Geminal Poly(1-pyrazolyl)alkanes and Their Coordination Chemistry

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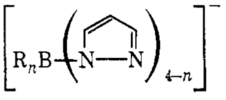
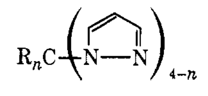
Abstract: Geminal bis(1-pyrazolyl)alkanes have been synthesized by (1) the reaction of pyrazole with methylene bromide at 150°, (2) the reaction of pyrazolide ion or C-substituted pyrazolide ion with methylene iodide (tetrakis-(1-pyrazolyl)methane was prepared analogously), and (3) the acid-catalyzed reaction of pyrazole or C-substituted pyrazole with acetals or ketals. At 200° route 1 leads to 4,4′-dipyrazolylmethane which, upon reaction with boranes, gives a pyrazabole polymer. Similar polymers were prepared from 3,5,3′,5′-tetramethyl-4,4′-xylylene-dipyrazole. Tris(1-pyrazolyl)methane, $HC(pz)_3$, acts as a neutral tridentate ligand of C_{3v} symmetry, isosteric with the hydrotris(1-pyrazolyl)borate, ion and displays a wealth of coordination chemistry. It forms water-soluble octahedral complexes with Ni(II) and Co(II) which can be precipitated as PF_6^-, I^-, or SiF_6^{2-} salts. Compounds $HC(pz)_3M(CO)_3$, where M is Cr, Mo, or W, $[HC(pz)_3Mn(CO)_3]PF_6$, and the stereochemically nonrigid $[HC(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5]PF_6$ were also prepared, as were the nitroso and arylazo derivatives such as $[HC(pz)_3Mo(CO)_2NO]PF_6$ and $[HC(pz)_3Mo(CO)_2N{=}NAr]PF_6$. The bidentate ligands $R_2C(pz)_2$ react with R'_2BX compounds, where X is a leaving group, to form boronium cations $[R_2C(pz)_2BR'_2]^+$ isosteric with pyrazaboles and isolable as their $B_{12}H_{12}^{2-}$ or PF_6^- salts. From π-allyl PdX dimer the cations $[R_2C(pz)_2Pd\text{-}\pi\text{-allyl}]^+$ are obtained. Nmr spectra indicate rapid intramolecular exchange of coordinated and uncoordinated pyrazolyl groups in $[HC(pz)_3Pd\text{-}\pi\text{-allyl}]^+$ and $[C(pz)_4Pd\text{-}\pi\text{-allyl}]^+$ but not in $[HC(pz)_3BEt_2]^+$ or $[C(pz)_4BEt_2]^+$.

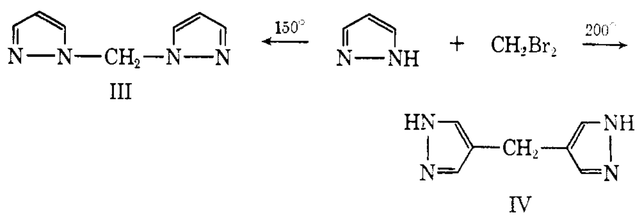
Poly(1-pyrazolyl) borates,[1] I, are a broad and versatile class of uninegative ligands which form a variety of novel coordination compounds with transition metals. In this context it was of interest to compare the coordination behavior of the isosteric but neutral poly-(1-pyrazolyl)methanes, II, of which only scattered examples were known.[2,3] This paper describes several synthetic approaches to compounds of structure II, particularly those where $n = 2$, and including those with diverse substituents on both the bridging carbon and on the pyrazole nucleus, and their coordinating behavior toward transition metal ions, metal carbonyls, and boranes.


I

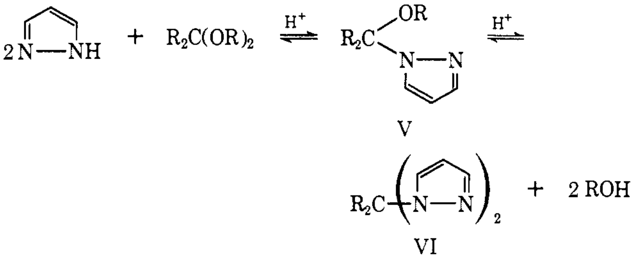

II

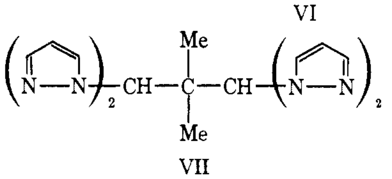
Synthesis of Poly(1-pyrazolyl)alkanes

When pyrazole was heated to 150° in an autoclave with methylene bromide, 1,1′-methylenedipyrazole, III, was obtained in 46% yield. Raising the temperature to 200° gave an isomeric $C_7H_8N_4$ compound identified as 4,4′-methylenedipyrazole, IV, by conversion to a diacetyl derivative and by its nmr spectrum, which showed only three singlets at τ −1.8, 2.62, and 6.43. These are reasonable chemical shifts for the NH, 3,5-H's, and CH_2 hydrogen singlets. It is thought that IV had arisen *via* a carbonium-type rearrangement of III. A better preparation of III or its analogs containing alkyl groups on the pyrazole carbons was the reaction of an alkali metal pyrazolide (or C-substituted pyrazolide) with methylene iodide—much like the synthesis of tris(1-pyrazolyl)methane by Hückel and Bretschneider.[4] Tetrakis(1-pyrazolyl)methane was also prepared in this fashion from carbon tetrachloride although in modest yield.



Difficulties arising from dehydrohalogenation in basic media were anticipated in trying to apply this method for the synthesis of compounds III containing alkyl groups on the methylene bridge. Accordingly, another approach was adopted which consisted of heating acetals or ketals, readily available from a carbonyl compound and methyl orthoformate, with pyrazole in the presence of *p*-toluenesulfonic acid. An equilibrium is rapidly established and the reaction is driven to completion by distillation of the low-boiling alcohol. For instance, 2,2-dimethoxypropane




VII

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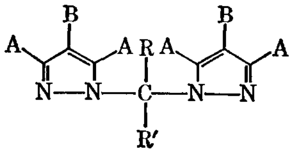
(1) S. Trofimenko, *J. Amer. Chem.Soc.*, **89**, 3170, 6288 (1967); **91**, 588 (1969).

(2) D. E. Wright, U. S. Patent 2,979,512 (1961).

(3) P. Yates, D. G. Farnum, and D. W. Wiley, *Chem. Ind. (London)*, 69 (1958).

(4) W. Hückel and H. Bretschneider, *Chem. Ber.*, 70, 2024 (1939).

