Molybdenum Complexes with Noninert-Gas Configuration
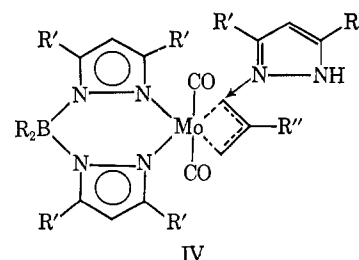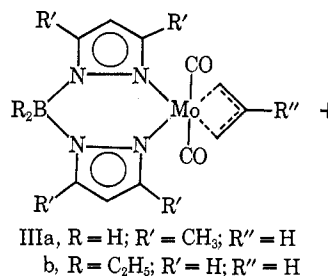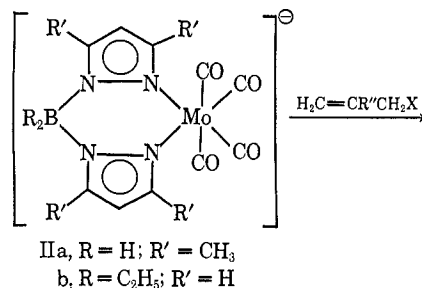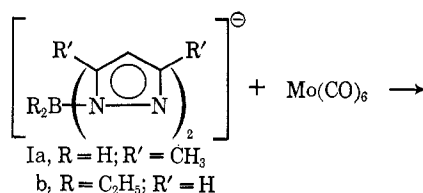
By S. TROFIMENKO

A variety of bidentate ligands $R_2B(3,5-R'_2pz)_2^-$ react with molybdenum hexacarbonyl to yield the oxidatively unstable anions $R_2B(3,5-R'_2pz)_2Mo(CO)_4^-$ which have been converted to the stable π-allyl derivatives $R_2B(3,5-R'_2pz)_2Mo(CO)_2$-$\pi$-allyl. These are 16-electron systems. When R = H, R' = alkyl or aryl, the compounds exhibit stereochemical nonrigidity interpreted in terms of a rotational mechanism. They do not react with nucleophiles. When R = alkyl or aryl (R' = H), the compounds add nucleophiles achieving 18-electron configuration. Allylation of related W anions yielded the pyrazole complexes $R_2B(pz)_2W(CO)_2$-π-C_3H_5·Hpz. From $H_2B(3,5-(CH_3)_2pz)_2Mo(CO)_4^-$ and CH_3I the compound $H_2B(3,5-(CH_3)_2pz)_2MoCH_3(CO)_3$·$3,5-(CH_3)_2pzH$ was obtained, while $H_2B(3,5-(CH_3)_2pz)_2Mo(CO)_2C_7H_7$ resulted from $H_2B(3,5-(CH_3)_2pz)_2^-$ and $C_7H_7Mo(CO)_2I$.

The chemistry of transition metal carbonyls containing also uninegative bidentate ligands such as β-diketonate[1] or oxalate[2] has been little explored. We had found earlier[3] that rather stable π-allyl compounds with a noninert-gas configuration may be synthesized from molybdenum hexacarbonyl and $R_2B(3,5-R'_2pz)_2$ ligands.[4] This paper presents the details of that work and some other chemistry of this ligand system.

The bidentate ligands I react in warm polar solvents with molybdenum hexacarbonyl to yield the tetracarbonyl anions II. These can be isolated as tetraethylammonium salts, but their air stability is much lower than that of the analogous $RB(pz)_3Mo(CO)_3^-$ salts. Consequently, the reactions of the anions II were carried out without their isolation. The most interesting results were obtained from allylation experiments. In each case the reaction proceeded with loss of 2 equiv of CO and formation of a π-allyl derivative containing a 16-electron configuration. The characteristics of these compounds fell into two distinct categories depending on whether the ligand contained substituents (alkyl or aryl groups) on boron or in the 3,5 positions. Each of these cases will be discussed separately.

The compound IIIa, which was also prepared from Ia and $(CH_3CN)_2MoBr(CO)_2$-π-C_3H_5, had extraordinary stability toward air, water, acids, and bases and did not exhibit the electrophilicity expected of an electron-deficient structure.

The infrared spectrum of IIIa showed only a sharp singlet in the B–H stretch region in contrast to pyrazaboles[5] and pyrazolylborates,[6] $[H_2B(pz)_2]_2M$, in which the BH_2 group gives rise to a complex multiplet. The intactness of the BH_2 group in IIIa was established by ^{11}B nmr which consisted of a well-defined triplet. The room-temperature ^1H nmr spectrum was hazy and indicative of stereochemical nonrigidity. It was easy, however, to obtain limiting spectra by heating to 60° or

Ia, R = H; R' = CH₃
b, R = C₂H₅; R' = H

IIa, R = H; R' = CH₃
b, R = C₂H₅; R' = H

IIIa, R = H; R' = CH₃; R'' = H
b, R = C₂H₅; R' = H; R'' = H

IV

cooling to −40° (see Figure 1). The high-temperature spectrum indicates a normal π-allyl group and C_{2v} symmetry of the bidentate ligand. On cooling one of the methyl signals collapses as do the signals of the syn and anti protons of the π-allyl group. In the low-temperature limiting spectrum there are three types of methyl groups and all the π-allyl hydrogens are different. This finding can be accommodated by either of the two "frozen" structures A and B (Figure 2). In

