well as the nmr spectrum, which had two singlets at τ 2.96 and 8.60 and a multiplet at τ 9.42 in a 2:3:10 ratio, assigned to the 4,5-H, methyl, and ethyl hydrogens, respectively. This compound melts sharply at 346–347° and is sublimable *in vacuo.* It is unaffected by boiling alkali or hydrochloric acid, nitric acid, or dichromate ion.

Molecular models indicate that this tetramer is devoid of strain. In fact, unstrained models of oligomers IIIc with $n \neq 4$ cannot be constructed.

A wide variety of substituted imidazoles and boranes has been found to react as shown in eq 1. These results, along with the details of this work, will be reported in a forthcoming publication.

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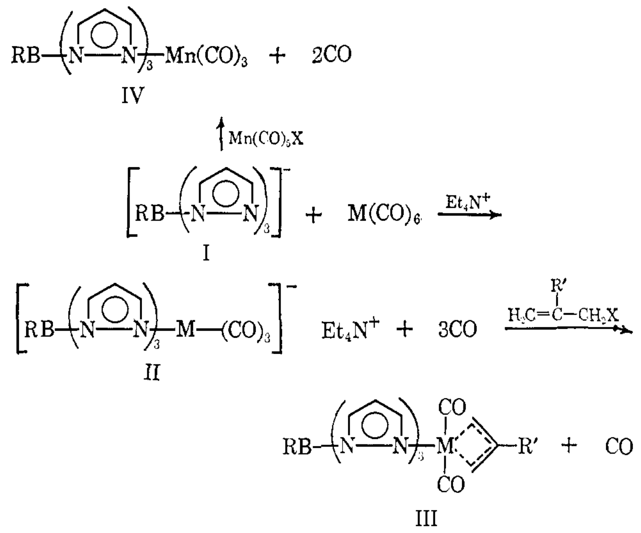
Transition Metal Poly(1-pyrazolyl)borates Containing Other Ligands

Sir:

The recently discovered[1] poly(1-pyrazolyl)borates are a versatile new class of uninegative ligands which may be either bidentate or tridentate. The latter, of structure I, possess C_{3v} symmetry (or local C_{3v} symmetry) and form a host of stable octahedral complexes,[2] $M[RB(pz)_3]_2$, with divalent transition metal ions.[3] The ligand I formally resembles the cyclopentadienide ion, or the more recently discovered carbollide[4] ion, in being uninegative and occupying three coordination sites in its metal complexes. Therefore, chemistry analogous to that exhibited by the $C_5H_5^-$ ligand might be expected in transition metal carbonyls, π-allyls, etc., in which ligand I would be substituted for $C_5H_5^-$. This communication presents some results indicating that this is indeed the case and that a comparable, if not more extensive,[5] area of chemistry based on I may be envisaged.

The anion I (R = H, pz) reacts at 90–120° with group VIb hexacarbonyls to yield the yellow species II, isolable as the air-stable tetraethylammonium salts. Structure II (R = pz, M = Mo, mp 283–285° dec) was assigned on the basis of the stoichiometry of carbon monoxide evolution, elemental analysis (*Anal.* Calcd for $C_{20}H_{30}BMoN_7O_3$: C, 45.8; H, 5.74; N, 18.7. Found: C, 45.3; H, 5.82; N, 18.7), the infrared spectrum (strong carbonyl bands at 1890 and 1750 cm^{-1} (very broad with shoulders at 1760 and 1720 cm^{-1})), and the nmr spectrum which indicated three coordinated (doublet (J = 1.6 cps) τ 2.25, doublet (J = 2.3 cps) τ 2.50, and triplet (J = 2.1 cps) τ 3.84 in 3:3:3 ratio) and one uncoordinated (doublet (J = 2.2 cps) τ 1.88, doublet (J = 1.5 cps) τ 2.07, and triplet (J = 1.9 cps) τ 3.37 in 1:1:1 ratio) pyrazolyl residues. Other compounds of structure II (R = pz, M = Cr, mp 294–296° dec; R = pz, M = W, mp 325–327° dec; R = H, M = Mo, mp 283–285° dec) were identified similarly.