Table I. Compounds of Structure



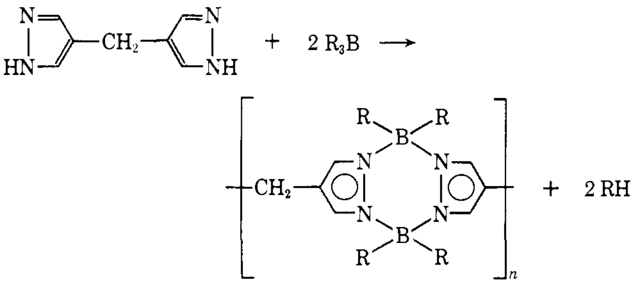
A	B	R	R′	Bp or mp, °C	% yield	% C		% H		% N		Misc	Nmr^{e}
						Calcd	Found	Calcd	Found	Calcd	Found		
H	H	H	H	111–112, mp	75	56.7	56.7	5.44	5.75	37.8	38.0	Mol wt^{a} 148	
CH_3	H	H	H	83–84,^{b} mp	82	64.7	64.8	7.90	7.79				s 3.97, s 4.23, s 7.58, s 7.80 (1:1:3:3)
CH_3	CH_3	H	H	145–146,^{c} mp	37	67.2	67.2	8.68	8.73				
H	H	H	CH_3	91–93 (4.1), bp 56–57, mp	80	59.2	58.7	6.21	6.29	34.6	34.6	n_D 1.5273	2d (overlap) 2.47, q (7) 3.38, t (2) 3.79, d (7) 7.89 (4:1:2:3)
H	H	CH_3	CH_3	84–85,^{b} mp	68	61.3	61.0	6.86	6.89	31.8	32.1		d (1.9) 2.48, d (2.3) 2.63, t (2.0) 3.80, s 7.77 (1:1:1:3)
H	H	C_2H_5	C_2H_5	63–64,^{d} mp	63	64.7	64.1	7.85	6.40	27.45	28.4		2 d (unres) 2.51, t (2.0) 3.76, q (7.0) 7.25, t (7.0) 9.23 (4:2:4:6)
H	H	R,R′ =	$(-CH_2-)_4$	136–137, mp	45	65.3	65.5	6.98	7.13	27.7	28.1		2d (overlap) 2.53, t (2.1) 3.82, m 7.08, m 8.17 (2:1:2:2)
H	H	R,R′ =	$(-CH_2-)_5$	78–79, mp	56	66.6	66.5	7.46	7.12	25.9	25.9		d (1.6) 2.50, d (2.5) 2.62, t (2.0) 3.82, m 7.20, m 8.43 (1:1:1:2:3)
H	H	CH_3	C_2H_5	56–57, mp	42	63.1	63.4	7.42	7.04	29.5	29.8		d (2.0) 2.45, d (2.7) 2.58, t (2.1) 3.78, q (7.0) 7.29, s 7.82, t (7.0) 9.17 (2:2:2:2:3:3)
H	H	H	$CH(CH_3)_2$	81–82, mp 68–74 (0.6), bp	52	63.1	63.0	7.42	7.44	29.5	30.3		d (2.4), 2.30, d (1.8) 2.52, t (2.1) 3.83, d (11) 4.00, m 6.92, d (7) 9.18 (2:2:2:1:1:6)
H	H	H	C_2H_5	71–72, mp	34	61.3	61.6	6.86	6.71	31.8	31.9		d (2.4) 2.40, d (1.7) 2.51, t (7.4) 3.70, "t" (2.4 and 1.7) 3.80, quint (7.4) 7.41, t (7.4) 9.13 (2:2:1:2:2:3)
CH_3	CH_3	H	CH_3	108–109, mp	68	66.0	65.4	8.31	8.29	25.7	25.9		quad (7.0) 3.48, s 4.19, s, 7.80, s 7.92, d (7.0) 7.86 (1:2:6:6:3)

[a] Osmometric in benzene.
[b] Recrystallized from hexane.
[c] Recrystallized from toluene.
[d] Recrystallized from petroleum ether.
[e] Listed are, in order, multiplicity (coupling constant), chemical shift, τ (relative ratio of peaks).

was converted to the dipyrazole VI (R = CH_3) in 75% yield. Polyfunctional systems such as VII were also prepared. In some instances the intermediate monoalkoxymonopyrazolylalkanes, V, were also isolated and identified. Similar results were obtained using enol ethers (derived from the appropriate acetals or ketals by the cracking out of alcohol) or even mixtures of ketals and enol ethers (see Table I).

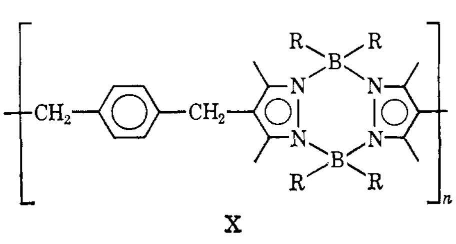
Coordinating Behavior of Polypyrazolylalkanes with Boranes

Formation of Polymeric Pyrazaboles. 4,4′-Methylenedipyrazole is one of the few examples of a 4,4′-linked dipyrazole unsubstituted at the 1 position, the others being 4,4′-dipyrazolyl[5] and 4,4′-methylenebis-(3,5-dimethylpyrazole).[6] The availability of such a compound prompted a study of its behavior with boranes since the normal mode of reaction of this dipyrazole should lead to a polymer consisting of pyrazabole[7] units linked in 2,6 fashion by methylene bridges. This proved to be the case as compound IV and

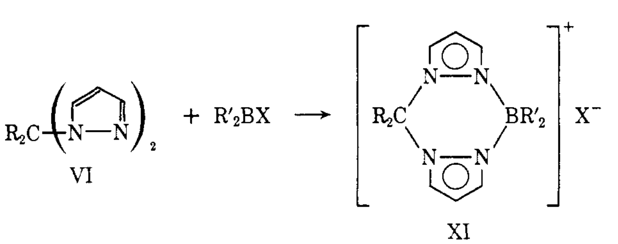

VIII, R = Et
IX, R = H

triethylborane formed exothermally a complex at room temperature, and at 110–120° ethane was evolved smoothly and a toluene-soluble polymer, VIII, was obtained in 95% yield. When trimethylamine–borane was used, the corresponding B-unsubstituted polymer, IX, was obtained. Both are thermally stable, 5% weight losses occurring at 327° for VIII and at 210° for IX, followed, in the case of IX, by weight gain (oxidation).

An analogous polymer, X, was synthesized from 3,5,3′,5′-tetramethyl-1,4-xylylene-4,4′-dipyrazole available from the known tetraone. This polymer softens above 360°.


X

Formation of Boronium Salts. The reaction of dipyrazolylalkanes of structure VI with boranes containing a leaving group gave the boronium ions XI, isolated conveniently as their $B_{12}H_{12}^{2-}$ or PF_6^- salts (see Table II). Ions XI are isostructural with pyrazaboles. Among the leaving groups used in this scheme, alkyl or arylsulfonate[8] groups were quite useful. A trifluoroacetoxy group gave the boronium salts in lower yield, while the yields from acetoxy groups were in the order of 1–2%.


VI
XI
$\cdot X = R''SO_3$, CF_3COO, CH_3COO

Just as in asymmetrically substituted pyrazaboles, two questions were pertinent to the structure of the boronium ions XI. Firstly, are they planar or puckered and, if the latter, do they invert easily? Secondly, if R = pz, is there intramolecular exchange of the coordinated and uncoordinated pyrazolyl groups?

Molecular models indicate that XI should be nonplanar and be in a boat form. If so, then the axial and equatorial substituents R should display different chemical shifts if the inversion rate is slow on the nmr time scale. Actually, in $[MeCH(pz)_2BEt_2]^+$ and $[Me_2C(pz)_2BEt_2]^+$ only one type of methyl group is observed which is compatible with a planar or rapidly inverting structure.

As far as intramolecular exchange of pz groups is concerned, the nmr spectra indicate, as they did in pyrazaboles, that the coordinated and uncoordinated pz groups do not exchange at room temperature. The spectrum of $[(pz)_2C(pz)_2BEt_2]^+$ was instructive in that it showed two different pairs of identical pyrazolyl groups and only one sharp spike (half-height width 1.6 Hz) at τ 9.41 for all ten BEt_2 hydrogens. This implies identical environment for both Et groups and thus either a planar or a rapidly inverting structure. In the latter, both Et groups would be interacting equally with the uncoordinated pz groups. In the ion $[(pz)HC(pz)_2BEt_2]^+$ the pz groups fall into the expected 2:1 pattern.

Coordination with Transition Metals

Geminal poly(1-pyrazolyl)alkanes represent a large family of chelating agents which should parallel the behavior of poly(1-pyrazolyl)borates and yield complexes differing only in the overall charge (higher by 1+ per ligand). This generalization has been supported by the synthesis of a variety of representative complexes containing the $R_nC(pz)_{4-n}$ ligand in place of $R_nB(pz)_{4-n}$. The similarity between these classes of compounds has been indeed remarkable.

The reaction of $R_nC(pz)_{4-n}$ and of its substituted analogs with π-allylpalladium chloride dimer rapidly formed water-soluble cations $[R_nC(pz)_{4-n}Pd\text{-}\pi\text{-}C_3H_5]^+$, *e.g.*, XII, isolated as PF_6^- salts. In these ions, just as in the boron analogs,[9] nmr spectra indicated rapid exchange of all pyrazolyl groups at room temperature, even for $n = 0$. This is in sharp contrast to the lack of observable exchange in $[RC(pz)_3BEt_2]^+$ cations, and it may be attributed to the presence in Pd of suitable low-lying d orbitals which make such an exchange possible through a five-coordinated Pd intermediate. The Pd cations were, in general, more thermally stable

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(5) S. Trofimenko, *J. Org. Chem.*, **29**, 3046 (1964).

