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Syntheses and Properties of New (Alkyl)dioxo[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(VI) Complexes

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Synopsis. New (alkyl)dioxo[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(VI) complexes, where "alkyl" refers to methyl and trimethylsilylmethyl groups, were prepared as white microcrystals, and were characterized by NMR and IR spectroscopic techniques.

In many catalytic reactions with an early transition-metal deposited on solid oxide supports such as silica and alumina, catalytically active sites have been described to contain the metal in its high-valent oxidation state, frequently with a d^0 electron system.[1] To understand the chemistry of various metal species formed on the surface of the oxides, some organo transition-metal complexes, for example, (alkyl)(oxo) complexes,[2,3] have been prepared as homogeneous molecular models for the species. Considering that some molybdenum(VI) intermediates incorporated with organic substrates, involving those with molybdenum–carbon σ bonds, have been proposed as key role-playing species in catalytic olefin-oxidation reaction cycles,[4] we wish to report here the syntheses and properties of new (alkyl)dioxo[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(VI) complexes $[\mathrm{Mo(R)(BHPz^*_3)(O)_2}]$ (Pz* = 3,5-dimethyl-1-pyrazolyl) {(**1**) and (**2**) with CH_3 and $CH_2Si(CH_3)_3$ as R, respectively} (Fig. 1), which were obtained in the course of our study of the transition-metal poly(1-pyrazolyl)borate complexes.[5] Recent publications by Young and his co-workers on unsuccessful attempts[6] to obtain the organomolybdenum(VI) complexes and on the syntheses[7] of similar tungsten(VI) analogues, prompted us to report our investigation results as a Note.

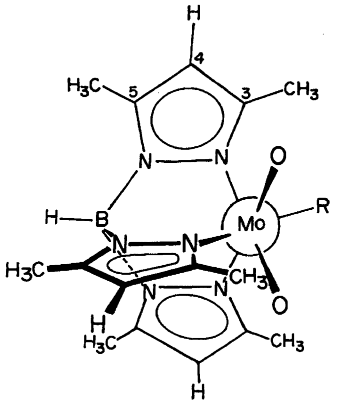

Fig. 1. The new (alkyl)dioxo[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(VI) complexes. **1**, R=CH_3; **2**, R=$CH_2Si(CH_3)_3$.

The molybdenum(VI) complex $[\mathrm{MoCl(BHPz^*_3)(O)_2}]$[8] was treated with excess Grignard reagents, CH_3MgI and $(CH_3)_3SiCH_2MgCl$,[9] at −78 °C, and the mixtures were stirred for 1 h at ca. −10 °C. After solvent removal at ca. 5 °C, the resulting solids were recrystallized or chromatographed on silica gel to give white microcrystals of the (alkyl)dioxo[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(VI) complexes. FAB Mass spectra of **1** and **2** showed the $(M+H)^+$ parent-ion signals centered at m/z 443 and 515, respectively, and confirmed their formulation as $[\mathrm{Mo(R)(BHPz^*_3)(O)_2}]$ {R=CH_3 and $CH_2Si(CH_3)_3$}. Fragment signals, $[M+H-O]^+$ and $[M+H-R]^+$, were observed also. The organomolybdenum(VI) complexes were soluble in organic solvents such as benzene, THF, dichloromethane, and diethyl ether. They were stable in the solid state, but slowly decomposed in chloroform under air.

The Grignard reagent CH_3MgI gave some highly-colored (usually violet or yellow) impurities as by-products, and in the reaction performed at room temperature, did not form **1** at all. These findings were in accord with Young's results,[6] whereas we obtained the organomolybdenum(VI) complexes from the reactions at ca. −10 °C (vide ante).

^1H and ^{13}C NMR spectra were measured for **1** and **2**, and their data are summarized in Table 1. NMR signal assignments were made with the aid of ^{13}C–^1H COSY observation (Fig. 2). Three coordinated 3,5-dimethyl-1-pyrazolyl groups were divided into two classes in a 1 : 2 ratio. The classification was readily interpretable by an end-view (i.e. Newman projection along the B–Mo axis) of the tridentate $\mathrm{BHPz^*_3}$ ligand with local C_{3v} symmetry (Fig. 1). That is, the tridentately-coordinated $\mathrm{BHPz^*_3}$ ligand did not rotate around the B–Mo axis at room temperature.

