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Transition Metal Tris(1-pyrazolyl)borates Containing Nitroso and Arylazo Ligands

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Anions $RB(pz)_3M(CO)_3^-$, obtained by the reaction of $RB(pz)_3^-$ with group VIb hexacarbonyls, react with nitrosating agents to yield the orange nitroso compounds $RB(pz)_3M(CO)_2NO$ which have been converted to the green, very stable $RB(pz)_3M(NO)_2Cl$ compounds (M = Mo, W). Reaction of $HB(3,5\text{-}(CH_3)_2pz)_3M(CO)_2NO$ (M = Mo, W) with ClNO produces the stable monomeric derivatives $HB(3,5\text{-}(CH_3)_2pz)_3MCl_2NO$ which have a 16-electron configuration. The reaction of $RB(pz)_3M(CO)_3^-$ with diversely substituted aryldiazonium salts yields the metal–arylazo compounds $RB(pz)_3M(CO)_2N{=}NAr$ (M = Mo, W) of remarkable thermal and chemical stability. Their ^{19}F shielding parameters (for Ar = *m*- or *p*-fluorophenyl) have been studied.

The tris(1-pyrazolyl)borate ligand, $RB(pz)_3^-$, has proved to be quite versatile in the area of coordination chemistry, forming both full sandwiches of structure $[RB(pz)_3]_2M$[1,2] and half-sandwiches[3] containing one tridentate $RB(pz)_3$ ligand attached to the metal with the other coordination sites occupied by ligands such as CO, π-allyl, alkyl, hydrogen, π-C_5H_5, C_7H_7, etc. Compounds of this type also include those bearing diverse substituents on carbon or boron. In terms of thermal and chemical stability and wealth of derivative chemistry, these complexes appear to surpass their C_5H_5 analogs. This paper reports the synthesis and characterization of poly(1-pyrazolyl)borate half-sandwiches containing nitroso and arylazo groups bonded to group VIb transition metals. In the discussion they are compared to their C_5H_5 analogs.

Nitrosyl Compounds

The chemistry of group VIb compounds containing cyclopentadienyl and nitrosyl ligands dates back to 1955 when Fischer and co-workers[4,5] reported the synthesis of $C_5H_5Cr(CO)_2NO$ by the reaction of NO with $[C_5H_5Cr(CO)_3]_2$. The analogous Mo and W compounds could not be obtained in this fashion but were synthesized by the reaction of NO with the anions $C_5H_5M(CO)_3^-$.

Simultaneously, Piper and Wilkinson[6-8] reported the preparation of $C_5H_5Cr(NO)_2Cl$ and its derivatives, obtained by nucleophilic attack on Cr by diverse bases. Examples of groups replacing Cl in $C_5H_5Cr(NO)_2Cl$ were Br, I, CH_3, C_2H_5, CH_2Cl, C_6H_5, and SCN. The compound $C_5H_5Cr(NO)_2C_5H_5$ was later studied by Cotton, *et al.*,[9] as an example of a fluxional molecule in which the rapidly exchanging C_5H_5 groups are spectroscopically equivalent at room temperature but at −110° the σ- and π-bonded C_5H_5 groups become distinguishable. Fischer and Strametz[10] investigated the reaction of $C_5H_5Cr(NO)_2Cl$ with various amines and found that not only Cl but also NO may be replaced yielding ions such as $C_5H_5Cr(NO)_2(\text{amine})^+$ and $C_5H_5Cr(NO)(\text{amine})_2^+$.

King has reported the dimer[11] $[C_5H_5Cr(NO)_2]_2$ which contains bridging nitrosyl groups. He also prepared compounds such as $[C_5H_5M(NO)_2S_2C_2(CF_3)_2]_2$, where M = Mo or W, by the reaction of $C_5H_5M(CO)_2NO$ with bis(trifluoromethyl)dithietene, and the iodine-bridged dimer $[C_5H_5Mo(NO)I_2]_2$ by the treatment of $C_5H_5Mo(CO)_2NO$ with I_2.[12] The compounds $(C_5H_5)_2MoNOI$, $(C_5H_5)_2MoNOCH_3$, and $C_5H_5Mo(NO)_2Cl$ have been synthesized recently,[13] the first two apparently representing the first examples of a *trihapto*-C_5H_5 group. This was supported by Cotton and Legzdins,[14] who synthesized $(C_5H_5)_3MoNO$ by the reaction of $C_5H_5MoNOI_2$ with excess TlC_5H_5 and found by nmr studies that this compound had three types of C_5H_5 rings, *viz. penta-*, *tri-*, and *monohapto*, which were interconverting at room temperature but could be observed separately at low temperatures. An X-ray structure determination of this compound,[15] however, revealed one *monohapto*-C_5H_5 and two identical *polyhapto*-C_5H_5 rings.