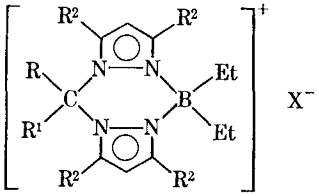
(6) C. F. H. Allen and B. D. Wilson, U. S. Patent 3,106,367 (1963).

(7) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 4948 (1967).

(8) S. Trofimenko, *ibid.*, **91**, 2139 (1969).

(9) S. Trofimenko, *ibid.*, **91**, 3183 (1969).

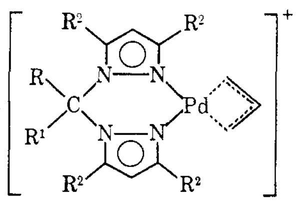
Table II. Compounds of Structure



R	R¹	R²	X⁻	% yield	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	Z Calcd	Z Found	Nmr[a]
H	H	H	$^1/_2B_{12}H_{12}$	30	260 dec	45.8	45.4	8.34	8.88	19.4	19.4	B 26.4	B 26.6	d (3) 1.95, d (3) 2.25, s 3.44, t 3.52, m 9.6 (1:1:1:5)
Me	Me	H	$^1/_2B_{12}H_{12}$	32	273–274 dec	49.4	49.2	8.87	9.45	17.7	17.7			d (3.2) 1.17, d (2.6) 1.50, t (2.9) 2.94, s 7.79, m 9.2–9.9 (1:1:1:3:5)
H	Me	Me	PF_6	51	196–197	44.5	44.4	6.43	6.31	12.9	12.9			q (6.5) 3.56, s 3.77, s, 7.78, d (6.5) 8.80, m 9.2–9.8, t (7.5) 10.39 (1:2:12:3:7:3)
R,R′ = $(CH_2)_4$		H	PF_6	16	182–184	43.0	43.0	5.73	5.55	13.8	13.5			d (2.9), 1.36, d (2.9) 1.60, t (2.9) 2.86, m 7.1, m 7.7, m 8.7–9.6 (1:1:1:2:2:5)
H	pz[b]	H	PF_6	35	185–187	39.2	39.1	4.67	4.77	19.6	19.9	F 26.2	F 26.5	s 0.61, 2d (overlap) 1.55, d (2.5) 2.17, d (1.5) 2.35, t (2.6) 3.07, t (2.5) 3.57, m 9.1–10.0 (1:4:1:1:2:1:10)
Me	Me	H	PF_6	17	193–195	40.0	40.0	5.64	5.73	14.4	14.7			d (3.0, 0.8), 1.50, d (2.7, 0.8) 1.74, t (2.8) 2.95, s 7.65; m 8.8–9.7 (1:1:1:3:5)
Me	H	H	PF_6	14	177–179	38.3	38.6	5.32	5.61	14.9	15.3			d (3.0) 1.85, d (2.4) 2.14, q (6.0) 3.36, t (2.7) 3.53, d (6.0) 7.89, m 9.2–10 (2:2:1:2:3:10)
H	H	H	PF_6	21	164–165	36.5	36.8	4.98	5.15	15.5	15.5			d (2.9) 1.96, d (2.7) 2.10, s 3.37, t (2.8) 3.53, m 9.3–10 (1:1:1:1:5)
pz[b]	pz[b]	H	PF_6	86	223–225	40.9	41.3	4.46	4.49	22.7	23.1			

[a] The secondary splitting of the doublets has been measured only for some of the compounds. It can be seen at the highest resolution of the A-60. [b] pz = 1-pyrazolyl.

Table III. Compounds of Structure



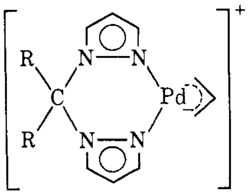
PF_6^-

R	R^1	R^2	% yield	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	Nmr (CD_3CN)
H	H	H	89	202–203 dec	27.3	27.3	2.95	2.98	12.7	12.6	d (2.8) 2.20, d (2.2) 2.37, t (2.5) 3.71, m ~4.3, d (7.2) 5.84, d (12.5) 6.82 (2:2:2:2:1:2:2)
Me	Me	H	98	208–209 dec	30.7	30.6	3.63	3.47	12.0	11.8	d (2.9) 2.13, d (2.1) 2.35, t (2.5) 3.71, m ~4.3, d (7.0) 5.85, d (12.5) 6.80, s 7.81 (2:2:2:1:2:2:6)
H	pz	H	81	235–236 dec	30.8	30.9	2.96	2.86	16.6	16.4	s 1.42, d (2.9) 2.17, d (2.1) 2.32, t (2.5) 3.62, m ~4.5, d (7.0) 5.90, d (12.5) 6.94 (1:3:3:3:1:2:2)
pz	pz	H	78	240–245 dec	33.5	33.5	2.97	2.91	19.6	19.5	d (1.9) 2.19, d (3.1) 3.07, t (2.5) 3.55, m 4.6, d (7.0) 5.98, d (12.5) 7.05 (4:4:1:2:2)
H	3,5-Me_2pz	Me	98	dec from 210	38.6	38.5	4.58	4.58	14.2	14.1	s 2.14, s 4.05, m 4.8, d (7.0) 6.02, d (12.5) 7.35, s 8.00, s 8.06 (1:3:1:2:2:9:9)

Table IV

	Z = C, m = 1 ν_{CO} and ν_{NO}, cm^{-1}	Z = B, m = 0 ν_{CO} and ν_{NO}, cm^{-1}	$\Delta\nu_{CO}$ or $\Delta\nu_{NO}$
$[HZ(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5]^{m+}$	1966	1958	−8
	1881	1874	−7
$[HZ(pz)_3Mo(CO)_2NO]^{m+}$	2037	2025	−18
	1953	1933	−20
	1691 (NO)	1666 (NO)	−25
$[Hz(pz)_3Mo(CO)_2N{=}NPh]^{m+}$	2003	1994	−9
	1919	1904	−15
$[HZ(pz)_3Mo(CO)_2C_7H_7]^{m+}$	1953	1953	0
	1878	1872	−6
$[HZ(3,5\text{-}Me_2pz)_3Mo(CO)_2NO]^{m+}$	2031	2016	−15
	1945	1925	−20
	1686 (NO)	1673 (NO)	−13
$[HZ(pz)_3W(CO)_2NO]^{m+}$	2022	2010	−12
	1931	1910	−21
	1677 (NO)	1651 (NO)	−26
$[HZ(pz)_3Mn(CO)_3]^{m+}$	2059	2041	−18
	1961	1941	−20

than the neutral $R_nB(pz)_{4-n}Pd\text{-}\pi\text{-}C_3H_5$ species. In particular, while $H_2B(pz)_2^-$ reduced Pd(II) to Pd^0 immediately and $HB(pz)_3^-$ did so on moderate heating, $H_2C(pz)_2Pd\text{-}\pi\text{-}C_3H_5$ and other such compounds were stable beyond 200° (see Table III).



XII

Tris(1-pyrazolyl)methane, $HC(pz)_3$, which is isosteric with the $HB(pz)_3^-$ ion, formed compact octahedral ions of D_{3d} symmetry $[HC(pz)_3M(pz)_3CH]^{2+}$ with aqueous solutions of Ni^{2+} and Co^{2+}. These complex ions could be isolated as nitrates or the very sparingly soluble iodides, hexafluorophosphates, or hexafluorosilicates. Their optical spectra were very similar to those of the corresponding $[HB(pz)_3]_2M$ chelates.[10] Anhydrous ferric chloride reacted with $HC(pz)_3$ giving the yellow $HC(pz)_3FeCl_3$, a high-melting complex of low solubility. It should be noted that the other known tridentate ligands of C_{3v} or local C_{3v} symmetry such as 1,1,1-tris(dimethylaminomethyl)ethane[11] and tetrakis(diphenylphosphinomethyl)methane[12] do not form L_2M-type complexes (for steric reasons) nor do they possess a uninegative counterpart.