In the ^1H NMR spectra of **1** in $CDCl_3$, the CH_3 group on molybdenum showed a singlet at $\delta=1.47$, a considerably higher field than that at $\delta=4.26$ for the CH_3O group of the corresponding (methoxy)molybdenum(VI) $[\mathrm{Mo(BHPz^*_3)(O)_2(OCH_3)}]$.[8] In view of the apparent similarities of tridentate polypyrazolylborate and η^5-cyclopentadienyl ligands in coordination and electronic structures,[5] NMR chemical shifts of the alkyl groups on molybdenum in the present $\mathrm{BHPz^*_3}$ complexes were compared with those in the corresponding Legzidins' η^5-cyclopentadienyl complexes, $[\mathrm{Mo(R)(\eta^5\text{-}C_5H_5)(O)_2}]$,[3] among which the methyl complex in C_6D_6 shows CH_3 signals at $\delta=1.19$ and 11.6 in the ^1H and ^{13}C NMR spec-

Table 1. ^{1}H and ^{13}C NMR Data of $[\mathrm{Mo(R)(BHPz^*_3)(O)_2}]$[a,b]

Complex	R	NMR	Alkyl groups		Pz* groups					
			CH_3	CH_2	Class[c]	CH_3		4-CH	3 and 5-C	
1	CH_3	^{1}H	1.81		X	2.12	2.82	5.62		
					Y	1.94	2.57	5.21		
		^{13}C	27.74		X	12.29	14.70	107.53	143.49	152.75
					Y	12.29	15.29	107.10	146.45	153.07
2	$CH_2Si(CH_3)_3$	^{1}H	0.54	2.13	X	2.14	2.85	5.63		
					Y	1.95	2.57	5.20		
		^{13}C	1.43	50.94	X	12.33	15.05	107.53	143.49	152.21
					Y	12.33	15.33	107.02	145.90	152.91

a) δ Values from TMS; in C_6D_6. b) ^{1}H NMR resonances of the alkyl groups on molybdenum in $CDCl_3$; **1**, $\delta=1.47$ (CH_3); **2**, $\delta=0.20$ (CH_3) and 1.93 (CH_2). c) X, two spectroscopically equivalent Pz* groups; Y, unique Pz* group.

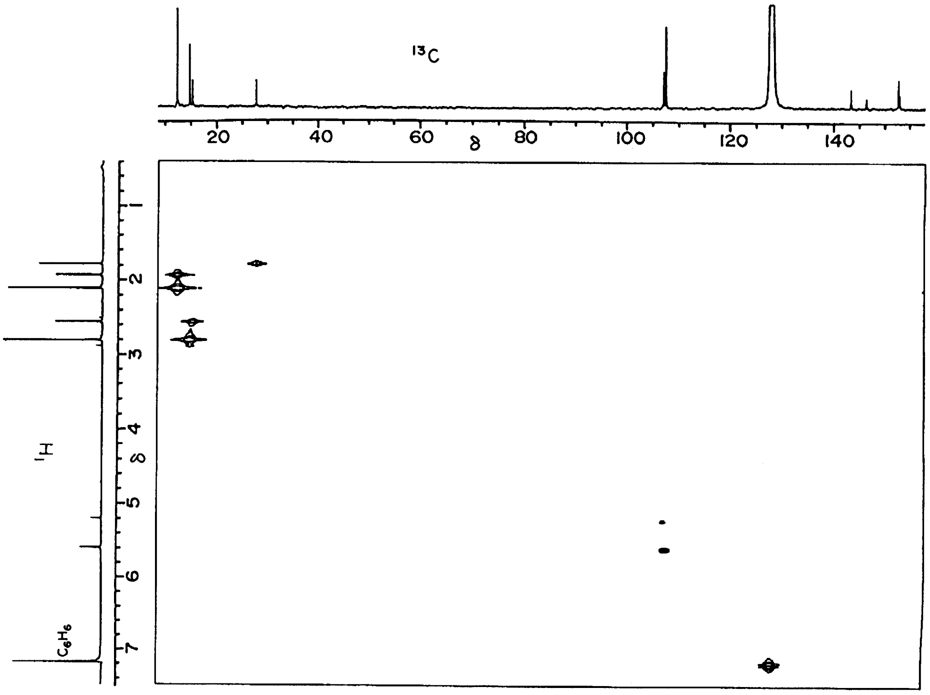

Fig. 2. The ^{13}C–^{1}H COSY spectrum of the methyl complex **1** in C_6D_6.