The expectation of comparable chemistry based on the $RB(pz)_3$ ligand has been realized. When the anions $RB(pz)_3M(CO)_3^-$ (where R = H, pz; M = Cr, Mo, W) are treated with a source of NO^+ such as nitrosyl chloride or alkyl nitrite, a rapid reaction gives compounds of structure $RB(pz)_3M(CO)_2NO$ in good yield. The same type of product is obtained from $HB(3,5\text{-}(CH_3)_2pz)_3M(CO)_3^-$. These nitrosyl complexes are high-melting, sublimable, orange compounds which show no sign of decomposition on storage for several years (see Table I).

Their ν_{CO} absorptions exhibited the trends previously observed in $RB(pz)_3M(CO)_2$-π-C_5H_5 compounds. Thus in $RB(pz)_3M(CO)_2NO$, ν_{CO} decreased in the order Cr > Mo > W, while for the same metal ν_{CO} decreased

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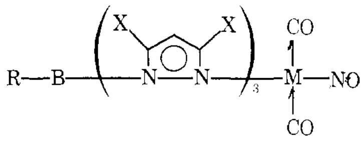
[1] S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
[2] S. Trofimenko, *ibid.*, **89**, 6288 (1967).
[3] S. Trofimenko, *ibid.*, **91**, 588 (1969).
[4] E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955).
[5] E. O. Fischer, *Rec. Trav. Chim.*, **75**, 629 (1956).
[6] T. S. Piper and G. Wilkinson, *Chem. Ind.* (London), **41**, 1296 (1955).
[7] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 28 (1956).
[8] T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).
[9] F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.*, **89**, 6136 (1967).
[10] E. O. Fischer and H. Strametz, *J. Organometal. Chem.* (Amsterdam), **10**, 323 (1967).
[11] R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **85**, 2527 (1963).
[12] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).
[13] R. B. King, *ibid.*, **7**, 90 (1968).
[14] F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6232 (1968).
[15] J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, **91**, 2528 (1969).

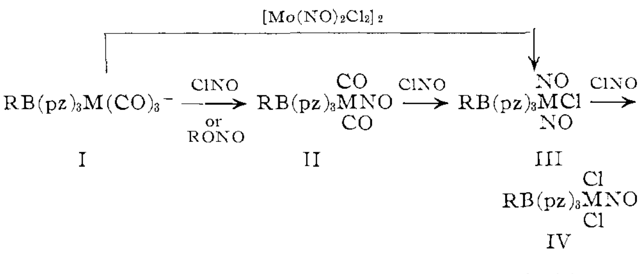
TABLE I
COMPOUNDS OF STRUCTURE



R	X	M	% yield	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Z Calcd	% Z Found	Ir, cm^{-1}	Uv,^{b} mμ (ε)
H	H	Mo	49^d	229–230 dec	33.4	33.2	2.53	2.56	2.48	24.8			2025 (CO)^f 1933 (CO) 1666 (NO)	426 (237)^f 255 (16,500)
pz	H	Mo	61^c	233–234 dec	36.5	36.5	2.61	3.05	27.3	27.4			2024 (CO)^g 1937 (CO) 1685 (NO)	420 (252)^g 258 (15,500)
H	CH$_3$	Mo	85^c	Grad dec from ~270	42.6	42.6	4.58	4.62	20.4	20.4	O, 10.0 (mol wt 479)	O, 9.7 (mol wt^a 474)	2016 (CO)^g 1925 (CO) 1673 (NO)	433 (254)^g 290 sh (8250) 250 sh (18,800)
H	H	W	52^d	287–288 dec	27.3	27.7	2.07	1.99	20.3	20.4			2010 (CO)^f 1910 (CO) 1651 (NO)	480 sh (168)^f 417 (305) 275 sh (14,500) 252 (18,800)
pz	H	W	88	252–253	30.6	30.9	2.19	2.04	22.9	22.9			2010 (CO)^g 1917 (CO) 1674 (NO)	
H	CH$_3$	W	62^c	Grad dec from ~335	36.0	36.3	3.88	4.22	17.3	16.9			2001 (CO)^g 1905 (CO) 1662 (NO)	424 (310)^g 277 (13,500) 250 sh (19,600)
H	H	Cr	60^e	Grad dec from ~180	37.6	37.7	2.85	2.84	27.9	27.9			2038 (CO)^g 1951 (CO) 1718 (NO)	470 (200)^g 360 sh (890) 280 (7140)
pz	H	Cr	43^e	Grad dec from ~180	40.4	40.5	2.88	2.96	30.2	30.4			2039 (CO)^g 1951 (CO) 1712 (NO)	470 (220) 360 sh (880) 285 (6300)
H	CH$_3$	Cr	14^e	Grad dec from ~190	46.8	46.6	5.06	5.47	22.5	22.2			2029 (CO)^g 1941 (CO) 1698 (NO)	

[a] By vapor pressure osmometry in chloroform at 37°. [b] λ_{max}. [c] From isolated salt $(C_2H_5)_4NRB(pz)_3$. [d] *In situ* (DMF) preparation. [e] Nitrite method; recrystallized C_2H_5OAc. [f] In methylene chloride. [g] In cyclohexane.

by about 10 cm^{-1} on going from HB(pz)$_3$ to HB(3,5-(CH$_3$)$_2$pz)$_3$. While changing R from H to pz resulted in no net change of ν_{CO}, it raised ν_{NO} by over 20 cm^{-1}, and going from HB(pz)$_3$ to HB(3,5(CH$_3$)$_2$pz)$_3$ raised ν_{NO} by only about 10 cm^{-1}. The above is valid for Mo and W only; in the Cr compounds ν_{NO} drops in going from HB(pz)$_3$ to B(pz)$_4$ to HB(3,5-(CH$_3$)$_2$pz)$_3$ from 1718 to 1712 to 1698 cm^{-1}. It thus appears that ν_{NO} is a more sensitive probe than ν_{CO} with respect to electron density on the metal.