(1) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964); F. A. Hartman, M. Kilner, and H. Wojcicki, *Inorg. Chem.*, **6**, 34 (1967); F. Bonati and R. Ugo, *J. Organometal. Chem.*, **11**, 341 (1968).
(2) H. tom Dieck and H. Friedel, *ibid.*, **14**, 375 (1968).
(3) S. Trofimenko, *J. Amer. Chem. Soc.*, **90**, 4754 (1968).
(4) pz stands for 1-pyrazolyl.
(5) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3165, 4948 (1967).
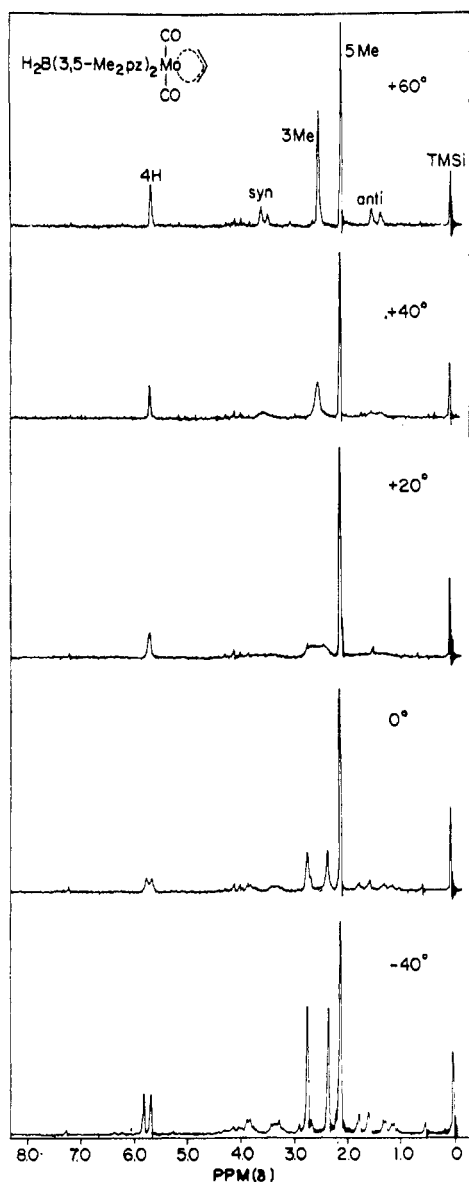(6) S. Trofimenko, *ibid.*, **89**, 3170, 6288 (1967).

Figure 1.—The temperature-dependent nmr spectrum of $H_2B(3,5-(CH_3)_2pz)_2Mo(CO)_2-\pi-C_3H_5$.
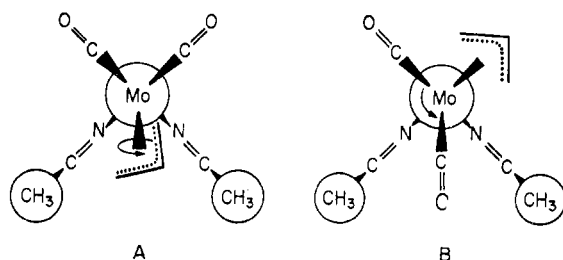
Figure 2.—Possible structures of $H_2B(3,5-(CH_3)_2pz)_2Mo(CO)_2-\pi-C_3H_5$.

each, the environments of the 3-methyl groups, as well as of the π-allyl termini, are different and compatible with the nmr spectra. Upon heating, in the case of A the π-allyl group would begin to rotate around its center of gravity, a type of motion established[7] for $C_5H_5Mo(CO)_2-\pi-C_3H_5$, thus averaging the environ-

(7) A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967).

ments of the 3-methyls and the π-allyl termini and resulting in dynamic C_{2v} symmetry for the molecule. On the other hand, in structure B the same type of dynamic C_{2v} symmetry can be achieved by rotation of the $Mo(CO)_2-\pi-C_3H_5$ group around the B–Mo axis, a process established in the $RB(pz)_3Mo(CO)_2-\pi-C_3H_5$ system.[8]

Of the two possibilities, structure B is preferred on several grounds. First, the π-allyl group is obviously less hindered being remote from the methyl groups. Second, the compound $HB(3,5-(CH_3)_2pz)_3Mo(CO)_2-\pi-C_3H_5$ has been prepared and shown[8] to be stereochemically rigid to over $100°$. In the nmr spectrum of this "frozen" conformation the π-allyl group looks "normal," yet it obviously must reside between two flanking 3-methyl groups and be in the least hindered configuration. Therefore, structure A would also be expected to have the π-allyl group symmetrically disposed with regard to the 3-methyl groups.

The lower barrier to rotation in $H_2B(3,5-(CH_3)_2pz)_2-Mo(CO)_2-\pi-C_3H_5$ as compared with $HB(3,5-(CH_3)_2pz)_3-Mo(CO)_2-\pi-C_3H_5$ is a natural consequence of the former's less strained structure (ring vs. cage). A qualitative comparison of the influence of various R'' substituents in $H_2B(3,5-(CH_3)_2pz)_2Mo(CO)_2-\pi-CH_2CR''-CH_2$ compounds on the height of the rotational barrier gave results similar to those obtained with tridentate analogs;[8] i.e., the lowest rotational barrier was for $R'' = CH_3$ rather than $R'' = H$ (Figure 3). Again, the reason for this is not clear. On the other hand, the $\pi-CH_2CC_6H_5CH_2$ group hindered rotation most (Figure 4) as all methyl groups became nonequivalent in the frozen configuration and splitting of the methyl peaks became pronounced already at $30°$, the splitting temperatures for the 3-methyl peak in the $\pi-C_3H_5$ and $\pi-CH_2CCH_3CH_2$ compounds being 10 and $-10°$, respectively.

