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ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS XX*. SOME REACTIONS OF ACETONITRILE DERIVATIVES OF MOLYBDENUM AND CHROMIUM CARBONYLS WITH OLEFINIC AND ACETYLENIC COMPOUNDS

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INTRODUCTION

Recently we described[2-4] the use of tris(acetonitrile)tricarbonyltungsten, $(CH_3CN)_3W(CO)_3$, as an intermediate in the synthesis of olefinic and acetylenic complexes of tungsten including the following types (triene)$W(CO)_3$ [triene = cycloheptatriene, 1,3,5-cyclooctatriene, cyclooctatetraene, and 6-(dimethylamino)fulvene], (diene)$W(CO)_4$ (diene = 1,5-cyclooctadiene, bicyclo[2.2.1]heptadiene, or dicyclopentadiene), $(1,3\text{-}C_6H_8)_2W(CO)_2$, $(CH_3COCH{=}CH_2)_3W$, and $[(CF_3)_2C_2]_3WNCCH_3$.

Most of the molybdenum analogues to these complexes can be prepared efficiently from the readily available hexacarbonylmolybdenum and the appropriate ligand. These include the cycloheptatriene complex[5,6] $C_7H_8Mo(CO)_3$, the 1,3,5-cyclooctatriene complex[7] $C_8H_{10}Mo(CO)_3$, the 6-dimethylaminofulvene complex[8] $C_5H_4CHN(CH_3)_2Mo(CO)_3$, the 1,5-cyclooctadiene complex[9-11] $C_8H_{12}Mo(CO)_4$, and the bicyclo[2.2.1]heptadiene complex[12,13] $C_7H_8Mo(CO)_4$. However, the cyclooctatetraene complex $C_8H_8Mo(CO)_3$ requires the diglyme[14] complex $(CH_3OCH_2CH_2OCH_2CH_2OCH_3)Mo(CO)_3$ for its preparation[15]. Photochemical techniques[16] are required for the preparation of the 1,3-cyclohexadiene complex $(C_6H_8)_2Mo(CO)_2$; reaction between hexacarbonylmolybdenum and 1,3-cyclohexadiene gives a low yield of a material of the same composition[17] but with the isomeric formulation[16] $(C_6H_9)(C_6H_7)Mo(CO)_2$. The dicyclopentadiene complex $C_{10}H_{12}Mo(CO)_4$, the methyl vinyl ketone complex $(CH_3COCH{=}CH_2)_3Mo$, and the hexafluoro-2-butyne complex $[(CF_3)_2C_2]_3MoNCCH_3$ have never been reported.

This paper describes the use of the acetonitrile complex $(CH_3CN)_3Mo(CO)_3$ as an intermediate for the synthesis of the complexes cited above which cannot be obtained readily from hexacarbonylmolybdenum itself. Some related reactions of $(CH_3CN)_3Cr(CO)_3$ are also described.

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium,

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* For Part XIX of this series see ref. 1.

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Bonn, Germany. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin–Elmer model 21 spectrometer. In addition, the metal carbonyl regions of selected compounds were investigated in cyclohexane solutions and recorded on a Beckman IR-9 spectrometer with a scale expanded by a factor of 2.5 or 4. Ultraviolet spectra were taken in dichloromethane or cyclohexane solution and recorded on a Cary Model 14 spectrometer. Mass spectra were taken at 70 e.v. electron energies using an Associated Electrical Industries MS-9 mass spectrometer. Proton and ^{19}F NMR spectra were taken on an A-60 spectrometer a 60 Mc and on an HR-60 spectrometer at 56.4 Mc, respectively. Melting points were taken in capillaries and are uncorrected.

Reagents

The metal hexacarbonyls were commercial samples obtained from Climax Molybdenum Company, New York City, and Pressure Chemical Company, Pittsburgh, Pennsylvania. In order to convert them to the acetonitrile derivatives, small portions (~10 mmoles) of the hexacarbonyls $M(CO)_6$ (M = Cr and Mo) were boiled overnight (~16 h) with excess (50 to 75 ml) of acetonitrile. After cooling and removal of excess acetonitrile at ~25°/30 mm, air-sensitive crystals of the tris(acetonitrile)-metal tricarbonyls remained[18]. The pale yellow molybdenum compound $(CH_3CN)_3Mo(CO)_3$ turned black in air after a few minutes; the golden yellow chromium compound $(CH_3CN)_3Cr(CO)_3$ turned green even more rapidly, sometimes with ignition. Because of their air-sensitivity, the intermediate $(CH_3CN)_3M(CO)_3$ (M = Mo or Cr) compounds were not weighed; instead, the entire batch from a weighed portion of metal hexacarbonyl was used for further reaction with the olefin or acetylene. The formation of $(CH_3CN)_3Mo(CO)_3$ from $Mo(CO)_6$ and acetonitrile by this procedure appeared quantitative since neither unreacted $Mo(CO)_6$ nor significant amounts of insoluble decomposition products appeared to be present. Therefore, for the purposes of yield calculations, etc., the molar amount of $(CH_3CN)_3Mo(CO)_3$ used for a reaction was assumed to be the same as that of the hexacarbonylmolybdenum used for its preparation.

