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π-CYCLOPENTADIENYL-π-CYCLOHEPTATRIENYL DERIVATIVES OF CHROMIUM AND MOLYBDENUM

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The recent report by Fischer and Breitschaft[1] of a two-step synthesis of $C_5H_5CrC_7H_7$ from the difficultly accessible $C_5H_5CrC_6H_6$ prompts us to report a much more convenient one-step synthesis of $C_5H_5CrC_7H_7$ from the readily available anhydrous chromium (III) chloride.[2]

A mixture of anhydrous chromium (III) chloride (0.1 mole), cyclopentadiene (0.12 mole), and cycloheptatriene (0.25 mole) was treated with a solution of isopropylmagnesium bromide (0.5 mole) in diethyl ether at -78°. The reaction mixture was allowed to warm slowly to room temperature and stirred for several hours at room temperature. It was then decomposed by the gradual addition of methanol at -78°. From the resulting very air-sensitive green-brown solution, dark green crystals of $C_5H_5CrC_7H_7$, m.p. ~225° (lit.[1], m.p. ~230°), could be isolated by evaporation at 20 mm and sublimation of the residue at 100-150°/0.1 mm. The crude product was purified further by washing with pentane and resublimation at 80-100°/0.1 mm. (Anal: Calc. for $C_{12}H_{12}Cr$: C, 69.2; H, 5.8; Cr, 25.0; mol. wt., 208. Found: C, 69.4; H, 5.9; Cr, 24.8; mol. wt., 218 [Mechrolab vapor pressure osmometer in benzene solution].)

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[1] E. O. Fischer and S. Breitschaft, Angew. Chem. **75**, 94 (1963).

[2] Available inexpensively from Diamond Alkali Company, Philadelphia, Pennsylvania.

The infrared spectrum of the $C_5H_5CrC_7H_7$ obtained by our method is in agreement with that reported by Fischer and Breitschaft.[1] We have determined the proton n.m.r. spectra of the deep blue-violet solutions of $C_5H_5CrC_7H_7$ in benzene and carbon disulfide. The cycloheptatrienyl resonance was observed at $\tau = 4.45$ (CS_2) or $\tau = 4.59$ (C_6H_6) and the cyclopentadienyl resonance at $\tau = 6.28$ (CS_2) or $\tau = 6.38$ (C_6H_6). The assignments of these resonances were confirmed by integration. Fischer and Breitschaft[1] report observing the cycloheptatrienyl resonance at $\tau = 5.08$ and the cyclopentadienyl resonance at $\tau = 6.90$. The reasons for the discrepancies between our data and those of Fischer and Breitschaft are not clear.

This synthesis of $C_5H_5CrC_7H_7$ probably proceeds via an unstable alkylchromium derivative analogous to the original synthesis of chromium hexacarbonyl[3] from anhydrous chromium (III) chloride, an alkylmagnesium halide derivative, and carbon monoxide and to the recently described synthesis of dibenzenechromium[4] from anhydrous chromium (III) chloride, an alkylmagnesium halide derivative, and 1,3-cyclohexadiene. Variations of this general method of synthesis for the preparation of other organometallic compounds of transition metals are currently being explored in this laboratory.

As a possible approach to the molybdenum analogue $C_5H_5MoC_7H_7$ the reaction between sodium cyclopentadienide (0.1 mole) and $C_7H_7Mo(CO)_2I$[5] (0.03 mole) in tetrahydrofuran solution at room temperature was investigated. From the resulting orange reaction mixture an orange crystalline solid of composition $C_5H_5Mo(CO)_2C_7H_7$ was obtained in yields up to 77% by evaporation of solvent at ~30 mm, extraction of the residue with

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[3] A. Job and A. Cassal, Comptes Rendus, 183, 392 (1926); Bull. Soc. Chim. [iv] 41, 814, 1041 (1927).

[4] E. O. Fischer and J. Müller, Z. Naturforschg. 17b, 776 (1962).

[5] D. J. Bertelli, Ph.D. Dissertation, University of Washington, 1961.

dichloromethane, and removal of the dichloromethane from the orange filtered extract at ~30 mm. Further purification was carried out by chromatography and/or crystallization from pentane followed by sublimation at 100°/0.1 mm to give orange crystals, m.p. 111-112°. Cyclopentadienylcycloheptatrienyl molybdenum dicarbonyl appears to be more stable to air oxidation both in the solid state and in solution but less stable to thermal decomposition during sublimation than $C_5H_5CrC_7H_7$.

The ultraviolet spectrum of a cyclohexane solution of $C_5H_5Mo(CO)_2C_7H_7$ exhibited a maximum at 306 mμ (ϵ = 7000). The visible spectrum of the cyclohexane solution exhibited a very shallow maximum at ~758 mμ (ϵ = 315). (Anal; Calc. for $C_{14}H_{12}MoO_2$: C, 54.5; H, 3.9; Mo, 31.2; O, 10.4; mol. wt., 308. Found: C, 54.8; H, 3.9; Mo, 31.3; O, 10.5; mol. wt., 318 [Mechrolab vapor pressure osmometer in benzene solution].