The inertness of compound IIIa toward oxygen or nucleophiles can be ascribed to steric hindrance as approach to the molybdenum atom is restricted by the $3-CH_3$ groups. That this restriction is not unduly severe follows from the synthesis of $H_2B(3,5-(CH_3)_2-pz)_2Mo(CO)_2-\pi$-cyclohexenyl, V, and $H_2B(3,5-(CH_3)_2-pz)_2Mo(CO)_2C_7H_7$, VI. The latter compound was prepared by the reaction of Ia with $C_7H_7Mo(CO)_2I$. Its nmr spectrum shows a sharp C_7H_7 singlet and indicates nonidentity of each methyl group as well as the 4-H's. This can be rationalized in terms of a $\pi-C_7H_7$ system with Ia acting as a monodentate ligand or in terms of a bidentate Ia and a dynamic pentahapto-C_7H_7[9] if an inert-gas configuration is presuppossed. However, just as in the case of compound IIIa one could regard VI as a 16-electron compound with a dynamic trihapto-C_7H_7 ligand. The present data do not provide an unequivocal answer to this question. In the nmr spectrum of the π-cyclohexenyl compound, V, the $3-CH_3$ groups were already sharp and well separated at room temperature, yet, in contrast to the $\pi-CH_2CC_6H_5-$

(8) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 3183 (1969).
(9) F. A. Cotton, *ibid.*, **90**, 6230 (1968).
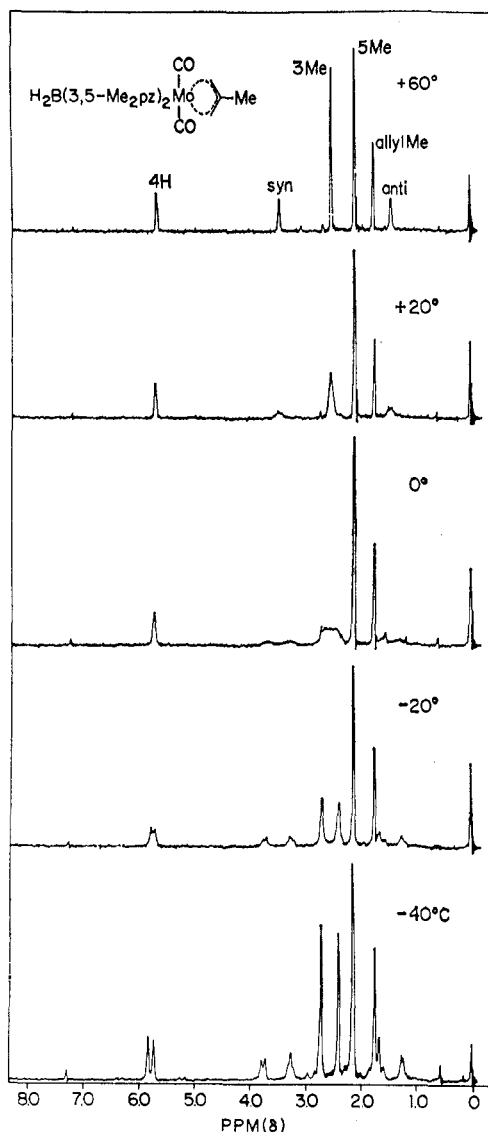
Figure 3.—The temperature-dependent nmr spectrum of H_2B-$(3,5-(CH_3)_2pz)_2Mo(CO)_2-\pi-CH_2CCH_3CH_2$.
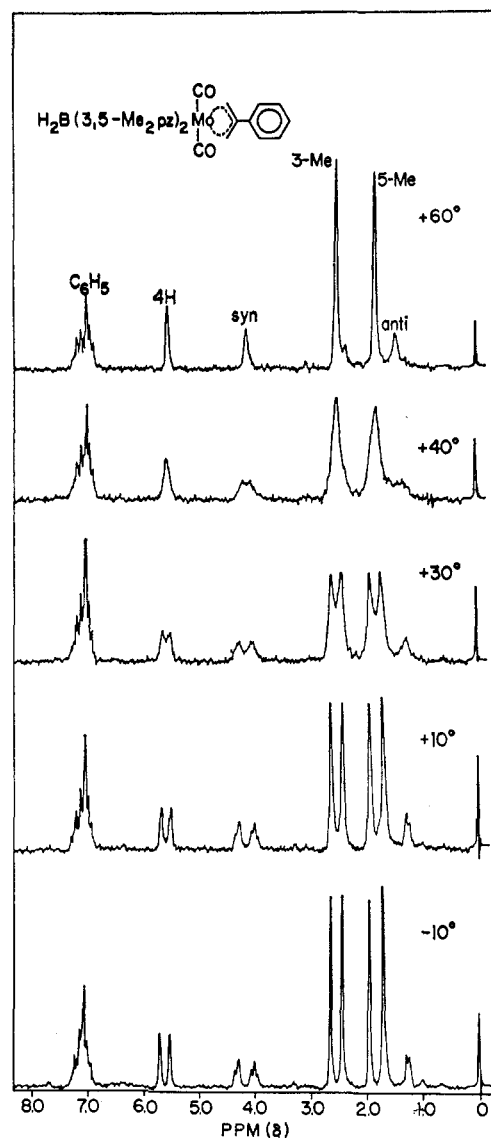
Figure 4.—The temperature-dependent nmr spectrum of H_2B-$(3,5-(CH_3)_2pz)_2Mo(CO)_2-\pi-CH_2CC_6H_5CH_2$.

CH_2 system, the two 5-CH_3 groups were a sharp singlet.
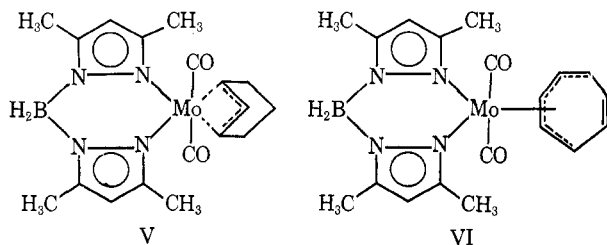
In order to check whether the even more sterically hindered ligand $KH_2B(3,5-(C_2H_5)_2pz)_2$ reacts similarly, it was prepared *in situ* and identified by conversion to the orange nickel derivative $[H_2B(3,5-(C_2H_5)_2pz)_2]_2Ni$ and the corresponding violet cobalt derivative. Compounds of structure III (R = H, R' = C_2H_5, and R'' = H, CH_3, C_6H_5) were prepared in good yield and were just as stable as IIIa, as was the compound $H_2B(3,5-(C_6H_5)_2pz)_2Mo(CO)_2-\pi-C_3H_5$ obtained from the ligand prepared *in situ*. Their nmr spectra indicated stereo-

chemical nonrigidity, but were not investigated in detail.