Of the two nitrosating agents, nitrosyl chloride was more reactive and had to be used in stoichiometric amounts. If not, the reaction proceeded further to form RB(pz)$_3$M(NO)$_2$Cl, which was, in fact, an impurity in the preparation of RB(pz)$_3$M(CO)$_2$NO and could be prepared by its reaction with an additional equivalent of ClNO. This reaction was not clean and resulted in a mixture of products containing M in higher oxidation states along with unreacted starting material. It was possible, however, to separate out the green RB(pz)$_3$M(NO)$_2$Cl from the other products by careful chromatography. A superior way of preparing RB(pz)$_3$Mo(NO)$_2$Cl compounds was by metathetical reaction of an RB(pz)$_3^-$ ion with [Mo(NO)$_2$Cl$_2$]$_n$. Unfortunately, this method could not be used to make RB(pz)$_3$W(NO)$_2$Cl as [W(NO)$_2$Cl$_2$]$_n$ could not be made by the reaction of W(CO)$_6$ with ClNO. Even by the reaction of HB(pz)$_3$W(CO)$_2$NO with ClNO the yield was very poor (~1%).

The compounds RB(pz)$_3$M(NO)$_2$Cl are emerald green, high melting, sublimable *in vacuo*, and soluble in halocarbons and aromatics from which they may be recrystallized. In contrast to C$_5$H$_5$Mo(NO)$_2$Cl, which is said to decompose unpredictably within a matter of days[13,16] with evolution of nitric oxide, the compounds RB(pz)$_3$Mo(NO)$_2$Cl are indefinitely stable to storage. Their properties are listed in Table II. Noteworthy is the considerably higher ν_{NO} in HB(pz)$_3$Mo(NO)$_2$Cl [1796, 1690, 1685 (in CH$_2$Cl$_2$) cm^{-1}] than in C$_5$H$_5$Mo(NO)$_2$Cl [reported:[13] 1759, 1665 cm^{-1} and 1737, 1668, 1648 cm^{-1} (mull[15])].

Finally, exhaustive reaction of HB(3,5-(CH$_3$)$_2$pz)$_3$M(CO)$_2$NO with excess nitrosyl chloride at room temperature yields emerald green (M = W) or orange (M = Mo) compounds of structure HB(3,5-(CH$_3$)$_2$pz)$_3$M(NO)Cl$_2$. These compounds have no counterparts in the C$_5$H$_5$ system. Molecular weight determination indicates they are monomeric in contrast to the analogous compound [C$_5$H$_5$MoNOI$_2$]$_n$ reported to be

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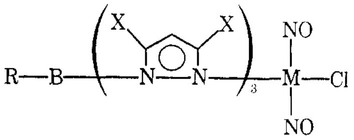
(16) M. L. H. Green, T. R. Sanders, and R. N. Whiteley, *Z. Naturforsch.*, **23b**, 106 (1968).

TABLE II

COMPOUNDS OF STRUCTURE



			%		% C		% H		% N		% Z			
R	X	M	yield	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Ir, cm^{-1}	Uv, mμ (ε)
H	H	Mo	34	297–298 dec	26.7	26.8	2.47	2.38	27.7	27.4	Cl, 8.77 O, 7.9	Cl, 8.84 O, 7.5	1797, 1690, 1685 (CH_2Cl_2)	750 (52), 536 (1180), 360 s (30), 300 sh (1370)
pz	H	Mo	28	264–265 dec	30.6	30.7	2.55	2.37	29.7	29.4			1792, 1688 (cyclohexane)	
H	CH_3	Mo	9	Grad dec from 380	36.8	37.1	4.50	4.39	22.9	22.6			1784, 1678 (cyclohexane)	760 (49), ~620 (25), 440 (1100), 360 sh (830), 300 sh (1570)
H	H	W	<1	348–349 dec	21.9	22.1	2.03	1.85	22.7	22.3				

dimeric.[17] The monomeric nature of the $HB(3,5\text{-}(CH_3)_2pz)_3M(NO)Cl_2$ compounds would make them another example of stable molybdenum complexes containing a 16-electron configuration around the metal. Like the other case[18] of a bis(pyrazolyl)borate–dicarbonylmolybdenum–π-allyl complex, this stability may be rationalized on steric grounds, *i.e.*, the inability of an external base to supply the missing two electrons on account of the interfering 3-methyl groups. The presence of two nonbridging NO stretching bands would imply presence of two isomers. They could result from distortion in the $HB(3,5\text{-}(CH_3)_2pz)_3$ ligand with one of the N–Mo bonds being longer or shorter than the other two. This may or may not include an interaction between the metal and one pair of hydrogens from a CH_3 group, akin to that found in $(C_2H_5)_2B(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$. The nmr spectra, however, apart from demonstrating diamagnetism and asymmetric environments of the pyrazolyl groups (2:1 ratio), did not indicate any upfield shifts of the 3-methyl groups.

