

A New Type of Intramolecular Aromatic Substitution Product for Transition Metal Complexes. μ -(Pentahapto:monohapto-cyclopentadienyl)-[(pentahapto-cyclopentadienyl)-carbonylmolybdenum][tetracarbonylmanganese] and Related Derivatives¹

Sir:

To investigate further the donor-acceptor interaction between two transition metal atoms in their complexes² we have combined $\text{CH}_3\text{Mn}(\text{CO})_5$ (I), a potential acceptor,³ with potential donors such as $(\text{C}_5\text{H}_5)_2\text{MH}_2$ [$\text{M} = \text{Mo}$ (II) or W (III)] and $(\text{C}_5\text{H}_5)_2\text{ReH}$ (IV). Mixtures of the acceptor with the donors in suitable solvents at room temperature showed only the resonances of the free components in the nmr and no signals which would have been expected⁴ if any appreciable formation of adducts had occurred. However, after several days at room temperature in tetrahydrofuran or more rapidly under gentle heating in benzene we observed evolution of gas identified as a mixture of H_2 and CH_4 in the reaction of I with II or III and a mixture of CO and CH_4 in the reaction of I with IV. This was reminiscent of the loss of molecular hydrogen, methane, or other small molecules from molecular addition compounds in derivatives of the main group elements,⁵ and now seems also to be related to intramolecular aromatic substitution⁶ in transition metal complexes and to newly reported chemistry of cyclopentadienylmetal hydrides.⁷

All experimental manipulations were carried out under an atmosphere of nitrogen, using reagents which had been previously dried and degassed. To a solution of 3.5 mmol of each of the donors, II, III, or IV, in 20 ml of benzene was added 5.0 mmol of I, and the mixture was refluxed until gas evolution ceased (time required: with II, 3 hr; III, 30 min; and IV, 16 hr) while the color changed from yellow to red. Solvent was removed under vacuum and excess I removed by sublimation at 40° for 12 hr. The new derivatives were dissolved in ether-hexane (1:1) and after filtration, crystallized at -20°, giving deep red crystals in yields of 50-70% based on donor. The crystals of each compound are moderately air stable but air sensitive in solution. Mass spectra showed, among other features, parent multiplets in agreement with the formulas $\text{C}_{15}\text{O}_5\text{H}_9\text{MoMn}$ (V), $\text{C}_{15}\text{O}_5\text{H}_9\text{WMn}$ (VI),⁸ and $\text{C}_{14}\text{O}_4\text{H}_{10}\text{ReMn}$ (VII). Additional multiplets were observed indicating loss of five CO groups for V and VI and four CO groups for VII.

(1) Work supported by National Science Foundation Grant No. 23267X. Departmental instruments used in this work were supported as follows: Varian A-60 nmr spectrometer, E. I. du Pont de Nemours and Co. and National Science Foundation Grant No. G 20207; Beckman IR-4, E. I. du Pont de Nemours and Co.; AEI MS9 mass spectrometer, National Science Foundation Grant No. GP 3672; Picker automated diffractometer, National Science Foundation Grant No. GP 10170.

(2) B. Deubzer and H. D. Kaesz, *J. Amer. Chem. Soc.*, **90**, 3276 (1968).

(3) See C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, **7**, 1806 (1968), and references cited therein.

(4) H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **1**, 125 (1965).

(5) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

(6) See G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970), and references cited therein.

(7) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).

(8) *Anal.* (A. Bernhardt, Mulheim (Ruhr), Germany) Calcd for $\text{C}_{15}\text{H}_9\text{MnO}_5\text{W}$ (VI): C, 35.46; H, 1.79; Mn, 10.81; O, 15.74; W, 36.19. Found: C, 35.23; H, 2.25; Mn, 10.71; O, 15.61; W, 35.98.

Table I. Nmr Data^a

Compound	-AB triplets ^b		J_{AB} , Hz	Singlet ^c τ , ppm
	τ , ppm			
	A	B		
$\text{C}_{15}\text{O}_5\text{H}_9\text{MoMn}$ (V)	5.57	5.67	1.7	5.84
$\text{C}_{15}\text{O}_5\text{H}_9\text{WMn}$ (VI)	5.56	5.58	1.8	5.83
$\text{C}_{14}\text{O}_4\text{H}_{10}\text{ReMn}$ (VII) ^d	5.20	6.12	2.0	5.97

^a Benzene solution, tetramethylsilane internal standard, Varian A-60 spectrometer, 60 MHz. A marked solvent shift is observed in cyclohexane, tetrahydrofuran, or pyridine; triplet B is observed to shift from 0.4 to 0.6 ppm upfield relative to the singlet, while triplet A remains unshifted. ^b Relative intensity 2 (each). ^c Relative intensity 5. ^d This derivative also displays a high-field signal, τ 24.7, relative intensity 1.