The infrared spectra of all these compounds had only one sharp BH spike, and their B^{11} nmr spectra were triplets around +33 ppm with J's in the 80–100-Hz range. The carbonyl stretching frequencies were lower by about 20 cm^{-1} than in the corresponding $HB(3,5-(CH_3)_2pz)_3Mo(CO)_2-\pi$-allyl systems.

The reaction of IIa with methyl iodide gave a red crystalline product which was assigned the structure
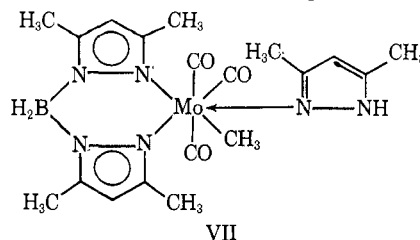
The reaction of IIb with allylic halides also gave the monomeric orange, coordinatively unsaturated deriva-

tives IIIb and analogs. They, however, were moderately air sensitive, especially in solution. Their structure was established from the infrared and nmr spectra which confirmed the presence of two carbonyl groups, one IIb ligand, and one "normal" π-allyl group. Rather unexpected was the finding that one of the methylene groups (from $B(C_2H_5)_2$) was shifted up to τ 12.4. If one considers that the ligand I is nonplanar and coordinates to metal in the boat form,[10] then it follows that the pseudoaxial methylene (which for steric reasons would be pointing toward the metal) would be approaching some empty orbitals of Mo and the electron-deficient metal would interact with the two hydrogens making them somewhat "hydridic" in nature. Support for this hypothesis may be found in the presence of CH stretch bands at remarkably low frequency (2704, 2664 cm^{-1}) implying again some sort of hydrogen bridging between the pseudoaxial methylene and the transition metal. These results are reminiscent of the situation involving exo and endo hydrogens in various Co and Fe complexes of cyclopentadiene[11,12] although, judging by the greater lowering of the ν_{CH}, the metal–hydrogen interaction in IIIb is more pronounced.

From a recent X-ray structure determination[13] of $[HB(pz)_3]_2Co$ one can estimate the Mo–H distances in IIIb to be about 2.5 Å assuming essential preservation of the established bond angles and distances and assuming the Mo–N distance[14] to be 2.3 Å. This appears beyond the range of any significant interaction. On the other hand, some of the assumptions might not be valid, resulting in a shorter Mo–H distance.

An alternative explanation of the unusual spectral data in IIIb, which invokes a ring-current effect of the two pyrazolyl rings on the methylene group, is unattractive since 4,4-diethylpyrazabole[15] and 4,4,8,8-tetraethylpyrazabole,[5] which have essentially the same geometry as metal complexes of the $(C_2H_5)_2B(pz)_2$ ligand, show neither such nmr nor infrared shifts of their methylene group, but $[(C_2H_5)_2B(pz)_2]_2Ni$ shows a CH_2 shift of comparable magnitude to that in IIIb, although it is in the opposite direction (downfield).[6]

Upon coordination of pyrazole (*vide infra*) or of any other base, the unique methylene disappears and both boron-bonded ethyl groups become normal (*i.e.*, resembling those in 4,4,8,8-tetraethylpyrazabole,[5] diethylborylimidazoles,[16] or N,N'-bis(diethylboryl)oxamidines.)[17] Furthermore, the low-frequency CH stretch bands disappear in the infrared spectrum.

A second product, isolated together with IIIb, was a yellow solid, assigned structure IV (R = C_2H_5, R′ = R″ = H) from analytical and spectroscopic data. The presence of one additional pyrazole followed from nmr where all the necessary hydrogens, including NH, were accounted for and the infrared spectrum where the NH band was also discernible. Significantly, the τ 12.4 methylene in IV disappeared, shifting back to its normal position at τ ~9.3, and the low-frequency CH stretch bands disappeared also. The same compound was obtained quantitatively upon treatment of IIIb with excess pyrazole. Compound IV must have thus arisen from the presence of pyrazole in the $(C_2H_5)_2B$-$(pz)_2^-$ ligand, where it is a frequent contaminant.

Compound IIIb formed yellow complexes with a number of other nucleophiles such as ammonia, methylamines, cyanide, azide ions, etc. These were not as stable as IV and on attempted recrystallization or chromatography were often converted back to IIIb. Unlike the related binuclear oxalate system[2] π-C_3H_5-$(CO)_2Mo(C_2O_4)Mo(CO)_2$-π-C_3H_5, IIIb does not add alcohols, water, etc.

Other analogs of IIIb containing different R″ substituents were synthesized similarly, as was the π-cyclohexenyl analog. In all instances the unique methylene appeared upfield from tetramethylsilane, usually in the τ 12.3–13.8 range. Other common features of these compounds were stereochemical rigidity as judged by their nmr spectra, which indicated overall C_{2v} symmetry, and fast reactions with nucleophiles to give coordinately saturated derivatives analogous to IV. Such coordination with, *e.g.*, pyrazole results in change of color from orange to yellow and a shift of ν_{CO} to lower frequencies by 15–20 cm^{-1}. The same holds true of $(C_6H_5)_2B(pz)_2$-$Mo(CO)_2$-π-allyl systems. In that compound one of the phenyl groups, presumably the pseudoaxial, had its ortho and meta hydrogen peaks shifted upfield in the nmr spectrum while the other phenyl group appeared normal.

The reaction of tungsten hexacarbonyl with R_2B-$(pz)_2$ ligands (R = C_2H_5, C_6H_5) followed by allylation gave the stable yellow pyrazole complexes $R_2B(pz)_2$-$W(CO)_2$-π-C_3H_5·Hpz. As the yields of these derivatives exceeded the anticipated amount of free pyrazole impurity in the ligand, the ligand must have degraded somewhat during the reaction.