A facile reaction takes place between compounds II and allylic halides. For instance, compound II (R = pz, M = Mo) reacts rapidly at room temperature with allyl bromide in dimethyl sulfoxide or dimethylacetamide. One equivalent of carbon monoxide is evolved, and III (R = pz, M = Mo, R′ = H) is obtained in 85% yield. This compound is an air-stable, sublimable yellow solid. It melts without decomposition at 253–255° and is thus the most thermally stable π-allyl complex known. Structure III was assigned on the basis of the stoichiometry of carbon monoxide evolution, elemental analysis (*Anal.* Calcd for $C_{17}H_{17}BMoN_8O_2$: C, 43.3; H, 3.61; N, 23.7; Mo, 20.3. Found: C, 43.4; H, 3.62; N, 23.7; Mo, 20.2), molecular weight determination (calcd 472, found 474 by osmometry in chloroform), the infrared spectrum resembling that of $C_5H_5Mo(CO)_2$-π-C_3H_5[6] (two strong carbonyl peaks of equal intensity at 1950 and 1860 cm^{-1}), and the nmr spectrum which, although complex,[7] showed the presence of 12 hydrogens of the $B(pz)_4^-$ ligand and 5 hydrogens of the π-allyl group.

Other compounds of structure III (R = pz, M = Cr, R = H, decomposes ~120°; R = H, M = W, R′ = CH_3, mp 268–270° dec; R = pz, M = Mo, R′ = CH_3, mp 218–219°; R = pz, M = W, R = H, mp 259–260°; R = pz, M = Mo, R′ = Br, mp 195–198° dec) were identified similarly.

The reaction of compounds II with alkyl halides, R″X, and with mineral acids yields compounds R″-$[RB(pz)_3M(CO)_3]$ and $H[RB(pz)_3M(CO)_3]$, respectively. They are less stable to oxidation than the π-allyl derivatives III, and their order of oxidative stability is W > Mo > Cr, just as in the case of the C_5H_5 analogs.

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(1) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966); **89**, 3170 (1967).

(2) pz = 1-pyrazolyl.

(3) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

(4) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965); M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965).

(5) Not only are salts of the type $MRB(pz)_3$ readily available and, in contrast to MC_5H_5 salts, quite stable to storage but the synthetic routes leading to C- and B-substituted ligands (S. Trofimenko, to be published) retain the original symmetry (or local symmetry) of the $RB(pz)_3^-$ ion. That such substitution can dramatically alter the properties of transition metal compounds without altering the molecular geometry around the metal atom has been demonstrated (J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3158 (1967).

(6) Peaks at 1961 (vs) and 1871 (vs) cm^{-1} are reported (M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(7) This temperature-dependent spectrum showed the existence of two sources of stereochemical nonrigidity: rotation of the noncoordinating pyrazolyl group around the N–B–Mo axis and changing of the environment of the 3-hydrogens in the $-B(pz)_3$ part. A detailed study of this and of related systems will be published.

Finally, the air-stable, sublimable compounds IV were obtained by the reaction of I with $Mn(CO)_5Br$. For instance, compound IV (R = pz) was obtained as pale yellow, sublimable crystals, mp 213–215° (*Anal.* Calcd for $C_{15}H_{12}BMnN_8O_3$: C, 43.0; H, 2.87; N, 26.8; Mn, 13.2. Found: C, 42.8; H, 3.10; N, 26.9; Mn, 13.4). The infrared spectrum of this compound contained carbonyl bands at 2055 (s) and 1940 (vs) cm^{-1}. The nmr spectrum had a peak at τ 2.10 (which included the 3- or 5-H of the coordinated pyrazole moieties and the 3- and 5-H of the uncoordinated pyrazolyl group), a doublet (J = 2 cps), and ill-resolved triplets at τ 3.41 and 3.80 in a 5:3:1:3 ratio. Compound IV (R = H), mp 206–208°, was identified similarly.

The details of this work and the chemistry of transition metal poly(1-pyrazolyl)borates containing other ligands will be the subject of subsequent publications.

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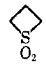
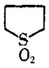
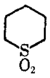
Acidities of Sulfones

Sir:

Using the method previously described[1] we have measured the pK_a's of a number of sulfones and find them to be much higher than commonly supposed (Table I).[2]

Table I. Acidities of Sulfones in Dimethyl Sulfoxide at 25°

Sulfone	pK_a^{a}	Sulfone	pK_a
Methyl	28.5		>30
Methyl phenyl	27		
Ethyl phenyl	29		
Benzyl	22		>31
α-Methylbenzyl	23.5		
			>31

^{a} *p*-Nitroaniline was used as the reference indicator.[1]