Another possible explanation would lie in an asymmetry-inducing specific solvation by one molecule of methylene chloride. This is considered less likely since a mineral oil mull spectrum also has two NO bands.

Arylazo Compounds

Since the original publication by Parshall, who prepared *trans*-$C_6H_5N{=}NPt(P(C_2H_5)_3)_2Cl$ and its analogs[19] and studied this compound in connection with the behavior of nitrogen reductase,[20] several publications have dealt with the MN=NAr bond. King and Bisnette[21] prepared a series of $C_5H_5Mo(CO)_2N{=}NAr$ compounds by the reaction of $C_5H_5Mo(CO)_3^-$ with ArN_2BF_4, where Ar was phenyl or substituted phenyl, and studied some of their reactions, although they were unable to synthesize the analogous W compounds. Nesmeyanov, *et al.*,[22] noted that $C_5H_5W(CO)_3^-$ reacts with $C_6H_5N_2BF_4$ and characterized the two products as $C_5H_5W(CO)_2N{=}NC_6H_5$ and $C_5H_5W(CO)_3C_6H_5$. Finally, Green, *et al.*,[16] prepared $C_5H_5M(CO)_2N{=}NC_6H_5$ (M = Mo, W) by the action of phenylhydrazine on the hydrides $C_5H_5M(CO)_3H$.

It was anticipated that analogous and probably more stable systems based on the $RB(pz)_3$ ligand should be obtainable. Indeed, the reaction of $RB(pz)_3M(CO)_3^-$ (M = Mo, W) with ArN_2BF_4 proceeds smoothly to yield red, air-stable compounds which were assigned the structure $RB(pz)_3Mo(CO)_2N{=}NAr$ (V) on the basis of evidence summarized below (see Table III).

$$RB(pz)_3M(CO)_3^- + ArN_2^+ \longrightarrow \underset{\text{V}}{RB(pz)_3M(CO)_2N{=}NAr}$$

Elemental analysis and molecular weight determinations were in agreement with structure V. The infrared spectra contained two sharp carbonyl peaks around 2000 and 1900 cm^{-1}, along with a band at 1620 cm^{-1}, possibly due to the –N=N– chromophore or the aromatic ring.

The well-resolved nmr spectra, apart from demonstrating diamagnetism, contained bands characteristic of the poly(pyrazolyl)borate ligand and of the benzene ring. The peaks were in the proper ratio. As could be anticipated from a bulky substituent such as the arylazo group, the nmr spectra indicated no rotation of the $RB(pz)_3$ ligand and were in that sense similar to those of $RB(pz)_3M(CO)_2NO$.

The CO frequency mirrored the electron-release tendency of the $RB(pz)_3$ ligand, as well as of the substituents on the phenyl group. The compounds $RB(pz)_3Mo(CO)_2N_2C_6H_5$ had their ν_{CO} absorption at about 10 cm^{-1} lower frequencies than $C_5H_5Mo(CO)_2N_2C_6H_5$, in line with the better donor properties of the $RB(pz)_3^-$ ligand. In the molybdenum compounds the substitution of a *meta* or *para* hydrogen by fluorine on the phenyl ring raised the CO stretching frequency by about 10 cm^{-1} (the lower ν band experiencing a greater shift than the higher ν band), while a *para*-nitro group raised the frequency about 20 cm^{-1}.

These changes are comparable to those observed in the $C_5H_5Mo(CO)_2N_2C_6H_5$ system, upon substitution of electron-donating or -withdrawing substituents in the *para* position.[19] Surprisingly, substitution of one or even two *ortho* hydrogens by methyl groups had a

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(17) R. B. King, *Inorg. Chem.*, **6**, 30 (1967).

(18) S. Trofimenko, *J. Am. Chem. Soc.*, **90**, 4754 (1968).

(19) G. W. Parshall, *ibid.*, **87**, 2133 (1965).

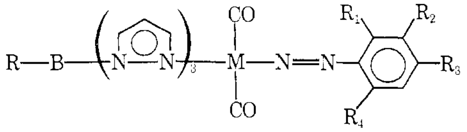
(20) G. W. Parshall, *ibid.*, **89**, 1822 (1967).

(21) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

(22) A. N. Nesmeyanov, Yu. A. Chapovskii, N. A. Ustyniuk, and L. G. Makarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 449 (1968).