In conclusion, it may be stated that Mo compounds with a 16-electron configuration, which have been postulated as intermediates in some dynamic processes[18] but are otherwise unknown,[19] can now be readily prepared by allylation of anions derived from $Mo(CO)_6$ and dipyrazolylborate ligands $R_2B(3,5-R'_2pz)_2^-$. The stability of these compounds is ascribed to screening of Mo by the alkyl or aryl groups R and R′. Of these, the R′ groups are much more effective making compounds of type IIIa indefinitely stable to storage and unreactive toward common nucleophiles. Lesser stability is

(10) The simplest way to visualize this is to remove one pyrazolyl group from a $RB(pz)_3M\equiv$ system replacing it with a noncoordinating R group, such as ethyl in the present case.

(11) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. I, American Elsevier, New York, N. Y., 1966, p 36 ff.

(12) G. E. Herberich and J. Schwarzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 143 (1969).

(13) M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, **9**, 1597 (1970).

(14) The Mo–N distances in an *o*-phenanthroline complex NCS(CO)$_2$-$(C_{10}H_8N_2)Mo$-π-C_3H_5 were 2.26 and 2.19 Å: A. J. Graham and R. H. Fenn, *J. Organometal. Chem.*, **17**, 405 (1969); in *cis*-(diethylenetriamine)Mo-(CO)$_3$ they were 2.31–2.35 Å: F. A. Cotton and P. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

(15) S. Trofimenko, *ibid.*, **8**, 1714 (1969).

(16) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3903 (1967).

(17) S. Trofimenko, *ibid.*, **89**, 7014 (1967).

(18) F. A. Cotton and T. J. Marks, *ibid.*, **91**, 1339 (1969).

(19) Except for the compound claimed to be (1,2,3,9,10-*pentahapto*-indenyl)dicarbonyliodomolybdenum: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).

imparted by more flexible R groups; compounds of type IIIb exhibit some air sensitivity and react readily with nucleophiles to afford complexes with an 18-electron configuration. Compounds IIIa and IIIb are thus a convenient vehicle for correlating the reactivity of a 16-electron Mo compound with its steric environment, particularly when their molecular dimensions become established.

Experimental Section

The nmr spectra were determined on a Varian A-60T spectrometer equipped with a variable-temperature probe in deuteriochloroform with external tetramethylsilane as standard. Some of the ligands were prepared by published methods.[6]

Potassium Dihydrobis(3,5-dimethyl-1-pyrazolyl)borate.—A mixture of 108 g (2 mol) of potassium borohydride and 422 g (4.4 mol) of 3,5-dimethylpyrazole in 2 l. of redistilled dimethylacetamide was stirred and refluxed until 95–100 l. of H_2 was evolved. The mixture was concentrated *in vacuo* at 70° to a thick slurry. This was stirred with 2 l. of ether and filtered. The product was purified further by restirring three times in 1 l. of ether, filtering, and air drying. It was obtained in 464-g (96.0%) yield.

The analytical sample was recrystallized twice from toluene and dried at 100° (2 mm). *Anal.* Calcd for $C_{10}H_{18}BKN_4$: C, 49.6; H, 6.62; N, 23.1. Found: C, 50.2; H, 6.95; N, 22.8.

Potassium Dihydrobis(3,5-diethyl-1-pyrazolyl)borate and Its Nickel and Cobalt Derivatives.—A mixture of 27 g (0.22 mol) of 3,5-diethylpyrazole and 5.4 g (0.1 mol) of KBH₄ in 200 ml of dimethylacetamide was stirred and refluxed overnight, the emanating gases being conducted through a −80° trap to a wet-test meter. About 4.4 l. of gas was evolved. The solution was stirred with Darco, cooled, and filtered. One-fourth of this solution was stirred with 30 ml of 0.5 M Ni(OAc)₂ solution and the resulting solid was taken up in methylene chloride. The extracts were filtered and stripped yielding the orange nickel derivative, mp 203–204°, in 3.5-g (51%) yield. The cobalt derivative was obtained similarly in 3.7-g (54%) yield as a violet solid, mp 90–91°.

Anal. Calcd for $C_{28}H_{48}B_2N_8Ni$: C, 58.3; H, 8.32; N, 19.4. The same figures are applicable to the Co compound. Found (Ni compound): C, 58.6; H, 7.97; N, 19.6. Found (Co compound): C, 58.1; H, 7.91; N, 19.3.

The nmr spectrum of the Ni compound had τ 4.42 s, 7.3 complex m, 8.2 complex m, 8.80 t ($J = 7.5$ Hz), and 8.98 t ($J = 7.5$ Hz) in 1:3:1:3:3 ratio.

Synthesis of the π-Allyl Compounds.—In general, the tetracarbonyl anions were not isolated but were converted immediately to the π-allyl compounds. The following procedures are typical, exemplifying the use of either previously prepared ligand or one synthesized *in situ*.

Method A. Dihydrobis(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum π-Allyl.—A mixture of 26.6 g (0.1 mol) of potassium dihydrobis(3,5-dimethyl-1-pyrazolyl)borate and 26.4 g (0.1 mol) of Mo(CO)₆ in 250 ml of DMF was stirred and heated to reflux until about 5 l. of gas was evolved. The solution was cooled under nitrogen to room temperature and 14 g (slight excess) of allyl bromide was added. The solution was stirred and warmed to 85° until another 5 l. of gas was evolved. The solution was then cooled and drowned in 600 ml of ice water. An orange solid precipitated. It was filtered and purified by chromatography on alumina followed by recrystallization from heptane. The compound was obtained as orange crystals, mp 165–166°, in 17.2-g (43.5%) yield. It can be sublimed *in vacuo*. Its properties are listed in Table I.