With group VIb hexacarbonyls, $HC(pz)_3$ reacted, forming very insoluble and nonvolatile compounds of structure $HC(pz)_3M(CO)_3$, XIII. Analytical data and infrared spectra of these compounds supported this structure, as did their chemical behavior (*vide infra*). Their insolubility and lack of volatility suggest cross-linking, since neutral compounds such as $HB(pz)_3$-$Mn(CO)_3$ and $HB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ sublime with ease.

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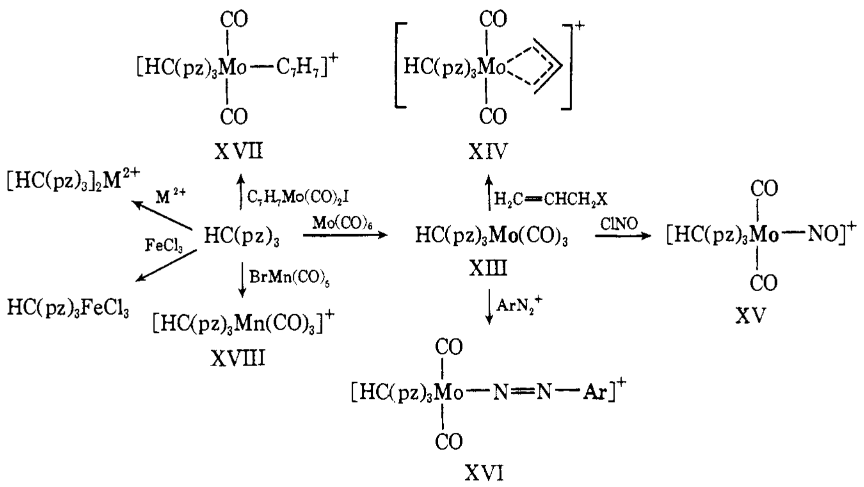
(11) W. J. Kasowski and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **91**, 3212 (1969).

(12) J. Ellerman and W. H. Gruber, *Angew. Chem.*, **80**, 115 (1968).

Scheme I



The reaction of $HC(pz)_3Mo(CO)_3$ with allyl bromide produced the cation $[HC(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5]^+$, XIV, in low yield, and the unreacted solid remained inert. The same cation was obtained more easily and in good yield by the reaction of $HC(pz)_3$ with $(MeCN)_2Mo(CO)_2\text{-}\pi\text{-}C_3H_5Br$.[13] The nmr spectrum of XIV is similar to that of $HB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ even to the point of indicating stereochemical nonrigidity similar to that observed in the $HB(pz)_3$ analogs.[9]

While the reaction of "polymeric" $HC(pz)_3M(CO)_3$ with allyl bromide proceeded sluggishly, the reaction with nitrosyl chloride or aryldiazonium fluoroborate proceeded very readily to give the cationic species XV and XVI which contain the metal bonded to –NO and –N=N—Ar groups (see Scheme I). These, and the other cationic species containing the $HC(pz)_3$ ligand, were isolated as PF_6 salts. Such salts are very soluble in acetonitrile and other polar solvents, and are insoluble in water and nonpolar solvents. The cycloheptatrienyl derivative, XVII, was obtained from $HC(pz)_3$ and $C_7H_7Mo(CO)_2I$, while the reaction of $HC(pz)_3$ with $BrMn(CO)_5$ gave the cation $[HC(pz)_3Mn(CO)_3]^+$.

The well-resolved nmr spectra of these compounds indicated diamagnetism and were quite similar to those of the corresponding $HB(pz)_3$ analogs. Hence, analogous structures were assumed.

If one compares the CO and NO stretch frequencies of compounds XIII–XVIII with their $HB(pz)_3$ counterparts (Table IV), one finds the expected lowering of ν_{CO} and ν_{NO} upon going from a cationic to a neutral complex, consonant with an increase in the M–C bond order. The absolute magnitude of these shifts varied, ranging from 0 to 6 cm^{-1} in the case of the $M(CO)_2N{=}NC_6H_5$ system to a more significant ~20 cm^{-1} for the $M(CO)_2NO$ compounds. The lower frequency ν_{CO} showed consistently greater shifts than the higher frequency ν_{CO}, and ν_{NO} in all instances displayed the greatest shifts.

From all the foregoing results it may be concluded that the $R_nC(pz)_{4-n}$ ligand closely resembles $[R_nB(pz)_{4-n}]^-$ in its coordinative behavior. The two ligand classes comprise thus a unique, mutually complementary pair of systems with essentially identical geometry, but differing by one charge unit per ligand. Advantage can be taken of this in predicting some properties of, *e.g.*, a $R_nB(pz)_{4-n}$ complex, having only the $R_nC(pz)_{4-n}$ ligand available (or *vice versa*), or else in situations where a BH_2 or BH grouping would cause reduction of the metal (*e.g.*, with Pd(II) systems). By contrast, neither $C_5H_5^-$ nor $AcAc^-$ and its analogs possess a neutral counterpart *of identical geometry* and bonding characteristics. The coordination chemistry of geminal polypyrazolylalkanes appears thus to be a fruitful new area for investigation.

Experimental Section

4,4′-Methylenedipyrazole. A mixture of methylene bromide (174 g, 1 mol) and pyrazole (136 g, 2 mol) was heated in an autoclave at 200° for 3 hr. The reaction product was a spongy, rock-like solid. It was dissolved in 900 ml of boiling water and the solution was made slightly basic with 50% sodium hydroxide. A brown solid precipitated. It was purified by recrystallization from boiling water and, finally, by sublimation.

From five such runs there was obtained a total of 116 g (31.4%) of white solid, mp 194–196°. It is water soluble, giving an immediate precipitate with Ag^+ ion.

Anal. Calcd for $C_7H_8N_4$: C, 56.7; H, 5.44; N, 37.8. Found: C, 56.6; H, 5.45; N, 38.6.

The infrared spectrum has strong broad absorption in the 2400–3400-cm^{-1} region characteristic of hydrogen bonding.

The nmr spectrum in $(CD_3)_2SO$ has a broad peak at τ −1.8 and singlets at τ 2.62 and 6.43 in a 1:2:1 ratio, assigned to the NH, the equivalent 3,5-pyrazole hydrogens, and the methylene group, respectively.

1,1′-Diacetyl-4,4′-methylenedipyrazole. 4,4′-Methylenedipyrazole (1.0 g, 0.0068 mol) was boiled for 5 min in 5 ml of acetic anhydride in the presence of a few milligrams of sodium acetate. The reaction mixture was evaporated to dryness and the product was purified by vacuum sublimation, yielding 1.3 g (83%) of crystals, mp 113–114°.

Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.9; H, 5.21; N, 24.1. Found: C, 56.7; H, 5.12; N, 24.2.

The infrared spectrum was devoid of –NH bands but had bands for the α-H at 3150 cm^{-1} and CO at 1725 cm^{-1}.

The nmr spectrum was confirmatory, containing four singlets with relative intensities 1:1:1:3 at τ 1.74, 2.21, 6.18, and 7.28, assigned, respectively, to the 5-H, 3-H, methylene, and methyl groups.

1,1′-Methylenedipyrazole. Dibromomethane (87 g, 0.5 mol) and pyrazole (34 g, 0.5 mol) were heated in an autoclave for 2 hr at 150°. The resulting syrup was dissolved in 1 l. of hot water and the solution was then neutralized with solid sodium bicarbonate and extracted with ether. The extracts were evaporated, yielding a solid which was purified by sublimation. There was obtained 17.9 g (46.5%) of material, mp 108–111°, raised to 111–112° after recrystallization from heptane.

Anal. Calcd for $C_7H_8N_4$: C, 56.7; H, 5.44; N, 37.8; mol wt, 148. Found: C, 57.7; H, 5.75; N, 38.0; mol wt (osmometry in benzene), 150.