Proton nmr data for the new complexes are summarized in Table I. In the carbonyl stretching region of the infrared, the following patterns were observed (cm^{-1}):⁹ V, 2033 (s), 1963 (s), 1950 (w), 1928 (s), 1919 (s); VI, 2038 (s), 1973 (s), 1954 (w), 1935 (s), 1924 (s); VII, 2043 (s), 1960 (s), 1946 (s), 1925 (s).

An X-ray study was undertaken to characterize the new derivatives; a sample of V was chosen. Crystals were found to belong to the triclinic system, space group $P\bar{1}$. Unit cell data are: $a = 8.056$ (1), $b = 9.322$ (3), and $c = 11.927$ (2) Å, $\alpha = 98.44$ (3), $\beta = 82.97$ (3), and $\gamma = 123.38^\circ$ (2), $\rho_{\text{obsd}}^{10} = 1.88 \text{ g cm}^{-3}$, ρ_{calcd} (for two formula units of V per unit cell) = 1.89 g cm^{-3} . Intensity data were collected with a Picker four-circle automated diffractometer to 2θ ($\text{Mo K}\alpha$) = 65° yielding 4900 independent observed reflections. The structure was solved and refined by standard procedures to a conventional R factor at present of 4.5%.

The structure is shown in Figure 1. All nine hydrogen atoms have been located. It is seen that Mn is bonded to four CO groups, the Mo, and C_{15} of one of the rings attached to the Mo atom. The geometry about the Mo atom is similar to that in II¹¹ with the exceptions that the mean planes of each of the rings are inclined at an angle of 35° to each other compared to that of 25° in II, and that an Mn and CO are bonded to the Mo rather than two hydrogens. The Mo-Mn bond length is 2.961 Å, significantly shorter than 3.083 Å in $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MoMn}(\text{CO})_5$ ¹² or 3.072 Å calculated as the mean of the Mo-Mo bond (3.222 Å) in $[(\text{C}_5\text{H}_5)(\text{CO})_3\text{Mo}]_2$ ¹³ and the Mn-Mn bond (2.923 Å) in $\text{Mn}_2(\text{CO})_{10}$.¹⁴

The C_{15} -Mn bond is an unusual one. If we define an approximate set of octahedral axes around Mn by the four CO groups, the C_{15} -Mn bond axis is displaced by an angle of approximately 20° from one of these axes and is bent by about 40° out of the plane defined by C_{11} , C_{14} , and C_{15} . The Mo-Mn bond is displaced from the octahedral axes by 20° . These features indicate that there may be some unusually "bent" bonds in this system which could explain the shortening of the Mo-Mn bond mentioned above and also of the C_{15} -Mn bond, which is observed to be 2.00 Å, compared to 2.19 Å

(9) Beckman IR-4 spectrophotometer equipped with LiF prism; cyclohexane solutions.

(10) The density was measured by the flotation method with a CCl_4 - $\text{C}_2\text{H}_2\text{Br}_4$ mixture.

(11) M. J. Bennett, M. Gerloch, J. A. McCleverty, and R. Mason, *Proc. Chem. Soc., London*, 357 (1962).

(12) B. P. Biryukov and Yu. T. Struchkov, *J. Struct. Chem. (USSR)*, **9**, 568 (1968).

(13) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

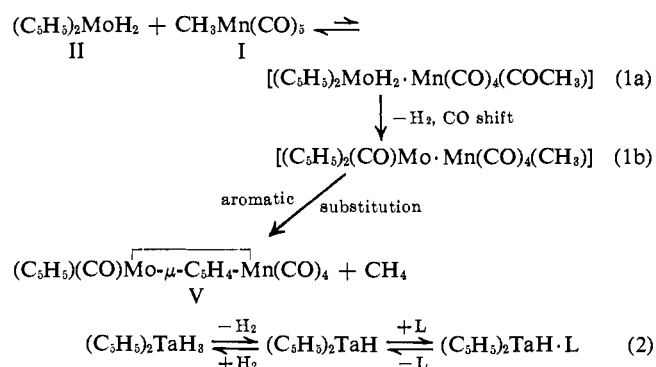
(14) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

expected for a C(sp²)-Mn bond (calculated from covalent radii).

The ring bonded to the two metal atoms is only slightly distorted from planarity; the mean plane formed by atoms C₁₁, C₁₂, C₁₃, and C₁₄ is bent at an angle of 4° to that formed by atoms C₁₁, C₁₄, and C₁₅. The ring appears nevertheless to have retained essentially aromatic character, as evidenced by the fact that the C-C bond lengths around the ring range between 1.40 and 1.44 Å, which compares well with the values of 1.40–1.43 Å in the other C₅H₅ ring and with the values expected for these rings.^{11–13}

We believe that the products VI and VII have structures analogous to that of V, with the variation that there will be a H atom instead of a CO group bonded to the Re atom in VII, as indicated by nmr and ir (which is required by the 18-electron rule).