Method B. Dihydrobis(3,5-diethyl-1-pyrazolyl)boratodicarbonylmolybdenum π-Allyl.—A mixture of 2.7 g (0.05 mol) of KBH₄ and 26 g (0.21 mol) of 3,5-diethylpyrazole[20] in 100 ml of

purified N,N-dimethylacetamide was stirred and heated until about 2.5 l. of hydrogen had been evolved. To the cooled solution was added 13.2 g (0.05 mol) of Mo(CO)₆ and heating was continued until another 2.5 l. of gas was evolved. After cooling under N₂, 10 ml of allyl bromide was added, and heating was resumed until another 2.5 l. of gas was evolved. The reaction mixture was poured into 600 ml of ice water and the product was extracted with methylene chloride and purified by chromatography on alumina. Stripping of the orange band gave an oil which was stirred with 200 ml of methanol and left standing overnight. Orange crystals separated. They were filtered, washed with CH₃OH, air dried, and obtained in 16.8-g (60.8%) yield. From the filtrate another 0.4 g of product was isolated. The compound was recrystallized from ethanol. Its properties are listed in Table I.

Dihydrobis(3,4,5-trimethyl-1-pyrazolyl)boratodicarbonylmolybdenum π-Allyl.—A mixture of 24.2 g of 3,4,5-trimethylpyrazole (0.21 mol) and 5.4 g of KBH₄ (0.1 mol) in 230 ml of DMAC was stirred and refluxed until ~5 l. of H₂ was evolved. After cooling, 26 g (0.1 mol) of Mo(CO)₆ was added and heating was resumed until another 5 l. of gas was evolved. After cooling, 15 ml of allyl bromide was added and the reaction mixture was heated until another 5 l. of gas came off. The reaction mixture was poured into ice water and the product was isolated by extraction with methylene chloride and purified by chromatography on alumina. It was obtained, after recrystallization from heptane, in 11-g (26%) yield, mp 190–192°. *Anal.* Calcd for $C_{17}H_{25}BMoN_4O_2$: C, 48.1; H, 5.89; N, 13.2. Found: C, 47.9; H, 5.95; N, 13.3.

The nmr spectrum indicates fluxional nature of the molecule. It has methyl peaks at τ 7.5 (broad), 7.94, and 8.13 in a 6:6:6 ratio. The π-allyl multiplet is at τ 6.0; the other peaks are at τ 6.5 and 8.6 (both broad). Ir (cyclohexane): 1961, 1872 cm⁻¹. Uv (cyclohexane): 390 mμ (ϵ 1320); 310 mμ (ϵ 5430).

Dihydrobis(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum π-Cyclohexenyl.—This compound was prepared in 17% yield by the above three-step reaction sequence using 3-chlorocyclohexene and was obtained, after recrystallization from heptane, as yellow crystals, mp 186–187°, sublimable *in vacuo*. *Anal.* Calcd for $C_{18}H_{25}BMoN_4O_2$: C, 49.5; H, 5.73; N, 12.9. Found: C, 49.5; H, 5.79; N, 12.9. Ir (cyclohexane): 1950 and 1864 cm⁻¹. Uv (cyclohexane): 390 mμ (ϵ 1230) 310 mμ (ϵ 5370).

Diethylbis(1-pyrazolyl)boratomolybdenum π-Cyclohexenyl.—This compound was prepared by method A, using K(C₂H₅)₂B(pz)₂, in 26% yield. The compound was recrystallized from heptane; mp 163–165°. *Anal.* Calcd for $C_{18}H_{25}BMoN_4O_2$: C, 49.6; H, 5.74; N, 12.8. Found: C, 49.6; H, 5.85; N, 12.8. Nmr: τ 1.90 d ($J = 2.1$ Hz), 2.56 d ($J = 2.2$ Hz), 3.78 t ($J = 2.15$ Hz), 5.58 centered m, 6.15 t ($J = 7.5$ Hz), 8.0 m, 9.2 m, 12.3 q (unresolved) in a 2:2:2:2:1:4:10:2 ratio.
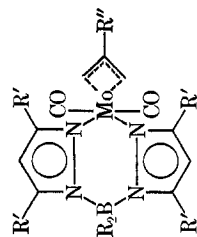
3,5-Dimethylpyrazole Complex of Dihydrobis(3,5-dimethyl-1-pyrazolyl)boratomethyltricarbonylmolybdenum.—A mixture of 27 g (0.11 mol) of potassium dihydrobis(3,5-dimethyl-1-pyrazolyl)borate and 26 g (0.1 mol) of molybdenum hexacarbonyl in 250 ml of DMF was stirred and heated. Gas evolution commenced at 75° and proceeded briskly at 85–95°; soon 4.6 l. was evolved. After cooling, 20 ml (large excess) of methyl iodide was added and the reaction mixture was stirred 2 hr at 50°. It was then poured into 600 ml of cold water and the product was extracted with methylene chloride. The extracts were chromatographed and the orange-red band was concentrated and chromatographed again on a hexane-packed column. After some yellowish green impurities were eluted with hexane, the main orange band came through with ether. It was stripped and the residue was stirred with hexane and filtered. There was obtained 9.1 g (18%) of orange solid, mp 190–193° dec with prior darkening from 170°. *Anal.* Calcd for $C_{19}H_{27}BMoN_6O_3$: C, 46.2; H, 5.47; N, 17.0; O, 9.7. Found: C, 46.2; H, 5.38; N, 17.0; O, 9.3.

The infrared spectrum had an NH band at ~3400 cm⁻¹ and strong carbonyl bands at ~1880 and 1770 cm⁻¹. Nmr: broad peak at τ 0.7, sharp singlets at τ 3.88, 4.15, 4.42, 7.38, 7.57,

(20) D. S. Noyce, E. Ryder, Jr., and B. H. Walker, *J. Org. Chem.*, **20**, 1684 (1955).