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[13] R. G. Hayter, *J. Organometal. Chem.*, 13, 1 (1968).

The nmr spectrum was confirmatory, consisting of doublets at τ 2.33 (J = 2.4 and 0.6) and 2.42 (J = 1.7) and a strong singlet at τ 3.70 with a small side peak at τ 3.87, the last two peaks being obviously overlapping signals of the methylene singlet and the 4-H triplet, as the areas were 2:2:4.

The same product was obtained by method A (*vide infra*) in 75% yield.

General Procedure for Preparing Geminal Dipyrazolylalkanes. The two general procedures for synthesizing geminal dipyrazoles—the reaction of pyrazolide ion with dihalomethanes and the acid-catalyzed reaction of pyrazole with 1,1-dialkoxyalkane (or the appropriate enol ether)—are exemplified by two specific preparations (see Table I).

Method A. 1,1′-Methylenebis(3,5-dimethylpyrazole). A solution of 106 g (1.1 mol) of 3,5-dimethylpyrazole in 500 ml of dry tetrahydrofuran was added to 39 g (1 g-atom) of potassium metal stirred under nitrogen in 600 ml of dry tetrahydrofuran. The reaction mixture was stirred and refluxed overnight. Methylene iodide (134 g, 0.5 mol) was then added and the reaction mixture was stirred and refluxed until neutral. It was then filtered and the filtrate was evaporated, yielding, after trituration with heptane and filtering, 84 g (82%) of solid. It was purified by recrystallization from heptane and melted at 83–84° (see Table I).

When the sodium, rather than the potassium, salt was used, the yields were lower.

Method B. Isopropylidene-1,1′-dipyrazole. A mixture of pyrazole (136 g, 2 mol) and 2,2-dimethoxypropane (104 g, 1 mol) was heated with 0.1 g of *p*-toluenesulfonic acid so that methanol distilled out slowly. After 80 ml (2 mol) had been collected, the melt was poured into 400 ml of heptane and cooled. There was obtained 120 g (68%) of first crop which, after recrystallization from heptane, melted at 84–85° (see Table I).

Similar results were obtained using the corresponding enol ether and distilling out 1 equiv of alcohol.

N-(1-Ethoxyethyl)pyrazole. A mixture of 136 g (2 mol) of pyrazole, 158 g of diethyl acetal (1 mol plus an additional 40 g to make up for distillation losses due to the 76:24 ethanol–acetal azeotrope) was stirred with 0.1 g of *p*-toluenesulfonic acid and heated at 100–130°, distilling out the azeotrope slowly over a Vigreux column. When all the azeotrope had been distilled, residual pyrazole and *p*-toluenesulfonic acid were destroyed by adding sodium hydride and the residue was distilled. There was obtained 104 g (74.3%) of the main cut, bp 71–74° (20 mm), $n^{25}\text{D}$ 1.4573.

Anal. Calcd for $C_7H_{12}N_2O$: C, 60.0; H, 8.63; N, 20.0. Found: C, 59.9; H, 8.89; N, 20.8.

The nmr spectrum has doublets at τ 2.31 (J = 2.4) and 2.47 (J = 1.9), a triplet at 3.70 (J = 2.2), a quadruplet (J = 7), further split into doublets at 6.67, a doublet (J = 6.0) at 8.40 and a triplet (J = 7) at 8.98.

Tetrakis(1-pyrazolyl)methane. A suspension of 1 mol of potassium pyrazolide and 0.25 mol of carbon tetrachloride in 800 ml of THF was refluxed with stirring for 48 hr. The reaction mixture was filtered, the filtrate was stripped, and the residue was chromatographed on alumina, packing and eluting with ether. There was obtained, on trituration with hexane, a solid in 12% (8.1 g) yield, melting at 146–147°.

Anal. Calcd for $C_{13}H_{12}N_8$: C, 55.7; H, 4.32; N, 40.0. Found: C, 55.8; H, 4.07; N, 40.6.

The nmr spectrum showed only three types of hydrogens at τ 2.88 (d, J = 1.8), 2.40 (d, J = 2.8), and 4.49 (quad, J = 1.8 and 2.8) in 1:1:1 ratio.

The molecular weight of this compound was determined by mass spectrometry. The parent ion, m/e 280, was strong; also, the abundance of the m/e 281 ion (^{13}C + ^{15}N isotope) was 16.5% of the m/e 280 peak, *vs.* 17%, theory. The base peak was m/e 213 (C(pz)$_3$). No ions above m/e 282 were observed.

Tris(3,5-dimethyl-1-pyrazolyl)methane. This compound was prepared in 17% yield by the above procedure from chloroform and sodium 3,5-dimethylpyrazolide. It sublimes readily at 100° (1 mm) and was obtained after recrystallization from toluene–heptane as silky fibrous needles, mp 153–154°.

Anal. Calcd for $C_{16}H_{22}N_6$: C, 64.5; H, 7.38; N, 28.2. Found: C, 64.5; H, 7.41; N, 28.4.

The nmr spectrum had singlets at τ 1.92, 4.05, 7.87, and 8.04 in 1:3:9:9 ratio.

1,1,3,3-Tetrakis(1-pyrazolyl)-2,2-dimethylpropane (A) and 1,1,3-Tris(1-pyrazolyl)-2,2-dimethyl-3-methoxypropane (B). A mixture of 96 g (0.5 mol) of 1,1,3,3-tetramethoxy-2,2-dimethylpropane,[14] 136 g (2 mol) of pyrazole, and 2 g of *p*-toluenesulfonic acid was stirred and heated until ~66 ml of methanol was collected. The reaction mixture was distilled *in vacuo* collecting, after a forerun, bp 120–135° (1.4 mm), the main fraction, bp 145° (1.4 mm), which was **B**. The pot residue was chromatographed on alumina, eluting with methylene chloride. There was obtained, after recrystallization from heptane–benzene and then from ethanol, 31 g (19%) of **A** as white crystals, mp 136–137°. Compound **B**, obtained in 25% (37 g) yield, solidified on standing and melted, after recrystallization from hexane, at 105–106°.

Anal. Calcd for $C_{17}H_{20}N_8$ (**A**): C, 60.7; H, 5.99; N, 33.3. Found: C, 60.8; H, 5.95; N, 33.4.

The nmr spectrum of **A** consists of a multiplet (2 overlapping doublets) at τ 2.41, a singlet at 3.25, a triplet (J = 2.1) at 3.80, and a singlet at 8.64 in the correct 4:1:2:3 ratio.

Anal. Calcd for $C_{15}H_{20}N_6O$ (**B**): C, 60.0; H, 6.71; N, 28.0. Found: C, 59.8; H, 7.00; N, 28.4.

The nmr spectrum of **B** had multiplets at τ 2.15 and 2.42, a singlet at 3.18, a multiplet at 3.72, and singlets at 5.13, 6.85, 8.87, and 8.92 in 2:4:1:3:1:3:3:3 ratio.

1-(1-Pyrazolyl)-1-ethoxy-2-methylpropane. A mixture of 164 g (1.1 mol) of isobutyraldehyde diethyl acetal, 160 g (2.35 mol) of pyrazole, and 1 g of *p*-toluenesulfonic acid was stirred and heated until about 1.1 mol of ethanol was evolved. The melt was cooled and poured into dilute aqueous bicarbonate solution. The organic product was extracted with pentane and the extracts were washed with water to remove pyrazole, dried, filtered, and distilled. The main cut boiled at 59° (1.3 mm) and was obtained in 66% yield (122 g). In addition, 9 g (4%) of another cut, bp 95–104° (1.4 mm) was obtained, which solidified and was identified as 1,1-dipyrazolyl-2-methylpropane.

Anal. Calcd for $C_9H_{16}N_2O$: C, 64.2; H, 9.59; N, 16.7. Found: C, 64.2; H, 9.47; N, 17.2.