Examination of Table I reveals that: (1) methyl substitution for hydrogen causes an increase of 1.5 to 2 pK_a units [compare $(PhCH_2)_2SO_2$ with $(PhCHMe)_2SO_2$ and CH_3SO_2Ph with $MeCH_2SO_2Ph$]; (2) phenyl substitution causes a decrease of 6.5 pK_a units [compare $(CH_3)_2SO_2$ with $(PhCH_2)_2SO_2$]; and (3) substitution of a phenyl group for a methyl group at a β position causes a decrease of 1.5 pK_a units (compare $MeSO_2CH_3$ and $PhSO_2CH_3$). It is of interest to compare these effects with those observed in nitroalkanes, the only other oxygenated carbon acids for which equilibrium data are available. Here methyl substitution causes a decrease, rather than an increase, in pK_a (CH_3NO_2, 10.2; $MeCH_2NO_2$, 8.5; Me_2CHNO_2, 7.7).[3] Phenyl substitution causes a decrease in pK_a, as in the sulfone series, but of only 3.3 units, as compared to 6.5 units.[4] Substitution of a phenyl group for a methyl group at a β position appears to have relatively little effect ($MeCH_2CH_2NO_2$, pK_a = 8.98;[3b] $PhCH_2CH_2NO_2$, pK_a = 8.68).[5]

In attempting to rationalize these differences it is important to note that the oxygen acids (nitric and methanesulfonic) produced by substitution of NO_2 and CH_3SO_2, respectively, for H in HOH are of a comparable order of acidity,[6] whereas the corresponding carbon acids (nitromethane and methyl sulfone) produced by substitution of a nitro group for H of CH_4 differ in acidity by over 12 pK_a units.[7]

A variety of effects must be operating to make NO_2 and CH_3SO_2 of about equal effectiveness in promoting the acidity of oxygen acids, but of markedly unequal effectiveness in promoting the acidity of carbon acids. One of the most important of these is no doubt the degree of resonance stabilization in the corresponding conjugate bases. Whereas the conjugate bases in the oxygen series, NO_3^- and $CH_3SO_3^-$, each have three equivalent resonance contributors, the resonance contributors for $CH_2NO_2^-$ and for $CH_3SO_2CH_2^-$ are not equivalent. For $CH_2NO_2^-$ the $CH_2{=}NO_2^-$ contributor is highly important, not only because of the concentration of the negative charge on oxygen, but also because of the near equivalence of the C=N and N=O bond energies (147 and 145 kcal/mole, respectively). In contrast, the relatively poor conjugative stabilization provided by the 2p–3d overlap in the $[CH_3SO_2{=}CH_2]^-$ contributor makes it of much less importance than the other two contributors.[8]

If it is assumed that there is indeed a high degree of C=N bond character in the $CH_2NO_2^-$ nitronate ion, the progressive increase in acidity caused by substitution of methyl groups for hydrogen atoms in this ion can be understood in terms of a stabilizing influence analogous to that observed for C=C bonds. No such effect would be expected for the $CH_3SO_2CH_2^-$ ion.[9]

Phenyl substitution in $CH_2NO_2^-$ and $CH_3SO_2CH_2^-$ should cause an appreciable increase in stability. The much larger effect in the sulfone series is expected in

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[1] E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

[2] (a) From an extrapolation based on the relationship of rates of proton abstraction and pK_a's of ketones, R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953), estimated a pK_a of 23 for methyl sulfone. (b) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, for a discussion of the acidities of carbon acids.

[3] (a) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943); (b) G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

[4] V. Pihl, V. Timotheus, A. Pihl, and A. Talvik, "Organic Reactivity," Vol. II, No. 4, Tartu State University, Estonian SSR, 1965, p 24, give pK_a = 6.88 for $PhCH_2NO_2$.

[5] S. Hiidman, A. Pihl, and A. Talvik, ref 4, Vol. III, No. 8, 1966, p 65.

[6] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 85.

[7] The difference is 18.3 units using the value for $CH_3SO_2CH_3$ of 28.5 (Table I) and 10.2 for CH_3NO_2,[3] but C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967), have found that pK_a for CH_3NO_2 in DMSO is 15.9.

[8] Note that for CH_3COCH_3, which is intermediate in acidity between CH_3NO_2 and $CH_3SO_2CH_3$, the contribution of $^-OC(CH_3){=}CH_2$ is reduced relative to $O{=}C(CH_3)CH_2^-$ in that the bond energy for C=O (179) is considerably higher than that for C=C (146).

[9] Methyl substitution causes a decrease in the rate of proton abstraction by base from nitroalkanes [see S. H. Maron and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 2588 (1938)] and also from sulfones (J. M. Williams, Jr., Ph.D. Dissertation, Northwestern University, 1966). Nitroalkane acidities increase with methyl substitution *despite* this effect.[10] It is uncertain yet whether the decrease in acidities of sulfones on methyl substitution is caused entirely by this effect or whether methyl substitution also destabilizes the conjugate base and thereby causes it to react more rapidly in the reverse reaction.

[10] See H. M. Cardwell, *J. Chem. Soc.*, 2442 (1951), for a discussion.