TABLE I

COMPOUNDS OF STRUCTURE

R	R'	R''	Mp	% yield	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	Mol wt Calcd	Mol wt Found[a]	Ir, cm⁻¹	Uv max, mµ (ε)	¹¹B nmr[b,c]	¹H nmr[c]
H	CH₃	H	165–166°	44	45.4	45.6	5.31	5.31	14.1	14.1	396	396	1963, 1874, 2483 (BH)		t (J = 90) +33.2	See Figure 1
H	CH₃	CH₃	179–180°	22	46.8	46.8	5.62	5.54	13.7	13.8			1963, 1872		t (J = 99) +33.6	See Figure 3
H	CH₃	C₆H₅	156–157°	38	53.4	53.2	5.30	5.17	11.9	11.9			1966, 1880			See Figure 4
H	CH₃	Br	158–160°	27	37.1	37.7	4.13	4.17	11.5	11.5			1974, 1889	384 (1100), 277 (9900)		s 4.24, s 6.19, s 7.48, 7.87, s 8.05 [1:1:3:3:1]
H	C₂H₅	H	104–105°	61	50.5	50.4	6.43	6.72	12.4	12.5			1963, 1874	387 (1240), 295 sh (4750)	t (J = 76) +33.4	s 4.10, m 5.73, d (7) 6.49, q (7.3) 7.17, d (9.7) 8.07, t (7.3) 8.77 [2:1:2:8:2:12]
H	C₂H₅	CH₃	109–110°	96	51.5	51.2	6.65	6.44	12.0	12.1			1962, 1783	390 (1370), 300 sh (4200)	t (J = 80) +32.9	s 4.22, m 6.3–7.8, s 8.31, m 8.5–9.1 [2:10:3:14]
H	C₂H₅	C₆H₅	91–92°	72	56.8	56.8	6.25	6.39	10.6	10.6			1966, 1879	372 (2760), 282 (13,700)	t (unres) +33.8	m 2.85, m 4.25, d (11) 5.83, m 4.97, m 7.77; m 8.3–9.3 [5:2:2:4:4:12]
H	C₆H₅	H	246–247°	67	65.3	65.4	4.51	4.82	8.70	8.73			1968, 1963, 1872	390 (1390), 240 (48,400)	t (unres) +31.0	m 1.9–2.7, s 2.70, s 7.45, m 6.2, broad d 6.8, d (10.0) 8.92 [10:10:2:1:2:2]
C₂H₅	H	H	126–130° dec	40	45.4	45.2	5.31	5.38	14.1	14.3			1973, 1884			d (2.1) 1.85, d (2.3) 2.57, t (2.2) 3.78, m 5.8–6.3, m. 9.16, m 12.4 [2:2:2:3:2:8:2]
C₂H₅	H	C₆H₅	155–156° dec	60	53.4	53.2	5.31	5.48	11.9	11.9			1971, 1887	387 (2760), 275 sh (12,000)	s +20.1	d (2.1) 1.8, d (2.3) 2.66, m 2.85, t (2.2) 3.78, s 5.82, s 8.31, s 9.34, t (7.0) 9.73, q (7.0) 13.8 [2:2:5:2:2:2:5:3:2]
C₆H₅	H	H	215–218° dec	69	56.1	56.1	4.27	4.29	11.4	11.4	492	491	1961, 1878	397 (1270), 278 (7130)		s 1.72, m 2.2–2.9, m 3.1, m 3.47, m 3.7, m 7.0, d (7.0), 7.69, d (10.0) 8.95 [2:8:2:2:2:1:2:2]
C₆H₅	H	CH₃	200–204° dec	37	56.9	57.1	4.55	4.67	11.1	11.3			1960, 1876		s +19.3	d (2.0) 1.82, d (2.3) 2.47; m 2.72, m 3.24, t (2.1) 3.75, s 7.43, s 8.44, s 9.13 [2:2:5:5:2:2:3:2]

a By vapor pressure osmometry in chloroform.   *b* In ppm referred to external trimethyl borate.   *c* Listed are: multiplicity (*J* in hertz) τ [relative areas].

7.60, 7.78, 8.05, 8.13, and 8.29 in a 1:1:1:1:3:3:3:3:2:1:6 ratio.

Pyrazole Complex of Diethylbis(1-pyrazolyl)boratodicarbonyltungsten π-Allyl.—To 0.1 mol of K(C$_2$H$_5$)$_2$B(pz)$_2$W(CO)$_4$, prepared *in situ*, was added at room temperature 15 g of allyl bromide. On heating to 45°, 3.6 l. of gas was evolved. The solution was poured into 1 l. of ice water and the product was extracted with methylene chloride and purified by chromatography on alumina. There was obtained 32 g (58%) of air-stable yellow solid. It is very soluble in ether and halocarbons. Recrystallization from ethanol yielded yellow crystals, mp 147–148°. *Anal.* Calcd for C$_{18}$H$_{25}$BN$_6$O$_2$W: C, 39.2; H, 4.54; N, 15.2. Found: C, 39.7; H, 4.74; N, 15.5. Ir (cyclohexane): 1935 and 1846 cm^{-1}. Nmr: τ 2.1 d (with shoulder) (J = 2.0 Hz), 2.28 d (J = 2.3, J' = 0.5 Hz), 2.86 m, 3.80 t (J = 2.2 Hz), 6.8 m + s, 8.2 d (J = 8 Hz), ~9.1 m, 9.62 "s" in a 3:2:1:3:3:2:5:5 ratio.

Pyrazole Complex of Diphenylbis(1-pyrazolyl)boratodicarbonyltungsten π-Allyl.—This compound was prepared as in the preceding experiment but using Na(C$_6$H$_5$)$_2$B(pz)$_2$ instead of K(C$_2$H$_5$)$_2$B(pz)$_2$. The product was obtained in 49% yield as yellow crystals and recrystallized from chloroform; mp 202–204°. *Anal.* Calcd for C$_{26}$H$_{24}$BN$_6$O$_2$W: C, 48.3; H, 3.72; N, 13.0. Found: C, 48.4; H, 4.62; N, 12.7.