TABLE III

COMPOUNDS OF STRUCTURE

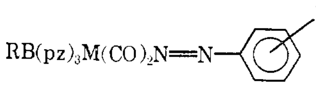


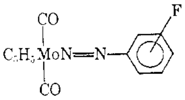
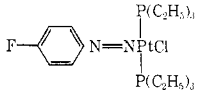
							%	% C		% H		% N		Mol wt				^{19}F
R	M	R_1	R_2	R_3	R_4	Mp, °C	yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Ir,[a] cm^{-1}	Uv, mμ (ε)	nmr,[b] ppm
H	Mo	H	H	H	H	225–226 dec	64	43.4	43.7	3.19	3.14	23.8	23.7			1994, 1904 (CH_2Cl_2)	420 (7430), 290 (50,300)	
H	Mo	H	H	F	H	206–208 dec	28	41.8	41.9	2.87	2.84	22.9	22.9			1996, 1914		+1.13
H	Mo	H	F	H	H	170–172 dec	20	41.8	42.3	2.87	2.81	22.9	22.8			2000, 1918	420 (8500), 290 (47,000), 240 sh (22,500)	−2.31
H	Mo	H	H	NO_2	H	188–190 dec	20	39.6	39.6	2.72	2.91	24.4	24.2			2009, 1930		
H	Mo	CH_3	H	H	H	149–150	29	44.7	44.8	3.51	3.58	23.1	22.8			1994, 1911	424 (7600), 290 (48,400), 250 sh (21,700)	
H	Mo	CH_3	H	H	CH_3	141–142	40	45.7	45.6	3.81	3.88	22.5	22.5	498	504[c]	1996, 1905	418 (1840), 304 (32,800), 342 sh (27,800)	
pz	Mo	H	H	H	H	180–181 dec	66	44.8	44.9	3.17	3.35	26.1	26.0			1996, 1913	530 (280), 420 (7350), 293 (50,200)	
pz	Mo	H	H	F	H	202–204 dec	54	43.2	43.0	2.89	2.79	25.2	24.7			1995, 1914	520 sh (300), 420 (6760), 288 (45,600)	+0.92
pz	Mo	H	F	H	H	174–175 dec	59	43.2	43.3	2.89	2.86	25.2	25.3			2001, 1919		−2.75
pz	Mo	H	H	NO_2	H	205–207 dec	9	41.3	41.7	2.76	2.73	26.5	26.4			2010, 1930	450 (19,600), 345 (13,900), 297 (21,400), 257 (26,900)	
H	W	H	H	H	H	251–252 dec	37	36.5	37.2	2.69	2.85	20.1	20.1			1983, 1894		
H	W	H	H	F	H	232–234 dec	22	35.4	35.4	2.43	2.39	19.4	19.0			1984, 1895		+2.34
H	W	H	F	H	H	180–182 dec	23	35.4	35.4	2.43	2.34	19.4	19.0			1987, 1901		−1.92
pz	W	H	H	H	H	218–220 dec	21	38.4	38.9	2.72	2.66	22.4	22.2			1984, 1896	420 (8800), 296 (48,400), 250 sh (19,100)	
pz	W	H	H	F	H	217–218 dec	63	37.4	37.4	2.49	2.54	21.8	21.4	642	631[c]	1984, 1897		+2.18
pz	W	H	F	H	H	187–188 dec	12	37.4	37.7	2.49	2.45	21.8	21.4			1989, 1901	420 (10,700), 293 (46,700)	−2.13

[a] In cyclohexane unless stated otherwise. [b] At 56.4 MHz, in acetone with fluorobenzene as internal standard. [c] By vapor pressure osmometry at 37° in chloroform.

TABLE IV

FLUORINE-19 SHIFTS[a] IN THE COMPOUNDS



M	R	p-F[b]	p-F[c]	m-F[b]	m-F[c]
Mo	pz	+0.92	−8.11	−2.74	−7.95
Mo	H	+1.13	−7.90[d]	−2.30	−7.86
W	pz	+2.18	−7.02	−2.13	−7.56
W	H	+2.32	−6.62[e]	−1.92	−7.45
		+0.39		−2.20	−7.75
		+2.32	−6.94		

[a] Measured in acetone with C_6H_5F as standard and expressed in parts per million at 56.4 MHz. [b] Internal standard, 10% C_6H_5F. [c] External standard. [d] With 10% $CF_3(CH_2)_4CH_3$ the shift was −7.72. [e] With 10% benzene or 10% chlorobenzene the shifts were −6.77 and −6.73, respectively.

negligible effect as did substitution of the boron-bonded hydrogen by a pyrazolyl group. In the tungsten compounds, on the other hand, which have ν_{CO} lower by about 10 cm^{-1} than the Mo compounds or the $C_5H_5W(CO)_2N_2C_6H_5$ analog,[21] introduction of fluorine into the phenyl ring produces no significant effect.

