 2032 and 1928 cm^{-1}.

Bis(ethylene)hydrotris(1-pyrazolyl)boraterhodium(I). A mixture of 0.84 g of bis(ethylene)rhodium(I) chloride dimer[32] and 2 g of $KHB(pz)_3$ in 30 ml of DMF was stirred overnight. The yellow solution was diluted with water to 100 ml, stirred for 10 min, and filtered. The solid was taken up in methylene chloride and was chromatographed on alumina, packing and eluting with methylene chloride. The yellow band was collected and evaporated to give 1.1 g (69%) of yellow crystals. The material decomposes on attempted sublimation. It darkens and decomposes gradually from 140° on.

Anal. Calcd for $C_{13}H_{18}BNRh$: C, 41.9; H, 4.84; N, 22.6. Found: C, 41.7; H, 4.93; N, 22.9.

The nmr spectrum (τ values) was as follows: d (J = 1.9 cps) 2.20, d (J = 2.3, J^1 = 0.5) 2.38, t (J = 2.1) 3.83, and "d" (J = 1.5–2.0) 7.46 in 3:3:3:8 ratio. This spectrum is not changed significantly upon cooling.

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