Polymer from 4,4′-Methylenedipyrazole and Trimethylamine–Borane. A mixture of 7.4 g (0.05 mol) of 4,4′-methylenedipyrazole and 7.3 g (0.1 mol) of trimethylamine–borane was refluxed in 50 ml of DMF. The emerging gases were led through a dilute H_2SO_4 scrubber to a gas meter. As about 2.4 l. of gas was registered on the meter (100% theory), solid started caking the walls of the flask, and the solution became viscous. The solid was filtered and washed with methanol. There was obtained 9.5 g of polymer which had a BH_2 doublet at 2330, 2410 cm^{-1} in the infrared. The material was dissolved with heating in 50 ml of commercial $(Me_2N)_3PO$ and poured into 200 ml of methanol. The solid thus obtained was filtered, washed, and dried, yielding 4.0 g (46%) of purified polymer. It softens around 250° and turns amber in the 380–430° range.

Anal. Calcd for $[C_7H_{10}B_2N_4]_n$: C, 48.8; H, 5.82; N, 32.6. Found: C, 48.9; H, 5.93; N, 32.8.

The inherent viscosity (0.1% in DMF at 25°) was found to be 0.09; TGA showed 5% weight loss at 210°, weight gain from 350 to 425° indicates oxidation, DTA showed a shallow endothermic crest at 250°.

Polymer from 4,4′-Methylenedipyrazole and Triethylborane. To a suspension of 7.4 g (0.05 mol) of 4,4′-methylenedipyrazole stirred in 300 ml of toluene was added 13.7 ml (0.097 mol) of triethylborane. The solid dissolved immediately with a small rise in temperature, but no gas was evolved. The solution was refluxed overnight and 2.5 l. of ethane was evolved. The clear solution was allowed to cool to room temperature, whereupon a solid separated. It was filtered, washed with toluene and then ether, and pressed dry. The yield was 13.4 g (94.5%). The polymer is soluble in hot toluene and can be precipitated by cooling or by adding methanol. The analytical sample was dried at 180° (2 mm) for 8 hr. It softens above 300°.

Anal. Calcd for $[C_{15}H_{26}B_2N_4]_n$: C, 63.4; H, 9.16; B, 7.61; N, 19.7. Found: C, 63.3; H, 9.18; B, 7.51; N, 18.9.

The inherent viscosity (0.1% solution in toluene at 25°) was found to be 0.37; TGA showed 5% weight loss at 327°, largest losses occur at 375–525°; DTA showed an endotherm beginning near 370° and cresting near 395°.

3,5,3′,5′-Tetramethyl-1,4-xylylene-4,4′-dipyrazole. A solution of 85 g (0.30 mol) of 1,4-bis(2,2-diacetylethyl)benzene[15] in 800 ml of ethanol at 60° was added to a solution of 32 g (0.64 mol) of hydrazine hydrate in 400 ml of methanol. An exothermic reaction took place and a solid separated. The mixture was boiled for 1 hr and

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(14) K. C. Brannock, *J. Org. Chem.*, 25, 258 (1966).

(15) D. F. Martin, W. C. Fernelius, and M. Shamma, *J. Amer. Chem. Soc.*, 81, 130 (1959).

then filtered, yielding 67 g (81%) of 3,5,3′,5′-tetramethyl-4,4′-xylylenedipyrazole as a white solid, mp 334–335°, which was recrystallized from 2800 ml of boiling DMF.

For characterization purposes, a small sample of this compound was converted to the diacetyl derivative in 75% yield by refluxing with excess acetic anhydride and evaporating to dryness. The product was recrystallized from a toluene–hexane mixture to yield colorless crystals, mp 153–154°.

Anal. Calcd for $C_{22}H_{26}N_4O_2$: C, 69.8; H, 6.92. Found: C, 69.7; H, 7.07.

The nmr spectrum of the diacetyl derivative was in accord with the assigned structure, having singlets at τ 2.96, 6.30, 7.33, 7.48, and 7.90 in the correct 2:2:3:3:3 ratio.

Polymer from 3,5,3′,5′-Tetramethylxylylene-4,4′-dipyrazole and Triethylborane. To a stirred and nitrogen-blanketed suspension of 14.7 g (0.05 mol) of 3,5,3′,5′-tetramethylxylylene-4,4′-dipyrazole in 300 ml of toluene was added, at room temperature, 13.7 ml (0.097 mol) of triethylborane. The mixture warmed up to 32° and most of the solid went in solution. The reaction mixture was refluxed overnight and the theoretical amount of ethane was evolved. The mixture was cooled to room temperature and filtered. The product was washed with ether and air dried, yielding 28.2 g of white solid. This was recrystallized from boiling xylene and obtained in 75% yield (16 g). The polymer softens above 360°. The analytical sample was dried at 200° (1 mm).

Anal. Calcd for $[C_{26}H_{40}B_2N_4]_n$: C, 72.6; H, 9.30; B, 5.02; N, 13.0. Found: C, 72.6; H, 9.46; B, 4.94; N, 13.2.

The inherent viscosity was found to be 0.24 (0.1% in tetralin at 125°); TGA showed 5% loss at 339°, largest losses at 375–575°; DTA showed endothermic peaking at 320 and 507°.

2,2′-*Dihapto*(1,1′-dipyrazolylmethane)diethylboronium Salt of $B_{12}H_{12}$. A solution of 14.1 ml (0.1 mol) of triethylborane and 7.5 ml (11.4 g, 0.1 mol) of trifluoroacetic acid in 150 ml of benzene was stirred and heated under nitrogen until the theoretical amount of ethane had been evolved (2.4 l.). Then a solution of 14.8 g (0.1 mol) of methylene-1,1′-dipyrazole in 100 ml of tetrahydrofuran was slowly added. The solution was concentrated to about 100 ml; benzene was added and the product was extracted with water until the extracts gave no test with $B_{12}H_{12}^{2-}$ ion. The aqueous extracts were combined and treated with an aqueous solution of 5 g of $Na_2B_{12}H_{12}$.[16] The product was recrystallized from acetonitrile and obtained in 30% yield (8.6 g). Its properties are listed in Table II.

An analogous procedure using acetic instead of trifluoroacetic acid gave only 1.4% of the boronium salt, and over 68% of unreacted 1,1′-methylenedipyrazole was recovered.

Better results were obtained using diethylboryl *p*-toluenesulfonate as in the example below. Other boronium salts were prepared similarly and are listed in Table II.

2,2′-*Dihapto*(tetrakis-1-pyrazolylmethane)diethylboronium Hexafluorophosphate. To a suspension of 2.8 g (0.01 mol) of $C(Pz)_4$ in 80 ml of toluene was added under N_2 11 ml of a 1.0 *M* solution of Et_2BOTs in toluene. The resulting solution was refluxed for 30 min and then stirred overnight at room temperature. The precipitated solid was dissolved in 50 ml of water and the organic layer was extracted once more with 50 ml of water. The combined water extracts were stirred with excess aqueous NH_4PF_6 solution and the resulting precipitate was filtered. The product was dissolved in methylene chloride. The solution was dried with $MgSO_4$, filtered, and evaporated. The residue was stirred with ether and filtered, yielding 4.2 g (86%) of product. Its properties are listed in Table II.

Other compounds were prepared similarly.

General Synthesis of $[R_nC(pz)_{4-n}Pd\text{-}\pi\text{-}C_3H_5]PF_6$ Compounds. These compounds were synthesized by a general procedure exemplified by one specific example. Their properties are listed in Table III.

Tetrakis(1-pyrazolyl)methane-π-allylpalladium Hexafluorophosphate. A mixture of 1.4 g (0.005 mol) of tetrakis(1-pyrazolyl)methane and 0.91 g (0.005 mol) of π-allylpalladium chloride dimer was stirred in 40 ml of a 3:1 water–methanol mixture. In a few minutes a clear solution resulted, whereupon 10 ml of 1.0 *M* NH_4PF_6 solution was added. The copious white precipitate that formed was filtered off and washed with water, dried, and obtained in 78% yield (2.2 g). It was purified by dissolving it in acetonitrile–acetone mixture and diluting the concentrated solution with ethyl acetate. Its properties are listed in Table III.

