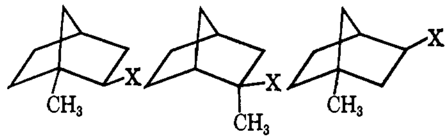
Table II. Products of Additions to 1-Methylnorbornene (VII)



Conditions	V	X	VI
HCOOH, 70°, X = OOCH	≈50%[a]		≈50%[a]
HCl-H_2O, reflux, X = Cl	43%[b]	6%[b]	51%[b]
HCl-Et_2O, 25°, X = Cl		54%[b]	46%[b]

[a] Analysis by analytical distillation of the alcohols V (X = OH), bp 177°, and VI (X = OH), bp 183°. Oxidation of VI (X = OH) gave 1-methyl-3-norbornanone, a low melting solid (2,4-DNP mp 133.2–133.4°), and 1-methyl 1,3-*cis*-cyclopentanedicarboxylic acid, mp 95.0–96.6°, anhydride mp 78.7–79.4°.[1,2c,6] (1-Methyl-2-norbornanone 2,4-DNP had mp 167.2–167.8°.) [b] Analysis by solvolysis.[1,2c,6]

rule is followed and rearrangements are observed, but the exact definition of the transition states has been difficult.[11] The present results show that no significant charge delocalization due to bridging is present in the transition state of the proton-addition step.

Unsymmetrical molecules such as 1-methylnorbornene (VII) and bornene should thus be ideal substrates for the study of the relationship between bridging and the stereochemistry of addition of unsymmetrical reagents, such as D^+Y^- and X^+Y^-. If the electrophilic fragments, D^+ and X^+, become attached indiscriminately to the 2 and 3 positions of the olefins, then bridging cannot be involved in the transition state for their addition. If, despite this lack of preference, these electrophiles become attached *exo*, then factors other than bridging must be responsible for this stereospecificity.

The results of addition reactions already described in the literature[4b,12] with symmetrically substituted norbornenes suggest that electrophiles tend to become attached *exo* in the kinds of reactions studied here, *even in the presence of hindering 7,7-dimethyl groups.*[13] Torsional effects[14] may contribute to the *exo* selectivity observed in such instances.

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(11) P. B. D. de la Mare and R. Boulton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966; M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, 3, 245 (1964); B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1965," John Wiley and Sons, Ltd., London, 1966, p 104 ff.

(12) S. J. Cristol, *et al.*, *J. Org. Chem.*, **31**, 2719, 2726, 2733, 2738, 2741 (1966), and previous papers; H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964); J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(13) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3898, 3900 (1967); T. T. Tidwell and T. G. Taylor, footnote 6, ref 3.

(14) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

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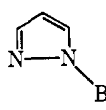
Received April 18, 1967

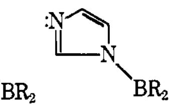
Poly(1-boryl)imidazoles

Sir:

The geometric and electronic features of a 1-borylpyrazole fragment (I), which is a 1,3-dipole, are suitable for the formation of a variety of novel boron heterocycles (pyrazaboles), coordinating ligands, and transition metal compounds (poly(1-pyrazolyl)-borates).[1,2] On the other hand, it would be expected that the electronically similar but geometrically disparate 1-borylimidazole fragment (II), which is a 1,4-dipole, would be incapable of forming comparable homoassociation products but would form polyassociated structures instead. This has been borne out by the following findings.

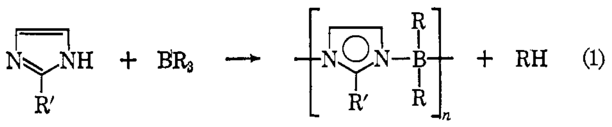


I



II

When an equimolar mixture of triethylborane and imidazole was refluxed in xylene, ethane was evolved (eq 1), although at a rate much slower than in the analogous reaction with pyrazole.[3] The resulting product was soluble in aromatic hydrocarbons and chloroform



IIIa, R = Et; R′ = H
b, R = Bu; R′ = H
c, R = Et; R′ = Me

but not in methanol. It was an elastomer, with an inherent viscosity of 0.5–0.7, which showed a 5% weight loss at 373°, underwent a glass transition at −12°, and displayed a sharp endotherm at 435°. Structure IIIa[4] was assigned on the basis of elemental analysis[5] (*Anal.* Calcd for $[C_7H_{13}BN_2]_n$: C, 61.8; H, 9.57; B, 7.94; N, 20.6. Found: C, 62.8; H, 9.82; B, 8.13; N, 20.0) and the nmr spectrum, which had singlets at τ 2.48, 3.24, and 9.67 in a 1:2:10 ratio assigned to 2-H, 4,5-H, and the ethyl hydrogens,[6] and was consistent with C_{2v} symmetry of the imidazolyl nucleus. The molecular weight ranged from about 6000 to 12,000 (osmometry in chloroform) giving n values in the 40–80 range. Poly(1-dibutylborylimidazole) (IIIb) was prepared and identified similarly.

These polymers are stable to air and boiling water, but are hydrolyzed slowly by boiling alkali and rapidly by boiling hydrochloric acid.

By contrast, the reaction of triethylborane with 2-methylimidazole gave the cyclic tetramer IIIc (n = 4) as the sole reaction product in 99% yield. The structure assignment was consistent with elemental analysis and molecular weight determination (*Anal.* Calcd for $[C_8H_{15}BN_2]_4$: C, 64.0; H, 10.0; B, 7.21; N, 18.7; mol wt, 600. Found: C, 64.5; H, 10.3; B, 7.31; N, 18.9; mol wt (ebullioscopic in benzene), 630) as

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

(2) S. Trofimenko, *ibid.*, **89**, 3165, 3170 (1967).

(3) This is understandable, since the imidazole–triethylborane complex cannot eliminate ethane through a low-energy, concerted intramolecular transition state, as is the case with the corresponding pyrazole complex, and this reaction has to proceed intermolecularly.

(4) It is understood that a positive charge is delocalized in the imidazole ring and a negative charge resides on boron.

(5) The high C, H, B, and low N values indicate contamination by triethylborane, probably as endcapping groups.

(6) The appearance of B-bonded ethyl group hydrogens as a singlet has been noted before: L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *Inorg. Chem.*, **4**, 1649 (1965).

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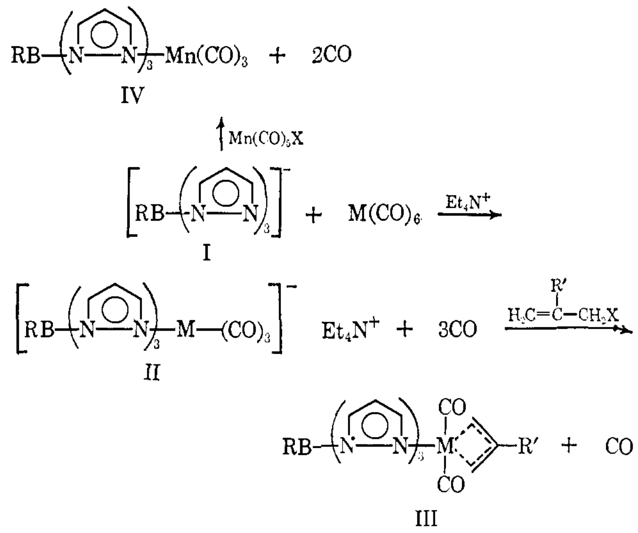
Transition Metal Poly(1-pyrazolyl)borates Containing Other Ligands

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.