Of interest were the ^{19}F nmr spectra of *m*- and *p*-fluorophenylazo derivatives as they, too, constitute a probe of the electronic effects. It is immediately apparent from Table IV that these shifts are indeed highly sensitive to a variety of influences. First, the ^{19}F nuclei in the *p*-fluorophenyl derivatives are considerably more shielded than in the *meta* compounds. Second, within a given series of *m*- or *p*-fluorophenyl compounds the shielding increases as one goes from a $B(pz)_4$ to a $HB(pz)_3$ group and also on going from Mo to W. Thus, in the *p*-fluorophenylazo system, on going from $B(pz)_4Mo(CO)_2N{=}NC_6H_4F$ to $HB(pz)_3W(CO)_2N{=}NC_6H_4F$, the ^{19}F shift changes from +0.92 to +2.32 ppm, which is identical with the value obtained from *trans*-$(P(C_2H_5)_3)_2ClPtN{=}NC_6H_4F$ under the same conditions.

While one can explain the various values for the ^{19}F shifts in terms of resonance structures such as those proposed by Parshall[19,20] in which the metal supplies electrons to the aromatic ring, some caution is necessary as the method of measurement does enter the picture. For instance, in $HB(pz)_3Mo(CO)_2N{=}NC_6H_4F$, Δδ between the *meta* and *para* compounds is 2.43 ppm when *internal* fluorobenzene standard is used while it becomes an insignificant 0.04 ppm with an *external* fluorobenzene standard. Moreover, in the latter case (as well as in the case of the B(pz)$_4$ analog) the *p*-fluoro compound is less shielded than the *m*-fluoro! This raises the possibility of a specific interaction between fluorobenzene and the particular organometallic compound. Addition of other solutes, such as $CH_3(CH_2)_4CF_3$, benzene, or chlorobenzene, instead of C_6H_5F, produced either positive or negative shifts, but these were uniformly small (±0.15 ppm). The same effect was observed in the platinum system.

The chemical stability of these arylazo compounds was remarkable. They were unaffected by 15-hr irradiation, by refluxing with CH_3SSCH_3, which reacts readily with $C_5H_5Mo(CO)_2N_2$-*p*-$C_6H_4CH_3$, and by mineral acids. Hot 70% sulfuric acid decomposed B(pz)$_4$Mo(CO)$_2$N$_2$C$_6$H$_5$ while HB(pz)$_3$Mo(CO)$_2$N$_2$C$_6$H$_5$ remained unaffected. The former's fourth pyrazolyl group, naturally, offers a ready protonation site from where decomposition may proceed. The N=N bond of HB(pz)$_3$Mo(CO)$_2$N=NC$_6$H$_5$ could not be reduced with H_2 (Pt catalyst) under conditions substantially more severe than those under which $C_5H_5Mo(CO)_2N{=}NAr$ or $(P(C_6H_5)_3)_2PtClN{=}NAr$ is hydrogenated and the starting material was quantitatively[23] recovered. Also, no decarbonylation took place upon refluxing B(pz)$_4$Mo(CO)$_2$N=NC$_6$H$_5$ with $P(C_6H_5)_3$.

Experimental Section

Synthesis of Compounds Rb(pz)$_3$M(CO)$_2$NO and Substituted Analogs.—These compounds were synthesized by the two general methods illustrated below by specific examples.

(a) **Alkyl Nitrite Method. Hydrotris(1-pyrazolyl)boratodicarbonylnitrosylchromium.**—To a solution of 0.1 mol of KHB(pz)$_3$Cr(CO)$_3$ prepared *in situ* in 250 ml of DMF was added dropwise at 25° 13 g (excess) of amyl nitrite. Gas was evolved briskly. When gas evolution stopped, the reaction mixture was poured into 600 ml of water and the product was extracted with methylene chloride. The extracts were washed several times with water, concentrated, and chromatographed on alumina. The product was obtained in 21-g (60%) yield as bright red crystals. Its properties are listed in Table I.

(b) **Nitrosyl Chloride Method. Hydrotris(3,5-dimethyl-1-pyrazolyl)boratodicarbonylnitrosylmolybdenum.**—Into a suspension of 60.7 g (0.1 mol) of $(C_2H_5)_4NB(pz)_4Mo(CO)_3$ in 1200 ml of methylene chloride was bubbled nitrosyl chloride (5 ml condensed at −20° or about 0.11 mol). Vigorous gas evolution took place and all of the solid dissolved. The solution was extracted with two 1:1 portions of water and the aqueous extracts were discarded. The organic layer was concentrated at reduced pressure until a saturated solution was obtained. It was chromatographed on alumina collecting the orange band. After the residue was stripped of solvent and washed with methanol, there was obtained 40.8 g (85%) of orange crystals the properties of which are given in Table I.

When a larger excess of nitrosyl chloride was used, the yield dropped to about 30%, and, on chromatography, a green band moved behind the orange one, partly overlapping it. The green product was subsequently identified as HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(NO)$_2$Cl.

Bubbling a stoichiometric amount of nitrosyl chloride into a DMF solution of KHB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3$ resulted in evolution of only ~10% of the required amount of CO and the reaction stopped. However, such a DMF solution could be used when butyl nitrite was employed instead of ClNO. Furthermore, nitrosyl chloride reacted well with DMF solutions of KRB(pz)$_3$M(CO)$_3$ (R = H, pz; M = Mo, W).

