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Reactions of Molybdenum Atoms with various Conjugated Dienes

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Tris(η^4-butadiene)molybdenum **1** was first obtained by Skell *et al.*[1] by cocondensation of the metal atoms with 1,3-butadiene. The structure of **1** has an *s-cis* conformation and **1** adopts a trigonal prismatic rather than a octahedral geometry about the metal atom.[2,3] And yet the bond lengths of the terminal and internal C-C bonds in **1** are not clearly defined. We are interested in π-complexes and have synthesized some stable π-complexes, tris(isoprene)molybdenum **2** and tris (2,3-dimethyl-1,3-butadiene)molybdenum **3**, by cocondensation method.

We would like to report the effect of methyl substituents of diene ligand and the structures of these π-complexes. Analytical and spectroscopic data for **1, 2,** and **3** are listed in Table 1. **1** forms yellow plates and **3** yellow needles. **1** decomposes after a week in air. **3** is the most stable among the three compounds. **3** is stable over 3 months in air and then decomposes slowly. However, **2** is a greenish yellow liquid at room temperature and turns a dark green sticky solid after a few days in air.

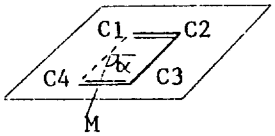

Table 1. Analytical and Spectroscopic Data

Compound and analysis^a(%)	I.R.^{b}(cm^{-1}) $\nu_{C=C}$, $\nu_{=CH}$	UV-Vis.^{c}(nm) λ_{max}	^{1}H nmr^d data δ(ppm)
1, $(C_4H_6)_3Mo$ C, –; H, –	1490w, 3050m	314	4.58(m,6H), 1.56(qut,6H) 0.45(dd,6H)
2, $(C_5H_8)_3Mo$ C, 60.09(60.00); H, 8.11(8.10)	1510m, 3040m	322	4.30(m,2H), 1.68(m,9H) 1.57(m,2H), 1.32(m,2H) 0.37(m,2H), -0.29(m,2H)
3, $(C_6H_{10})_3Mo$ C, 63.51(63.15); H, 8.82(8.83)	1513m, 3040m	330	1.58(s,18H), 1.27(d,6H) -0.47(d,6H)

[a]Calculated values are given in parentheses. [b]Spectra recorded for KBr disks or KBr windows. Intensity; w = week, m = medium. [c]Measured in *n*-hexane at room temperature. [d]Chemical shifts referenced to residual solvent in toluene-d_8 at room temperature. Multiplicity; s = singlet, d = doublet, dd = double doublet, qut = quintet, m = multiplet.

Yields and spectroscopic properties of **1, 2,** and **3** indicate that methyl groups at carbon 2 or 3 position in 1,3-butadiene affect the formation of these π-complexes. Since electron donating ability of the diene ligand increases with methyl substituents, we can expect the stability and yield increase in the order of **1**~**2**<**3.** Yields of **1, 2,** and **3,** based amount of molybdenum vaporized are 20-40, 30-40, and 60-70 percentages, respectively. The i.r. spectra of **1, 2,** and **3** suggest that there are strong π-bonding between Mo atom and diene ligand and methyl substituents affect the strength of π-bonding. The UV-Vis. spectra of **1, 2,** and **3** show broad absorption bands, due to *d-d* transition in the complexes. In these *d-d* transition bands, the red shifts occurred with methyl substituents indicate that the delocalization of electron increases with the methyl substituent. The methyl substituent effect is also observed in ^{1}H nmr spectra of these π-complexes. In-

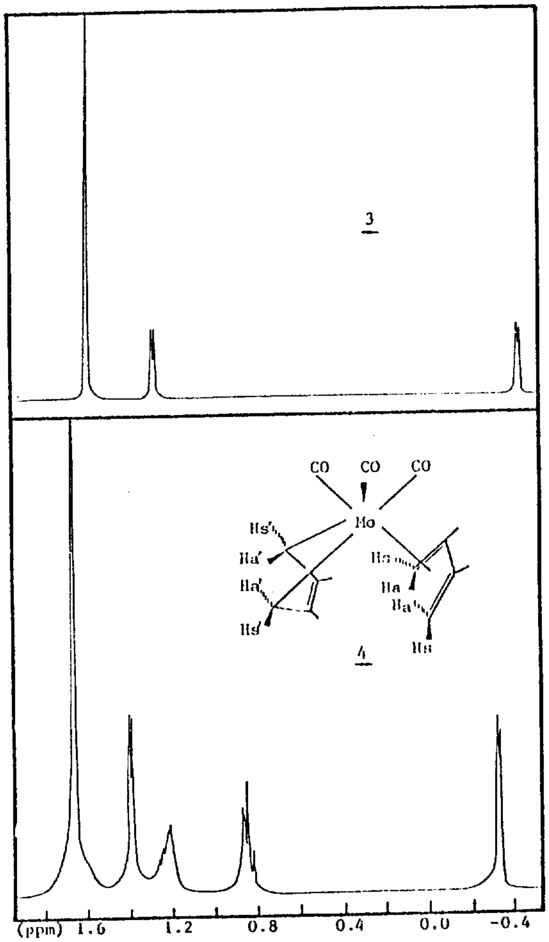

Figure 1. 300 MHz ^{1}H NMR spectra of $(C_6H_{10})_3Mo$, **3**, and $(C_6H_{10})_2(CO)_3Mo$, **4**, at room temperature in toluene-d_8 and benzen-d_6, respectively.

