Trimethylenemethane Complexes of Iron, Molybdenum, and Chromium

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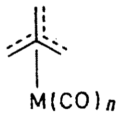
Summary Trimethylenemethane complexes of iron, molybdenum, and chromium are synthesized by methods which are also applicable to the synthesis of other organometallic complexes.

FOLLOWING the isolation of trimethylenemethaneiron tricarbonyl by Emerson and his co-workers,[1] several derivatives of this organo-iron complex have been reported.[2] The preparation of each of these involves reaction of $Fe_2(CO)_9$ with an organic substrate and, due to the unique reactivity of this metal carbonyl, the methods appear to be unsuitable for the preparation of complexes other than those of iron, none having been reported so far. We now report two methods for the synthesis of metal complexes of trimethylenemethane.

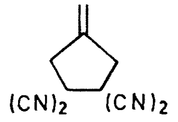
We had earlier shown that several cyclobutadiene–transition-metal complexes of metals other than iron could be prepared by treating 3,4-dichlorocyclobutene with various metal carbonyl anions.[3] We find that analogous treatment of 3-chloro-2-(chloromethyl)propene (I) produces trimethylenemethane–transition-metal complexes. For example, sodium tetracarbonylferrate reacted with (I) in tetrahydrofuran to give trimethylenemethaneiron tricarbonyl (IIa, 32%).

Since various reactive dienes can be liberated and then trapped by oxidizing their iron carbonyl complexes with electron-transfer oxidizing agents,[4] we investigated the oxidation of trimethylenemethaneiron tricarbonyl as a potential route to trimethylenemethane. Complex (IIa) was readily oxidized with Ce^{4+} in the presence of tetracyanoethylene to give white crystals of 3,3,4,4-tetracyanomethylenecyclopentane (III; m.p. 109°, 4%). The possibility of free trimethylenemethane being involved in this reaction is under investigation.

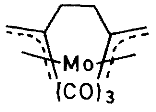
Sodium pentacarbonylmolybdenate reacted with (I) to give trimethylenemethanemolydenum tetracarbonyl (IIb) as yellow crystals (m.p. 50°, 1%) as well as the complex (IV) as orange needles [m.p. 62° (decomp.), 2%]. The reaction of $Ru_3(CO)_{12}$ with sodium amalgam in tetrahydrofuran and subsequent treatment with (I) gave a light-green crystalline compound [m.p. 90° (decomp.), 4%] to which we have assigned formula (V). We were unable to synthesize trimethylenemethane-chromium or -tungsten complexes by this metal anion reaction. However, we were able to synthesize the chromium complex by the following route.



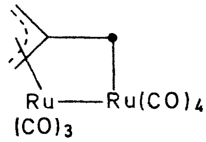
(II)	M	n
a	Fe	3
b	Mo	4
c	Cr	4



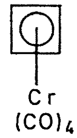
(III)



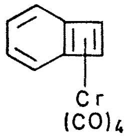
(IV)



(V)



(VI)



(VII)

Irradiation of an ether solution of $Cr(CO)_6$ in the presence of (I) gave trimethylenemethanechromium tetracarbonyl (IIc) as yellow needles (m.p. 83°, <1%). Similar irradiation of $Cr(CO)_6$ in the presence of 3,4-dichlorocyclobutene produced cyclobutadienechromium tetracarbonyl (VI) as yellow crystals (m.p. 46°, <1%). When the $Cr(CO)_6$ solution was first irradiated and then heated with 3,4-dibromobenzocyclobutene, orange crystals of benzocyclobutadienechromium tetracarbonyl (VII) were isolated

(10%). The *X*-ray structural analysis of benzocyclobutadiene–$Cr(CO)_3PPh_3$ [prepared by irradiation of (VII) in the presence of PPh_3] indicated that chromium was bonded to the cyclobutadiene portion of the organic ligand and that the compound is not an arene–chromium complex.[5] The mechanism of these photolysis reactions is not known, but presumably a chromium carbonyletherate complex is involved as an intermediate.[6]

TABLE

Compound	N.m.r. (δ)	I.r. (ν_{CO}, cm^{-1})
(IIa)	2·0 (s)	1998, 2064
(IIb)	1·60 (s)	1958, 2062
(IIc)	1·58 (s)	1955, 2020
(III)	3.78 (t, 2H), 5·48 (m, 1H), (J 2Hz)	
(IV)	2·15 (s, 1H), 2·32 (s, 1H), 3·35 (s, 1H)	1902, 1950, 2008
(V)	1·35 (m, 1H), 1·58 (m, 1H), 1·88 (m, 1H)	1990, 2030, 2040 2050, 2070, 2120
(VI)	3·88 (s)	1970, 2080
(VII)	4·35 (s, 1H), 6·92 (m, 2H)	1945, 1980, 2080

The pertinent physical properties of the new compounds are given in the Table.† In addition, the mass spectrum of each compound, with the exception of (VII), displayed a strong parent molecular ion and prominent fragments corresponding to successive loss of CO groups.

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† All new compounds, with the exception of (IIb) and (VI), gave satisfactory elemental analyses. Compounds (IIb) and (VI) gave consistent mass spectra.

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