Hydrotris(1-pyrazolyl)boratodinitrosylmolybdenum Chloride. Procedure A.—Into a suspension of 30 g (0.075 mol) of HB(pz)$_3$Mo(CO)$_2$NO in 300 ml of methylene chloride was bubbled nitrosyl chloride (from about 5 ml condensed at −20°, or approximately 0.11 mol). Gas evolution was rapid and soon 4.7 l. was evolved. The mixture was chromatographed on alumina, eluting with CH_2Cl_2. Three principal bands were obtained. The fastest moving orange band was starting material; next came a lime green band which was the product. A stationary brown band remained at the top. The green band was stripped of solvent and recrystallized from chlorobenzene; yield 4 g (13%). Properties of the product are listed in Table II.

Procedure B.—To a suspension of $[MoCl_2(NO_2)]_x$ prepared from 0.1 mol of $Mo(CO)_6$ in 1 l. of methylene chloride by the published procedure[23] was added enough tetrahydrofuran to effect dissolution of all of the solids. Then 0.11 mol of KHB(pz)$_3$ was added, and the reaction mixture was refluxed for 1 hr and then chromatographed on alumina collecting the green band. Evaporation gave green crystals which were stirred with methylene chloride and filtered. The product obtained in a 13.8-g (34.2%) yield was identical in all respects with that from procedure A. The tungsten analog was prepared by procedure A in ~1% yield.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratonitrosyltungsten Dichloride.—Nitrosyl chloride was bubbled into a solution of 43 g (0.077 mol) of HB(3,5-(CH$_3$)$_2$pz)$_3$W(CO)$_2$NO in 1 l. of methylene chloride until all gas evolution ceased. The mixture was stirred with Celite and filtered; the filtrate was stripped into a 1-l. flask containing 250 ml of toluene. After all methylene chloride was evaporated, the mixture was filtered yielding 38 g (87%) of emerald green crystals. The analytical sample was recrystallized from chlorobenzene and dried at 160° (1 mm). *Anal.* Calcd for $C_{15}H_{22}BCl_2N_7OW$: C, 31.0; H, 3.78; Cl, 12.2; N, 16.8; mol wt, 582. Found: C, 31.3; H, 3.89; Cl, 11.9; N, 16.7; mol wt (osmometric in chloroform), 572.

The infrared spectrum (in CH_2Cl_2) contained bands at 1677 and 1547 cm^{-1}.

The ultraviolet spectrum had λ_{max} 707 mμ (ϵ 290), 318 mμ (ϵ 8780), and 286 mμ (ϵ 8210).

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratonitrosylmolybdenum Dichloride.—Nitrosyl chloride was bubbled into a stirred solution of 24 g of HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_2$NO in 500 ml of methylene chloride until no further gas evolution was observed. The reaction mixture was stripped of solvent and the residue was stirred with methanol and filtered, to give 16.6 g (67%) of an orange solid.

The orange solid was recrystallized from toluene to give red crystals which contained toluene of crystallization. When heated, they lost liquid, became orange, and then gradually decomposed from ~300° on. *Anal.* Calcd for $C_{15}H_{22}BCl_2MoN_7O$: C, 36.5; H, 4.46; Cl, 14.4; Mo, 19.4; N, 19.8; mol wt, 494. Found: C, 36.8; H, 4.56; Cl, 14.3; Mo, 19.3; N, 19.8; mol wt (osmometric in $CHCl_3$), 504.

The ir spectrum (in methylene chloride) contained bands at 1723 and 1718 cm^{-1}.

General Method of Synthesizing RB(pz)$_3$M(CO)$_2$N=NAr Compounds.—The general synthesis of RB(pz)$_3$M(CO)$_2$N=NAr compounds consisted of adding a freshly made DMF solution of an aryldiazonium tetrafluoroborate to a DMF solution of KRB(pz)$_3$M(CO)$_3$, prepared *in situ*. The aryldiazonium tetrafluoroborates were prepared from commercially available substituted anilines in the usual fashion (they were stored in Dry Ice). The over-all procedure is illustrated by one specific example which follows.

Hydrotris(1-pyrazolyl)boratophenylazodicarbonylmolybdenum.—A mixture of 0.1 mol of $Mo(CO)_6$ and 0.1 mol of KHB(pz)$_3$ in 250 ml of DMF was stirred and heated until 7.5 l. of CO was evolved. The solution was cooled under nitrogen to room temperature and a freshly prepared solution of 0.1 mol of benzene-

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[23] The hydrogenation experiments were carried out by Dr. G. W. Parshall.

diazonium fluoroborate in ~100 ml of DMF was added dropwise. Gas evolution proceeded rapidly and stopped at 2.1 l. Another portion of $C_6H_5N_2BF_4$ dissolved in DMF was added dropwise until the total volume of gas evolved was 2.5 l. The reaction mixture was poured into 800 ml of water and $MgSO_4$ was added to facilitate filtration of the mixture. The red solid was purified by chromatography on alumina eluting with methylene chloride. The orange band was collected and stripped of solvent. The residue was triturated with hexane and filtered, yielding 30.2 g (64.3%) of solid. Recrystallization from toluene gave red crystals, mp 225–226° dec. Properties of the product and of other MN=NAr compounds are listed in Table III.