The infrared spectrum of this new molybdenum complex besides exhibiting bands due to the hydrocarbon residues exhibits two strong metal carbonyl bands at 1934 and 1858 cm^{-1} (NaCl optics). The proton n.m.r. spectrum in carbon disulfide solution besides demonstrating the complex to be diamagnetic exhibits two sharp resonances at $\tau = 4.94$ and $\tau = 5.21$ of relative intensities 5:7. However, a structure with all five carbon atoms of the cyclopentadienyl ring bonded to the molybdenum atom as in $[C_5H_5Mo(CO)_3]_2$[6] and with all seven carbon atoms of the cycloheptatrienyl ring bonded to the molybdenum atom as in $C_7H_7Mo(CO)_2I$[5] or $[C_7H_7Mo(CO)_3]^+$[7] would have a molybdenum atom with four electrons in excess of the inert gas configuration. For this reason two more reasonable structures for $C_5H_5Mo(CO)_2C_7H_7$ appear to be I and II. In structure I the cyclopentadienyl ring is bonded to the molybdenum atom with all five carbon atoms as in $[C_5H_5Mo(CO)_3]_2$ but the cycloheptatrienyl ring is bonded to the molybdenum atom with only three carbon atoms.

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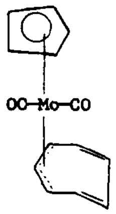
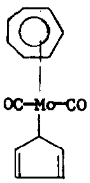
[6] T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem. **3**, 104 (1956).

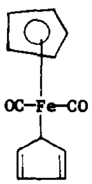
[7] H. J. Dauben, Jr. and L. R. Honnen, J. Am. Chem. Soc. **80**, 5570 (1958)



I



II



III

The cycloheptatrienyl-molybdenum bond in I would then resemble the cyclopentenyl-chromium bond in $C_5H_5Cr(CO)_2C_5H_7$[8] and the electronic configurations of the molybdenum atom in $C_5H_5Mo(CO)_2C_7H_7$ and the chromium atom in $C_5H_5Cr(CO)_2C_5H_7$ would be similar. In structure II the cyclopentadienyl ring is σ-bonded to the molybdenum atom with only one carbon atom as the σ-bonded cyclopentadienyl ring in $C_5H_5Fe(CO)_2C_5H_5$ (III)[6] but the cycloheptatrienyl ring is bonded to the molybdenum atom with all seven carbon atoms as in $C_7H_7Mo(CO)_2I$.[5] Structure II for $C_5H_5Mo(CO)_2C_7H_7$ seems to be relatively improbable, however, since the position of its cyclopentadienyl resonance in the n.m.r. at $\tau = 4.94$ is greatly different from the position of the resonance of the σ-cyclopentadienyl protons of the closely analogous $C_5H_5Fe(CO)_2C_5H_5$ (III) at $\tau = \sim 3.5$.[6] Moreover, attempts to make the methyl derivative $C_7H_7Mo(CO)_2CH_3$ by methods such as the reaction between $C_7H_7Mo(CO)_2I$ and CH_3MgI analogous to successful syntheses for $C_5H_5Fe(CO)_2CH_3$[6] have been unsuccessful.

If the structure of $C_5H_5Mo(CO)_2C_7H_7$ is indeed I its n.m.r. spectrum exhibiting only one sharp resonance due to all seven protons of the cycloheptatrienyl ring is unusual. On the basis of the n.m.r. spectra of most other known hydrocarbon complexes of transition metals, the three

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[8] E. O. Fischer and K. Ulm, Ber. 94, 2413 (1961).

[9] T. A. Manuel and F. G. A. Stone, Proc. Chem. Soc. 90 (1959), J. Am. Chem. Soc., 82, 366 (1960); M. D. Rausch and G. N. Schrauzer, Chem. and Ind., 957 (1959); A. Nakamura and N. Hagihara, Bull. Chem. Soc. Japan 32, 880 (1959).

[10] B. Dickens and W. N. Lipscomb, J. Am. Chem. Soc. 83, 4862 (1961).

protons of the three carbon atoms of the cycloheptatrienyl ring which are bonded to the molybdenum atom and the four carbon atoms of the two double bonds of the cycloheptatrienyl ring which are not bonded to the molybdenum atom would be expected to exhibit different chemical shifts, and, in addition, further complexities in the portion of the proton n.m.r. spectrum due to the cycloheptatrienyl ring would be expected. The presence of the single proton resonance in the proton n.m.r. spectrum due to the seven protons of the cycloheptatrienyl ring in $C_5H_5Mo(CO)_2C_7H_7$ is however entirely analogous to the presence of the single proton resonance in the proton n.m.r. spectrum due to the eight protons of the cyclooctatetraene ring in $C_8H_8Fe(CO)_3$.[9] X-ray structural studies[10] on $C_8H_8Fe(CO)_3$ have shown that only four of the eight carbon atoms of the cyclooctatetraene ring are bonded to the iron atom and that the ring is not planar. The n.m.r. spectra of $C_8H_8Fe(CO)_3$ and of $C_5H_5Mo(CO)_2C_7H_7$ appear to represent the first two examples of an unusual effect in the n.m.r. spectra of hydrocarbon complexes of transition metals and may be indicative of some unusual feature in the bonding in these complexes. It is to be hoped that the syntheses of additional related compounds and investigation of their n.m.r. spectra will clarify this phenomenon.