tra, respectively. Thus, the CH_3 NMR signals of **1** were found to be at significantly lower fields than those of the η^5-cyclopentadienyl analogue. A similar phenomenon was also observed for the CH_2 group on molybdenum in two kinds of $(CH_3)_3SiCH_2$ complexes.[3] Presently, we are trying to evaluate the electron densities on the alkyl groups in the complexes with two types of ligands, by means of extended Hückel molecular orbital calculations, and the results will be published elsewhere.

Experimental

The reagents, $[\mathrm{MoCl(BHPz^*_3)(O)_2}]$[8] and $(CH_3)_3SiCH_2MgCl$[9] were prepared according to the literature procedures. Solvents were dried and distilled by the usual methods. Preparative operations except chromatographic separations were performed under dry nitrogen by the standard Schlenk technique. IR spectra (KBr) were obtained by a JASCO A-100 spectrometer. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL model JNM GX-400 spectrometer operating at 399.7, 100.4, and 128.2 MHz, respectively, by use of tetramethylsilane (TMS) as an internal standard for the former two nuclei and trimethyl borate as an external one for the third. The chemical shifts (δ) are expressed in parts per million from these standards, and downfield shifts are noted as positive in all cases. The melting points were determined in evacuated capillary tubes on a Yanagimoto MP-S3 and are uncorrected. FAB Mass spectra were obtained on a JEOL JMS-DX-303, using *m*-nitrobenzyl alcohol as a matrix material.

Preparation of the Alkyl Molybdenum(VI) Complexes. To a THF solution (20 cm^3) of $[\mathrm{MoCl(BHPz^*_3)(O)_2}]$[8] (0.43 mmol) at −78 °C under nitrogen, an ether solution of excess CH_3MgI (e.g. 1.30 mmol) was added dropwise. The mixture was stirred for 1 h at ca. −10 °C, and was allowed to warm to ca. 5 °C. At this temperature, acetone (1 cm^3) was added to quench the unreacted Grignard reagent, and the solvents were removed under reduced pressure. The residue was recrystallized from benzene and hexane to afford slightly pink-tinged white microcrystals of [Mo(CH$_3$)(BHPz$^*_3$)(O)$_2$] **1**. For its analytically pure sample as a monohydrate,[10] chromatographic separation was performed on silica gel by elution with benzene (R_f, 0.45). Yield, 39%; mp 240—280 °C (decomp); ^{11}B NMR (CDCl$_3$) $\delta=-28.1$ (d, $J_{\mathrm{BH}}=110$ Hz); IR (KBr) 905 and 940 (Mo=O), 2540 cm^{-1} (B–H). Found; C, 42.21; H, 5.72; N, 18.11%. Calcd for $C_{16}H_{25}N_6BMoO_2 \cdot H_2O$: C, 41.94; H, 5.94; N, 18.34%.

(Trimethylsilylmethyl)molybdenum(VI) complex **2** was obtained as white microcrystals, by a similar treatment in diethyl ether with $(CH_3)_3SiCH_2MgCl$.[9] The crude product was purified by chromatographic separation on silica gel by elution with benzene (R_f, 0.54) and the analytical sample of **2** was isolated as a monohydrate.[10] Yield, 45%; mp 210—212 °C (decomp); ^{11}B NMR (CDCl$_3$) $\delta=-29.2$ (d, $J_{\mathrm{BH}}=96$ Hz); IR (KBr) 902 and 942 (Mo=O), 2545 cm^{-1} (B–H). Found; C, 43.13; H, 6.33; N, 16.20%. Calcd for $C_{19}H_{33}N_6BMoSiO_2 \cdot H_2O$: C, 43.03; H, 6.65; N, 15.85%.

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