Poly(1-pyrazolyl)methane Complexes. Bis(tripyrazol-1-ylmethane)nickel(II) Nitrate and Hexafluorophosphate. A mixture of 14.5 g (0.05 mol) of nickel nitrate hexahydrate and 21.4 g (0.1 mol) of tris(1-pyrazolyl)methane was stirred in 350 ml of distilled water at 90–95° and filtered. On cooling, violet crystals grew. They were filtered, washed with water and with methanol, air dried, and obtained in 56% yield (17 g). The filtrate was stirred with excess aqueous ammonium hexafluorophosphate solution. The resulting precipitate was filtered, washed with water and methanol, and air dried. It was obtained in 41% yield (16 g). The nitrate gradually darkens from about 310° and decomposes with a puff at about 360°. The hexafluorophosphate was purified by recrystallization from acetone; it darkens gradually from about 380°.

Anal. Calcd for $C_{20}H_{20}N_{14}NiO_6$ (nitrate): C, 39.3; H, 3.28; N, 32.1; Ni, 9.60. Found: C, 39.0; H, 3.36; N, 31.8; Ni, 9.58.

Anal. Calcd for $C_{20}H_{20}F_{12}N_{12}NiP_2$ (hexafluorophosphate): C, 30.9; H, 2.58; N, 21.6; Ni, 7.55. Found: C, 30.8; H, 3.19; N, 21.4; Ni, 8.06.

Bis(tripyrazol-1-yl)methanenickel(II) Iodide. To a stirred solution of 2.2 g (0.01 mol) of tris(1-pyrazolyl)methane in 50 ml of methanol was added 10 ml of 0.5 *M* nickel acetate solution. The solution was evaporated to dryness and the residue was dissolved in 50 ml of water and treated with excess aqueous potassium iodide. A pale lilac solid precipitated. It was filtered, washed successively with water, methanol, and ether, and air dried. The product, obtained in 73% (2.7 g) yield, is a very insoluble solid and decomposes gradually from ~390°.

Anal. Calcd for $C_{20}H_{20}I_2N_{12}Ni$: C, 32.4; H, 2.70; I, 34.3; N, 22.7. Found: C, 32.4; H, 2.59; I, 32.5; N, 22.6.

Bis(tripyrazol-1-ylmethane)cobalt(II) Nitrate and Hexafluorophosphate. These compounds were prepared by the same method as their nickel(II) analogs (*vide supra*) and were obtained in 69 and 27% yields, respectively. The nitrate darkens gradually from 280° and the hexafluorophosphate decomposes slowly from 360°, rapidly around 400°.

Anal. Calcd for $C_{20}H_{20}CoN_{14}O_6$ (nitrate): C, 39.3; H, 3.28; N, 32.1. Found: C, 39.2; H, 3.33; N, 31.7.

Anal. Calcd for $C_{20}H_{20}F_{12}CoN_{12}P_2$ (hexafluorophosphate): C, 30.9; H, 2.58; Co, 7.59; N, 21.6. Found: C, 30.7; H, 3.47; Co, 8.17; N, 21.4.

Bis(tripyrazol-1-ylmethane)cobalt(II) Iodide. This compound was obtained as a pale yellow solid, decomposing from 380°, in 89% yield by the procedure used for the nickel analog.

Anal. Calcd for $C_{20}H_{20}CoI_2N_{12}$: C, 32.4; H, 2.70; I, 34.3; N, 22.7. Found: C, 32.8; H, 2.52; I, 32.9; N, 22.8.

The infrared spectra of the cobalt and nickel complexes are identical.

Bis(tripyrazol-1-ylmethane)cobalt(II) Hexafluorosilicate. To a solution of 15.5 g (0.05 mol) of cobaltous hexafluorosilicate hexahydrate in 400 ml of water at 80° was added 21.4 g (0.1 mol) of tris(1-pyrazolyl)methane. The yellow precipitate that formed was digested with stirring at 90° for 15 min. The suspension was then cooled and filtered. The yellow solid was washed with distilled water and methanol and then air dried, being obtained in 81.4% yield (25.6 g). It gradually darkens and decomposes from about 380°.

Anal. Calcd for $C_{20}H_{20}CoF_6N_{12}Si$: C, 38.1; H, 3.18; F, 18.1; N, 26.7. Found: C, 37.7; H, 3.46; F, 18.1; N, 26.4.

Tris(1-pyrazolyl)methaneiron(III) Chloride. A solution of 3.24 g (0.02 mol) of anhydrous ferric chloride in 200 ml of anhydrous tetrahydrofuran was added to a solution of 4.28 g (0.02 mol) of tris(1-pyrazolyl)methane in 100 ml of anhydrous tetrahydrofuran, all the manipulations being carried out in a dry nitrogen atmosphere. A bright yellow precipitate formed immediately. The reaction mixture was boiled briefly and then evaporated to dryness at aspirator vacuum. The resulting yellow solid was insoluble in ether or benzene. It was purified by recrystallization from boiling DMF, mp 305–306°.

Anal. Calcd for $C_{10}H_{10}Cl_3FeN_6$: Cl, 28.3; Fe, 14.9; N, 22.3. Found: Cl, 28.3; Fe, 15.0; N, 22.2.

Tris(1-pyrazolyl)methanechromium Tricarbonyl. A mixture of 2.2 g (0.01 mol) of tris(1-pyrazolyl)methane and 3.0 g (0.014 mol) of chromium hexacarbonyl was heated in 50 ml of DMF. The subliming $Cr(CO)_6$ was periodically scraped off and returned to the flask. When about 0.7 l. of CO had been evolved, the reaction was stopped. The mixture was cooled, diluted with ether, and filtered. There was obtained 3.8 g (>100%) of yellow solid. It starts darkening from 320° on and turns black at 340°. The impurity of $Cr(CO)_6$ was removed by sublimation.

Anal. Calcd for $C_{13}H_{10}CrN_6O_3$: C, 44.6; H, 2.86; N, 24.0; Cr, 14.8. Found: C, 44.1; H, 3.04; N, 24.7, 23.5; Cr, 13.4.

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(16) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, 3, 1456 (1964).

Ir (Nujol mull): 1898, 1758 cm^{-1}.

Tris(1-pyrazolyl)methanemolybdenum Tricarbonyl. This compound was obtained in 77% yield by an analogous procedure. It darkened gradually from 260° on.

Anal. Calcd for $C_{13}H_{10}MoN_6O_3$: C, 39.6; H, 2.54; Mo, 24.4. Found: C, 41.8; H, 3.18; Mo, 23.1.

Ir (Nujol mull): 1882 and 1765 cm^{-1}.

Tris(1-pyrazolylmethane)tungsten Tricarbonyl. This compound was prepared on a 0.01 molar scale as above and obtained as a lemon yellow solid in 98% yield. It darkens gradually above 220°.

Anal. Calcd for $C_{13}H_{10}N_6O_3W$: C, 32.4; H, 2.08; N, 17.4; W, 38.1. Found: C, 32.5; H, 2.40; N, 17.2; W, 35.2.

Ir (Nujol mull): 1886 and 1759 cm^{-1}.

Tris(3,5-dimethyl-1-pyrazolyl)methanemolybdenum Tricarbonyl. A mixture of 6.0 g of tris(3,5-dimethyl-1-pyrazolyl)methane and 5.3 g of $Mo(CO)_6$ (both 0.02 mol) was stirred and heated in 50 ml of DMF until 1.5 l. of CO was evolved. The mixture was cooled, stirred with water, filtered, and dried, yielding 8.9 g (94%) of lemon yellow solid. It is insoluble in ethanol, ether, or toluene, but dissolves in boiling DMF. It does not sublime at 290° (1 mm).

Anal. Calcd for $C_{19}H_{22}MoN_6O_3$: C 47.6; H, 4.60; N, 17.6. Found: C, 47.4; H, 4.58; N, 17.7.

Ir (Nujol mull): 1900 and 1760 cm^{-1}.

