

References

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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 an 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.

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

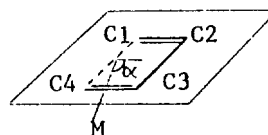


Table 1. Analytical and Spectroscopic Data

Compound and analysis ^a (%)	I.R. ^b (cm ⁻¹)		UV-Vis. ^c (nm)	¹ H nmr ^d data
	$\nu_{C=C}$	ν_{C-H}	λ_{max}	δ (ppm)
1 , (C ₄ H ₆) ₃ Mo C, —; H, —	1490w, 3050m		314	4.58(m,6H), 1.56(quot,6H) 0.45(dd,6H)
2 , (C ₅ H ₈) ₃ Mo 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 ₆ H ₁₀) ₃ Mo 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)

^aCalculated values are given in parentheses. ^bSpectra recorded for KBr disks or KBr windows. Intensity: w = weak, m = medium. ^cMeasured in *n*-hexane at room temperature. ^dChemical shifts referenced to residual solvent in toluene-*d*₆ at room temperature. Multiplicity: s = singlet, d = doublet, dd = double doublet, quot = quintet, m = multiplet.

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 ¹H nmr spectra of these π -complexes. In-

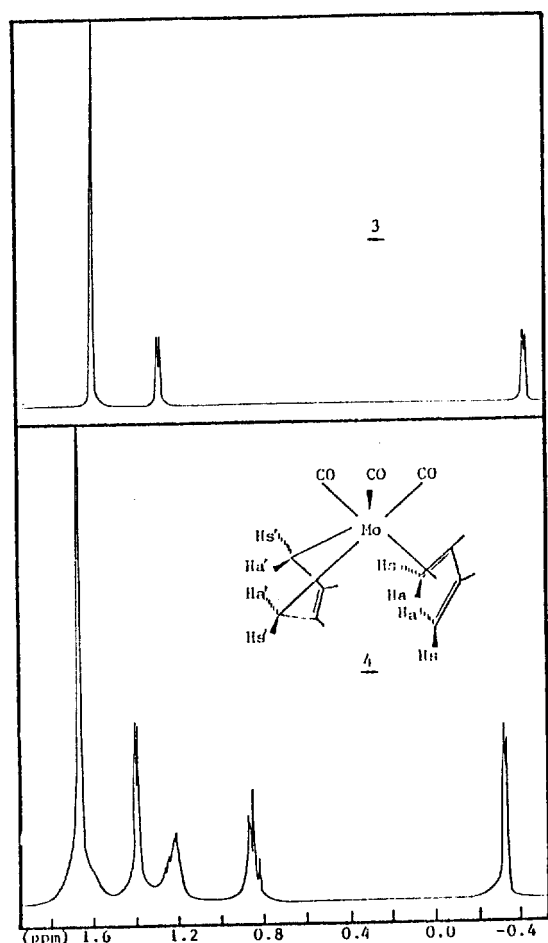


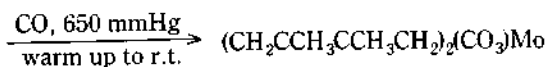
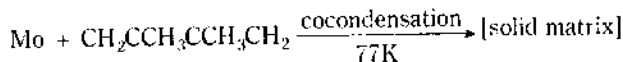
Figure 1. 300 MHz ^1H NMR spectra of $(\text{C}_6\text{H}_{10})_3\text{Mo}$, **3**, and $(\text{C}_6\text{H}_{10})_2(\text{CO})_3\text{Mo}$, **4**, at room temperature in toluene- d_8 and benzene- d_6 , respectively.

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 ^1H nmr data suggest that the dihedral angle (α) subtended by the C1-M-C4 and C1-C2-C3-C4 planes would increase by the methyl substituents on the diene ligands. The dihedral angle calculated from the x-ray structure analysis data² of **1** is 86.44°. Then the dihedral angles of **2** and **3** are expected larger than that of **1**. The x-ray structure analysis⁴ 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, ^1H 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 $\text{Mo}(\text{CO})_6$.⁶ However, **3** reacts with CO to give $(\text{C}_6\text{H}_{10})_2(\text{CO})_3\text{Mo}$, **4**, *via* following reaction.



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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. spectrum⁷ 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 ^1H nmr⁹ analysis. ^1H nmr spectrum of **4** is shown in comparison with ^1H nmr spectrum of **3** in Figure 1. ^1H 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 $\text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} = \text{C} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{C}$ 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**: $\nu_{\text{CO}} = 1950(\text{s,br}), 1860(\text{s,br}) \text{ cm}^{-1}$, $\nu_{\text{C}=\text{C}} 1513(\text{m}) \text{ cm}^{-1}$.
8. **3**: Fragment, m/e (% base) = M, 344 (28); M- C_6H_{10} , 262 (73); M- C_6H_{10} -6H, 256 (100); M-2 C_6H_{10} -4H, 176 (6); Mo, 98 (5); C_6H_{10} , 82 (6); C_3H_7 , 67 (26); C_4H_7 , 55 (8); C_3H_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); $\text{C}_5\text{H}_7(\text{CO})$, 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).