Contribution from the Lawrence Radiation Laboratory and Department of Chemistry,
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The Crystal and Molecular Structure of the Heptacoordinate Complex Tris(diphenylpropanedionato)aquoholmium, $Ho(C_6H_5COCHCOC_6H_5)_3 \cdot H_2O$[1]

By Allan Zalkin, David H. Templeton, and David G. Karraker

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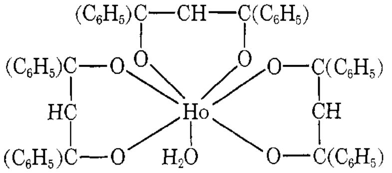
$Ho(C_6H_5COCHCOC_6H_5)_3 \cdot H_2O$, tris(diphenylpropanedionato)aquoholmium, crystallizes in space group R3 with one molecule per rhombohedral cell. The dimensions of the triply primitive hexagonal cell are $a = 22.713$ (12) and $c = 6.334$ (4) Å. The measured density is 1.48 g/cm³; the calculated X-ray density is 1.50 g/cm³. The structure was determined from measurements with Cu Kα radiation of 1365 reflections which included 120 Friedel pairs. It was refined to $R = 0.031$ with anisotropic temperature factors on all but the hydrogen atoms. The holmium atom, on the threefold axis, has a sevenfold coordination. The six oxygen atoms of the diphenylpropanedionato ligands are at distances 2.275 (4) and 2.305 (7) Å from holmium at the corners of a substantially distorted octahedron. The water molecule, also on the threefold axis, is 2.39 (2) Å from holmium and caps the above octahedron; its hydrogen atoms are presumed to be in disordered positions. The molecule as a whole has the appearance of a three-bladed propeller, each blade of which consists of a planar six-membered ring consisting of a holmium, two oxygen, and three carbon atoms; the planes of the two phenyl groups are twisted by 10 and 19° to the above plane.

Introduction

Holmium in the trivalent state, like other rare earths, reacts with dibenzoylmethane[2] to form a complex with the structure



The water molecule is known to be firmly bound, and Hoard[3] in 1961 suggested this heptacoordinate structure for some similar complexes. The structure determination was undertaken in order to ascertain the coordination geometry about the holmium atom and to investigate the nature of the hydration of the water molecule in this material. Recently the structures of tris(1-phenyl-1,3-butanedionato)aquoyttrium,[4] ytterbium acetylacetonate monohydrate,[5] and tris (acetylacetonato)aquoytterbium–hemibenzene[6] were reported which also have sevenfold coordination.

Experimental Section

$Ho(C_6H_5COCHCOC_6H_5)_3 \cdot H_2O$ was prepared by adding an aqueous solution of holmium trichloride to a refluxing mixture of dibenzoylmethane, acetone, and potassium hydroxide. Yellow crystals of the compound crystallized from the filtered and cooled solution. This procedure is from preparation no. 17 as described by Melby, *et al.*[2]

A crystal fragment of dimensions 0.15 × 0.15 × 0.10 mm was cleaved from a needle and glued to a Pyrex fiber. A preliminary set of Weissenberg films had shown the crystal to be rhombohedral with the fiber parallel to the hexagonal c axis. Cell dimensions were measured using a GE XRD-5 X-ray diffraction apparatus equipped with a quarter-circle Eulerian cradle and a molybdenum anode tube ($\lambda_{K\alpha_1}$ 0.70926 Å, $\lambda_{K\alpha_2}$ 0.71354 Å, and $\lambda_{K\beta}$ 0.632253 Å). Cell dimensions were determined from a series of 2θ measurements along the hexagonal $00l$ and $h00$ directions using peaks where Kβ, Kα_1, and Kα_2 X-rays were resolved. All measurements were made at room temperature, *i.e.* ~23°.

The crystal was transferred to a quarter-circle type of automatic GE XRD-5 diffractometer. The intensity measurements were made using a Cu anode X-ray tube set at a takeoff angle of 2° and operated at 35 kV and 20 mA. The diffracted beam was filtered by an Ni foil just ahead of the scintillation counter which was equipped with a pulse height analyzer. The θ–2θ scanning technique was used; scanning began 0.6° in 2θ lower than the Kα_1 position and continued to 0.6° beyond the Kα_2 position at a rate of 1°/min. Backgrounds were taken at 0.4° ahead of and beyond the scan limits. The net intensity I was then calculated to be $I = C - (B_1 + B_2)(T_c/2T_b)$. C is the total counts in the scan time T_c. B_1 and B_2 are the two stationary backgrounds which were each counted for $T_b = 10$ sec. The data included 1366 independent reflections. Fourteen intensities, of which two were actually recorded as zero, were less than their estimated standard deviations. One reflection, (24, −12,3), was deleted from the data set due to a recording error by the automatic diffractometer, *i.e.*, a background was

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