Pyrazole Complex of Diethylbis(1-pyrazolyl)boratodicarbonylmolybdenum π-Allyl.—From the preparation of IIIb a 10% yield of a yellow solid, purified by chromatography and recrystallized from hexane, was obtained. This compound, mp 131–132°, was also obtained in 100% yield by the reaction of IIIb with 1 equiv of pyrazole. *Anal.* Calcd for C$_{18}$H$_{24}$BMoN$_6$O$_2$: C, 46.5; H, 5.39; N, 18.1. Found: C, 46.2; H, 5.50; N, 18.0.

The infrared spectrum showed, apart from carbonyl peaks at 1942 and 1857 cm^{-1}, the NH band at 3398 cm^{-1}. The nmr spectrum clearly demonstrated the presence of the (C$_2$H$_5$)$_2$B(pz)$_2$ ligand and of one additional pyrazole: τ 1.30 s (broad), 2.02 d

(unresolved), 2.21 d (J = 2.0 Hz), 2.31 d (J = 2.4 Hz), 2.94 d (unresolved), 3.83 t (J = 2.2 Hz), 5.8 m, 6.62 d (J = 7.0 Hz), 8.43 d (J = 9.5 Hz), ~9.1 m, 9.66 "d" in a 1:1:2:2:1:3:1:2:2:5:5 ratio. These were assigned to the NH, 3-H of pyrazole, 3-H's of ligand, 5-H's of ligand, 5-H of pyrazole, 4-H's of pyrazole and ligand, allylic 1-H, allylic 2-H, allylic 3-H, pseudoaxial ethyl, and pseudoequatorial ethyl, respectively.

Pyrazole Complex of Diphenylbis(1-pyrazolyl)boratodicarbonylmolybdenum π-Allyl.—To a stirred solution of 1.50 g of (C$_6$H$_5$)$_2$B(pz)$_2$Mo(CO)$_2$ π-C$_3$H$_5$ in 20 ml of methylene chloride was added 1 g (large excess) of pyrazole. The color changed immediately from orange to yellow. Evaporation of the solution and washing of the residue with aqueous methanol gave 1.65 g (96%) of yellow solid which was purified by recrystallization from a toluene–heptane mixture; mp 206–208° dec with prior darkening from ~190°. *Anal.* Calcd for C$_{26}$H$_{25}$BMoN$_6$O$_2$: C, 55.7; H, 4.47; N, 15.0. Found: C, 55.5; H, 4.46; N, 14.9. Ir (cyclohexane): 1947, 1863 cm^{-1}.

Dihydrobis(3,5-dimethyl-1-pyrazolyl)boratocycloheptatrienylmolybdenum Dicarbonyl.—To a freshly prepared solution of 13.7 g (0.05 mol) of cycloheptatrienylmolybdenum dicarbonyl iodide[21] in 125 ml of DMF was added 14.1 g (0.06 mol) of KH$_2$B-(3,5-(CH$_3$)$_2$pz)$_2$. The mixture was stirred at 50° until the color changed from greenish to deep red. The solution was poured into 500 ml of ice water and the precipitated product was isolated by filtration and purified by chromatography. It was obtained in 13.6-g (60%) yield and was recrystallized from ethyl acetate; mp 179–181° dec. *Anal.* Calcd for C$_{19}$H$_{23}$BMoN$_4$O$_2$: C, 51.2; H, 5.38; N, 12.5. Found: C, 51.2; H, 5.48; N, 12.4. Ir (cyclohexane): 1961, 1883 cm^{-1}. Uv: two superimposed bands at 333 mμ (ε 8170) and 305 mμ (ε 8300). The nmr spectrum has singlets at τ 4.30, 4.36, 4.76, 7.53, 7.58, 7.87, and 7.90 in 1:1:7:3:3:3:3 ratio.

(21) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 141.

Mixed-Metal Complexes between Indium(III) and Uranium(VI) with Malic, Citric, and Tartaric Acids[1]

By ANTHONY ADIN, PAUL KLOTZ, and LEONARD NEWMAN*

The formation of mixed-metal complexes between indium(III) and uranium(VI) with various hydroxycarboxylic acids was studied using spectrophotometric, potentiometric, and solvent extraction methods. Over wide concentration ranges, it was shown that the reactions for the formation of the indium(III) uranium(VI) malate, citrate, and tartrate mixed-metal complexes can be written

$$In^{III}L_2 + 0.5(U^{VI}L)_2 \underset{}{\overset{K'_{mmc}}{\rightleftharpoons}} In^{III}U^{VI}L_2 + L$$
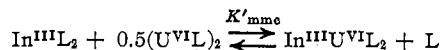
where L is the hydroxycarboxylic acid ligand. At 25° and pH 4 values of K'_{mmc} are as follows: malate, 30; citrate, 720; tartrate, 31. In order to study these reactions, it was first necessary to investigate the polymerization of indium(III) and dimerization of uranium(VI) complexes.

Introduction

The formation of mixed-metal complexes (henceforward denoted mmc) between a hydroxycarboxylic acid and a variety of different metal ions has been reported

in the literature.[2,3] It has been recently found that the basic malic acid structure is necessary for the formation of an mmc between Cr(III) and In(III).[2a] Some mmc's have been assigned the formula ABL$_2$ where A

(2) (a) T. W. Gilbert, L. Newman, and P. Klotz, *Anal. Chem.*, **40**, 2123 (1968); (b) H. M. N. H. Irving and W. R. Tomlinson, *Chem. Commun.*, 497 (1968).

(3) R. C. Srivastava and T. D. Smith, *J. Chem. Soc. A*, 2192 (1968).