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Synthesis of *Pentahapto*cyclopentadienyl Complexes *via* Metal-Assisted Cycloaddition Reaction

J. P. WILLIAMS and A. WOJCICKI

The McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, U.S.A.

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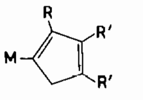
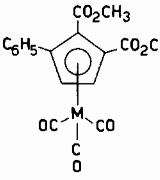
The metal-assisted (3+2) cycloaddition between metal-propargyl complexes ($MCH_2C{\equiv}CR$) and electrophilic molecules containing a double bond is a well known reaction.[1-3] The use of an electrophilic acetylene ($R'C{\equiv}CR'$) would not only expand the scope of this cycloaddition but would also afford a novel complex, I, with the transition metal σ-bonded to an sp^2 carbon of a cyclopentadienyl ring.*



I

We have found that the reaction of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ with $CH_3O_2CC{\equiv}CCO_2CH_3$ in 1,2-dichloroethane under nitrogen at 65 - 68 °C for 12 hr produces a red–orange solution. After removal of the solvent, extraction of the residue with pentane, and chromatography of the concentrated extract on an ethyl acetate-washed acid alumina column, a yellow solid, mp 101 - 102.5 °C, was isolated in *ca.* 15% yield. Its molecular formula was ascertained to be $Mn(CO)_3C_9H_7 \cdot C_6H_6O_4$.** This material has been characterized as II (M=Mn) from the following spectroscopic data.



II

The infrared spectrum in the ν_{CO} region shows bands at 2041, 1982, 1975, and 1723 cm^{-1} (pentane soln.), thus reflecting the presence of terminal Mn–CO groups and uncoordinated ester carbonyls.[5,6] The ^1H NMR spectrum in benzene consists of four singlets at 5.64 (CH), 5.89 (CH), 6.51 (CH_3), and 6.64 (CH_3) τ, besides a masked signal of the C_6H_5. The ^{55}Mn NMR spectrum exhibits a resonance with a chemical shift of 2588 ppm upfield from aqueous permanganate with $\nu_{1/2}$ = 5742 Hz, in good agreement with that of η^5-$C_5H_5Mn(CO)_3$ itself.[7]

However the ^{13}C NMR spectral data listed in the Table provide perhaps the most definite evidence for the assigned structure. The observation of all three CO carbon signals is in agreement with the non-equivalence of these ligands owing to the absence of a plane of symmetry. The ester CO_2 carbons, the ester methyl carbons, the phenyl carbons, and the cyclopentadienyl ring carbons all absorb in the expected regions.[8,9]

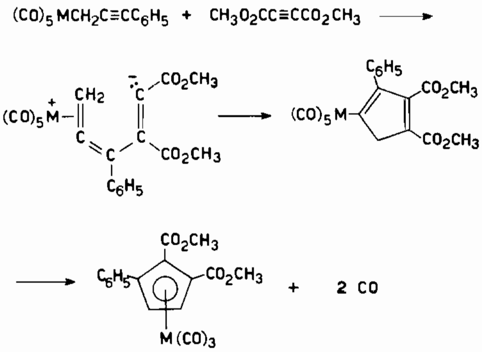
TABLE. ^{13}C NMR Spectrum of II (M = Mn).[a]

δ[b]	Assignment
225.89, 221.92, 220.24	$Mn(CO)_3$
167.58, 164.92	ester CO_2
131.11, 129.55, 127.8	C_6H_5
99.98, 98.22, 92.63, 89.38, 69.75	C_5 ring
53.69, 52.13	CH_3

[a] Recorded in $CDCl_3$ solution at −50 °C. [b] In ppm relative to tetramethylsilane.

The reaction of $Re(CO)_5CH_2C{\equiv}CC_6H_5$ with $CH_3O_2CC{\equiv}CCO_2CH_3$ in acetonitrile at 70 °C for 18 days gave after purification a small amount of white solid which appears to be II (M = Re) from its infrared ν_{CO} spectrum (bands at 2023, 1950, and 1910 cm^{-1}, as expected for a *pentahapto*cyclopentadienylrhenium tricarbonyl complex,[10] and at 1734 cm^{-1}).

It is likely that the reaction described herein involves the intermediacy of I (M = $Mn(CO)_5$ or $Re(CO)_5$; R = C_6H_5; R′ = CO_2CH_3) which rearranges readily to II (M = Mn or Re) with loss of two carbonyl groups. The proposed pathway is depicted below.



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*However binuclear compounds are known which contain one metal η^1-bonded and one η^5-bonded to a C_5H_4 ring, see ref. 4.

***Anal.* Calcd. for $C_{18}H_{13}MnO_7$: C, 54.6; H, 3.28. Found: C, 55.12; H, 3.46. Mass spectrum: calcd P^+, m/e 396.0042; observed P^+, m/e 396.0045. Metastable peaks were noted for P^+ −2CO and $(P{-}2CO)^+$–CO.

Acknowledgment

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