Tris(1-pyrazolyl)methane-π-allyldicarbonylmolybdenum Hexafluorophosphate. To 0.1 mol of crude $(MeCN)_2MoBr(CO)_2$-π-C_3H_5, prepared *in situ*, was added 0.1 mol of tris(1-pyrazolyl)methane. The reaction mixture was poured into aqueous NH_4PF_6 solution and the product was extracted with methylene chloride. It was purified by chromatography on alumina, eluting with acetone, and was obtained in 38% (21 g) yield as bright yellow crystals. The analytical sample was purified by dissolving the product in acetonitrile (in which it is very soluble) and diluting this solution with a tenfold volume of ethyl acetate. On standing, fine yellow needles were obtained. They retain tenaciously the solvent of crystallization and have to be dried at 150° (1 mm) for 1 hr before the solvent is removed completely. The product darkens gradually from 240°.

Anal. Calcd for $C_{15}H_{15}F_6N_6MoO_2P$: C, 32.6; H, 2.72; F, 20.7; N, 15.2. Found: C, 32.6; H, 2.73; F, 20.6; N, 15.2.

Ir (methylene chloride): 1966 and 1881 cm^{-1}.

The nmr spectrum indicated stereochemical nonrigidity (τ values): s 1.58, broad hump 1.85, d (J = 2.9) 2.02, t (J 2.5) 3.67, m 6.42 and d (J = 8.5) 8.62 in 1:3:3:3:3:2 ratio assigned to methinyl CH, 3-H's, 5-H's, 4-H's, and π-allyl-H's. On heating, the τ 1.85 peak becomes sharp and on cooling it splits into a 1:2 pattern, the small peak at τ 1.33 and the latter hidden under the 2.02 doublet.

The same product was obtained in 4% yield by the reaction of $HC(pz)_3Mo(CO)_3$ with allyl bromide in boiling DMF, followed by treatment with PF_6^-.

Tris(1-pyrazolyl)methane-π-cycloheptatrienyldicarbonylmolybdenum Hexafluorophosphate. A mixture of 13.7 g (0.05 mol) of $C_7H_7Mo(CO)_2I$ and 10.7 g (0.05 mol) of tris(1-pyrazolyl)methane was stirred in 100 ml of DMF until a red solution was obtained. This was poured into 300 ml of water containing 70 ml of 1.0 M NH_4PF_6. The resulting solid was filtered, then dissolved in acetonitrile and chromatographed on alumina, eluting with acetonitrile. The orange product was obtained in 70% (21 g) yield. It turns gradually gray at ~200° and more pronounced decomposition sets in at ~300°. It was recrystallized from acetonitrile.

Anal. Calcd for $C_{19}H_{17}F_6MoN_6PO_2$: C, 37.9; H, 2.83; F, 19.0; N, 13.9. Found: C, 37.7; H, 2.75; F, 19.0; N, 13.9.

Ir (CH_2Cl_2): 1953 and 1878 cm^{-1}.

A sharp C_7H_7 spike appeared in the nmr spectrum at τ 4.77; the other peaks were ill defined because the solution was dilute.

Tris(1-pyrazolyl)methanetricarbonylmanganese(I) Hexafluorophosphate. A mixture of 4.3 g (0.02 mol) of tris(1-pyrazolyl)methane and 5.5 g (0.02 mol) of $Mn(CO)_5Br$ was stirred and heated in 35 ml of DMF until about 0.9 l. of CO was evolved. The reaction mixture was poured into 400 ml of water containing excess KPF_6 and the resulting precipitate was filtered and purified by recrystallization from EtOH. The yellow crystals darken gradually from about 250°.

Anal. Calcd for $C_{13}H_{10}F_6MnN_6O_3P$: C, 31.3; H, 2.00; N, 16.7. Found: C, 30.8; H, 1.93; N, 16.7.

Ir (CH_2Cl_2): 2059 and 1961 cm^{-1}.

Tris(1-pyrazolyl)methanedicarbonylnitrosylmolybdenum Hexafluorophosphate. Into a suspension of 0.1 mol of freshly prepared $HC(pz)_3Mo(CO)_3$ in 250 ml of DMF was bubbled nitrosyl chloride until all the solid dissolved and an orange solution was obtained. It was poured into 1800 ml of water containing 0.3 mol of NH_4PF_6. The precipitated solid was isolated by filtration. It was taken up in hot acetone; the solution was stirred with Darco and filtered. On evaporation orange crystals were obtained in 50% (27 g) yield. The analytical sample was recrystallized from ethyl acetate, mp 273–275° dec.

Anal. Calcd for $C_{12}H_{10}F_6MoN_7O_3P$: C, 26.6; H, 1.85; N, 18.1. Found: C, 26.2; H, 1.81; N, 17.6.

Ir (CH_2Cl_2): 2037, 1953, and 1691 cm^{-1}.

Nmr (CD_3CN) (τ values): s 09.2, d (2.8) 1.53; d (2.8) 1.58; d (2.2) 1.73; d (2.2) 1.86; (2.5) 3.30; t (2.5) 3.37 in 1:2:1:2:1:2:1 ratio.

Tris(1-pyrazolyl)methanedicarbonylnitrosyltungsten Hexafluorophosphate. This compound was prepared as in the preceding experiment, starting with $HC(pz)_3W(CO)_3$, and was obtained in 68% yield. The crude product melts at 216–222°. It was recrystallized from acetone–ethyl acetate mixture.

Anal. Calcd for $C_{12}H_{10}F_6N_7O_3PW$: C, 22.9; H, 1.59; N, 15.6. Found: C, 22.5; H, 1.75; N, 15.3.

Ir (CH_2Cl_3): 2022, 1931, and 1677 cm^{-1}.

Nmr (CD_3CN) (τ values): s 1.00, overlapping doublets ~1.7; d (2.2) 1.93; t (2.7) 3.40, t (2.7) 3.49 in 1:5:1:2:1 ratio.

Tris(3,5-dimethyl-1-pyrazolyl)methanedicarbonylnitrosylmolybdenum Hexafluorophosphate. This compound was obtained in 96% yield by the above procedure, starting with $HC(3,5\text{-}Me_2pz)_3Mo(CO)_3$. The yellow solid was purified by concentration of its methylene chloride solution, mp 272–274°.

Anal. Calcd for $C_{18}H_{22}F_6MoN_7O_3P$: C, 34.5; H, 3.52; N, 15.6. Found: C, 34.4; H, 3.67; N, 15.5.

Ir (CH_2Cl_2): 2031, 1945, and 1686 cm^{-1}.

Nmr (CD_3CN) (τ values): s 2.34, s 3.99, s 4.08, s 7.71, s 7.74, s 7.82, s 7.92 in 1:2:1:6:3:6:3 ratio.

Tris(1-pyrazolyl)methanephenylazodicarbonylmolybdenum Hexafluorophosphate. A mixture of 21.4 g of $HC(pz)_3$ and 26.4 g of $Mo(CO)_6$ (both 0.1 mol) in 250 ml of DMF was stirred and heated until 7.5 l. of CO was evolved, as measured by a wet-test meter. The yellow slurry was cooled under nitrogen to room temperature and a solution of 0.11 mol of freshly prepared benzenediazonium fluoroborate was added. Gas was evolved and stopped after 2.5 l. The red solution was poured into 2 l. of water containing excess NH_4PF_6 and the resulting mixture was filtered; the orange solid was washed with water. The product was obtained, after drying, in 91% (56 g) yield. It was purified by dissolving in hot acetone and filtering, followed by concentration of the solution, which was then cooled and diluted with ether. The compound melts at 242–243°.

Anal. Calcd for $C_{18}H_{14}F_6MoN_8O_2P$: C, 35.1; H, 2.28; N, 18.2; F, 18.5. Found: C, 35.0; H, 2.33; N, 18.1; F, 17.9.

Ir (CH_2Cl_2): 2003 and 1919 cm^{-1}.

Nmr (CD_3CN) (τ values): s, 0.81; d (2.9) 1.52; d (2.0) 1.86; m 2.4–2.8 with sharp spike at 2.52; t (2.5) 3.37 in 1:3:3:5:3 ratio.