The products incorporate in a novel way interesting features of the chemistry of transition metal complexes that are of current interest. In the first place, the structure of V suggests a new possibility for the dimer recently reported for titanocene,¹⁵ namely, one containing intramolecular bridged C₅H₄ rings. In the second place, it is likely that the first step in the reactions leading to complex V or VI is probably loss of H₂ from a coordinated dicyclopentadienylmetal dihydride as shown in eq 1. This has a parallel in a reaction recently reported for dicyclopentadienyltantalum trihydride (2) by Barefield, Parshall, and Tebbe.⁷ We have tested the



hydrides II and III under the conditions of our reaction, but without acceptor I, and find that they do not lose hydrogen. Thus, although not favored by equilibrium, adduct formation (1a) most likely initiates the reaction sequence. Following closely behind the loss of H₂, or perhaps concerted with it, would be a shift of CO into the empty coordination site on the Mo (or W). This would be analogous to the addition of ligand as a second step reported in reaction 2. Finally, reaction 1 is completed by a novel intramolecular aromatic substitution of Mn on the adjacent cyclopentadienyl ring accompanied by elimination of CH₄, analogous to the similar irreversible elimination reported by Keim (reaction 3).¹⁶ To demonstrate this reaction for a derivative of Mn, we have heated VIII (reaction 4) for 3 hr in refluxing toluene to give the intramolecular aromatic substitution product IX, as shown.¹⁷

(15) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

(16) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

(17) *Anal.* (H. King, UCLA) Calcd for C₂₂H₁₄MnO₄P: C, 61.70; H, 3.27. Found: C, 61.65; H, 3.46. Mass spectrum, parent ion at *m/e* 428, shows successive loss of four CO's; ir (hexane) (cm⁻¹) 2067 (m), 1987 (s), 1983 (s), 1952 (s); nmr (acetone-*d*₆, external TMS), complicated phenyl resonance centered at τ 2.62, no Mn-CH₃ resonance.

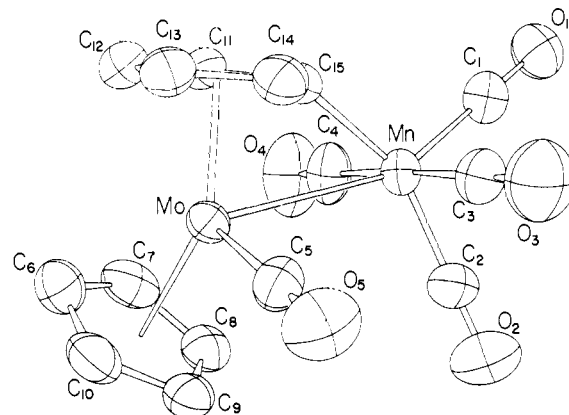
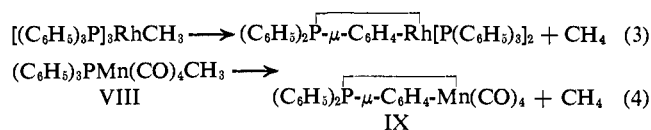
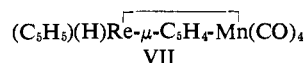


Figure 1. The structure of $(\text{C}_5\text{H}_5)(\text{CO})\overline{\text{Mo}}-\mu-\overline{\text{C}_5\text{H}_4}-\overline{\text{Mn}}(\text{CO})_4$; the molecule is rotated by 20° (clockwise) around the z axis and projected onto the y-z plane. The ellipsoids enclose 50% of the probability distribution and the hydrogens have been excluded for clarity.



In the formation of VII starting from IV, no H₂ can be lost after initial coordination, but a decarbonylation of the intermediate acyl derivative, followed by aromatic substitution with loss of CH₄, can account for the product. The decarbonylation will compete with the reverse of adduct formation, and this could account for the greater reaction time required for the formation of



The unusual ring system in these derivatives is susceptible to chemical attack. In the treatment of V with acid, the Mn-C₁₅ bond is cleaved and the C₅H₅ ring is restored (nmr) in an ionic derivative presently under study. We are attempting to cleave the Mn-C₁₅ bond with H₂ or simply to observe if with D₂ there is appreciable deuteration of the ring (which would proceed through a deuterated intermediate (C₅H₅)(C₅H₄D)(CO)Mo·Mn(CO)₄D). Also, we are attempting to obtain ring expansion by the reaction of CO and other carbenoid species with the new derivatives.

Acknowledgment. We wish to thank the members of the crystallographic group at UCLA, in particular Dr. J. Bell, M. Murphy, and E. Maverick, for helpful discussions in the structure determination reported here, and the UCLA Computing Center for an intramural grant to defray in part the computing expenses in this work.

(18) Publication No. 2752.

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Received November 21, 1970

Anodic Substitution. An Alternative to the ECE Mechanism

Sir:

The anodic reaction between pyridine and anthracene originally described by Lund¹ has received a great deal