creasing the number of methyl group at 2- or 3-position in 1,3-butadiene gives the high field chemical shifts, *i.e.* δ **1** 0.45, 1.56; **2** -0.29, 1.32; **3** -0.47, 1.27 ppm, for the terminal protons of the diene ligands. These ^{1}H nmr data suggest that the dihedral angle (α) subtended by the Cl-M-C4 and C1-C2-C3-C4 planes would increase by the methyl substituents on the diene ligangds. The dihedral angle calculated from the x-ray structure analysis data[2] of **1** is 86.44°. Then the dihedral angles of **2** and **3** are expected larger than that of **1**. The x-ray structure analysis[4] of **3** in this laboratory indicates the dihedral angle of **3** to be 95°.

For some η^4-butadiene-transition metal complexes, a fluxional behaviour of butadiene has been observed in solution.[5] However, ^{1}H nmr spectra of **3** show constant peaks in toluene-d_8 in the temperature range from room temperature to 100 °C. This indicates that the fluxional behavior of the ligands in **3** does not occur in this temperature range.

In conclusion, the methyl substituents on 2- and 3-position of 1,3-butadiene affect stability of π-complex of the butadiene by their electron donating ability to the π-system.

By the way, **1** reacts with CO to give isomeric 1,5,9-cyclododecatriene and $Mo(CO)_6$.[6] However, **3** reacts with CO to give $(C_6H_{10})_2(CO)_3Mo$, **4**, *via* following reaction.

$$\mathrm{Mo + CH_2CCH_3CCH_3CH_2 \xrightarrow[77K]{cocondensation} [solid\ matrix] \xrightarrow[warm\ up\ to\ r.t.]{CO,\ 650\ mmHg} \underset{\mathbf{4}}{(CH_2CCH_3CCH_3CH_2)_2(CO_3)Mo}}$$

4 is obtained as greenish yellow liquid in 20~30% yield (~50 mg). This is somewhat stable (a few hours) in the air. The i.r. spectrum[7] of **4** shows that the CO coordinates to the Mo atom and the vibrational mode of the coordinated diene is essentially similar to that in **3**. **4** was identified by elemental (Mo: 27.9%), mass spectrum,[8] and ^{1}H nmr[9] analysis. ^{1}H nmr spectrum of **4** is shown in comparisom with ^{1}H nmr spectrum of **3** in Figure 1. ^{1}H nmr spectrum of **4** shows that two ligands in **4** are coordinated differently, *i.e.* one ligand in **4** is indicated by the very high frequency signals of its terminal protons at δ-0.34 (*d*, Ha) and 1.40 (*d*, Hs) ppm, while the other ligand at δ 0.85 (*m*, Ha) and 1.21 (*m*, Hs). So we assume that the structure of **4** has that one of the 2,3-dimethyl-1,3-butadiene ligands binds to the molybdenum atom *via* π-interaction and the other via σ-interaction. Mass spectrum of **4** is very similar to that of **3**. However, there are several peaks which account for the combination of C_6H_{10} and CO fragments. Surprisingly, there are also peaks for $\mathrm{{}^{C}_{C}{>}C=C{<}^{C}_{C}}$ skeleton which do not appear in the mass spectrum of **3**. Further work on this and related mononuclear π-complexes is being directed toward obtaining more structural information and new stable π-complexes.

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7. **4**: ν_{CO} = 1950(s,br), 1860(s,br) cm^{-1}, $\nu_{C=C}$ 1513(m) cm^{-1}.
8. **3**: Fragment, *m/e* (% base) = M, 344 (28); M-C_6H_{10}, 262 (73); M-C_6H_{10}-6H, 256 (100); M-2C_6H_{10}-4H, 176 (6); Mo, 98 (5); C_6H_{10}, 82 (6); C_5H_7, 67 (26); C_4H_7, 55 (8); C_4H_6, 54 (10); C_4H_5, 53 (6), **4**: Fragment, *m/e* (% base) = M-2H, 344 (26); M-3CO, 262 (89); M-3CO-6H, 256 (100); M-3CO-C_6H_{10}-4H, 176 (13); C_5H_7(CO), 123 (13); Mo, 98 (11); C_6H_{10}, 82 (68); C_6H_2, 74 (95); C_5H_7, 67 (87); C_4H_7, 55 (45); C_4H_6, 54 (26); C_4H_5, 53 (24), Fragments of 2,3-dimethyl-1,3-butadiene: Fragment, *m/e* (% base) = C_6H_{10}, 82 (70); C_5H_7, 67 (100); C_4H_6, 54 (38); C_4H_5, 53 (22).
9. δ-0.34 (*d*, 2H), 0.85 (*m*, 2H), 1.21 (*m*, 2H), 1.40 (*d*, 2H), 1.66 (*s*, 12H) (ppm).