Hydrocarbons and other organic ligands required for this work were all obtained from commercial sources.

A nitrogen atmosphere was always provided for the following three operations: (*a*) carrying out reactions, (*b*) handling all filtered solutions of metal complexes, and (*c*) admission to evacuated vessels. A nitrogen atmosphere was mandatory to prevent rapid oxidation of the solid complexes $(CH_3CN)_3M(CO)_3$ (M = Cr and Mo), which appear to be far more air-sensitive than $(CH_3CN)_3W(CO)_3$.

Preparation of $(CH_3COCH{=}CH_2)_3Mo$

The $(CH_3CN)_3Mo(CO)_3$ obtained from 2.64 g (10 mmoles) of hexacarbonylmolybdenum was refluxed 18 h at the boiling point with 5.0 ml (4.31 g, 62 mmoles) of methyl vinyl ketone and 250 ml of hexane. The reaction mixture was then filtered hot and the brown residue* washed with two 30 ml portions of boiling hexane. Solvent was removed from the combined filtrates at 25°/30 mm leaving pale yellow

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* This brown residue appears to be an impure form of the previously reported[19] $[(CH_3COCH{=}CH_2)_2Mo(CO)_2]_n$. It was not investigated in detail.

crystals. These were extracted with ~80 ml of boiling hexane in four portions. The filtered (hot) hexane solutions were cooled overnight in a −78° bath. The resulting crystals were filtered and purified finally by sublimation at 70–80°/1 mm for 16 h to give 0.059 g (1.9% yield) of yellow air-stable crystalline $(CH_3COCH{=}CH_2)_3Mo$, m.p. 141–142°. (Found: C, 47.1; H, 5.8; Mo, 30.9; O, 15.8. $C_{12}H_{18}MoO_3$ calcd.: C, 47.1; H, 5.9; Mo, 31.4; O, 15.7%.)

Infrared spectrum. ν(CH) bands at 3000 (vw), 2900 (w), and 2870 (vw, sh) cm^{-1}; other bands at 1508 (w, sh), 1485 (s), 1416 (w), 1370 (m), 1363 (m), 1340 (m), 1328 (w), 1210 (w), 1147 (vw), 1048 (m), 1024 (w), 985 (vw), 900 (vw), 850 (m), 782 (vw), and 772 (vw) cm^{-1}.

Ultraviolet spectrum. Maximum at 309 mμ (ε 7520) in cyclohexane solution (nearly colorless).

Proton NMR spectrum. Resonances at τ 6.06 (triplet, $J = 7$ cps), τ 7.89 (sharp singlet), τ 8.07 (doublet, $J = 7$ cps) and τ 8.14 (doublet, $J = 7$ cps) of approximate relative intensities 1 : 3 : 1 : 1 due to the complexed vinyl proton adjacent to the ketonic carbonyl group, the three methyl protons, and the other two slightly non-equivalent complexed vinyl protons of each of the three equivalent methyl vinyl ketone ligands.

Mass spectrum. The following ions with $m/e > 180$ were observed: $(CH_3COCH{=}CH_2)_3Mo^+$ (m/e 306, rel. int. 18), $(CH_3COCH{=}CH_2)_2Mo^+$ (m/e 236, rel. int. 48), and $CH_3COCH{=}CH_2MoO^+$ (m/e 182, rel. int. 17).

Preparation of $[(CF_3)_2C_2]_3MoNCCH_3$

A 150 ml stainless steel vessel* was charged with the $(CH_3CN)_3Mo(CO)_3$ obtained from 2.64 g (10 mmoles) of hexacarbonylmolybdenum. After cooling and evacuation, 6.0 liquid ml (9.4 g, 58 mmoles) of hexafluoro-2-butyne was distilled in. The closed vessel was heated ~18 h at 100°. After the reaction period was over, the vessel was cooled to room temperature and excess pressure vented. The contents were rinsed out with six 25 ml portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at 25°/30 mm. The brown solid residue was sublimed at 70°/0.2 mm for 18 h to give a white crystalline sublimate which was purified further by a second sublimation at 70°/0.2 mm for 5 h to give 2.49 g (40% yield) of white air-stable crystalline $[(CF_3)_2C_2]_3MoNCCH_3$, m.p. 101–103°. (Found: C, 27.1; H, 0.7; F, 54.7; Mo, 15.6; N, 2.3. $C_{14}H_3F_{18}MoN$ calcd.: C, 27.0; H, 0.5; F, 54.9; Mo. 15.4; N, 2.2%.)

Infrared spectrum. ν(CH) band at 2925 (vw) cm^{-1}; ν(CN) band of complexed acetonitrile at 2290 (vw) cm^{-1}; ν(C=C) band of complexed hexafluoro-2-butyne at 1740 (m) cm^{-1}; ν(CF) bands at 1282 (s), 1267 (s), 1237 (sh), 1210 (vs), 1179 (s), 1150 (vs), and 1130 (vs) cm^{-1}; other bands at 1029 (vw), 970 (m), 947 (w), 817 (vw), 764 (w), and 694 (w) cm^{-1}.

Ultraviolet spectrum. Maximum at 267 mμ (ε 1900) in dichloromethane solution (colorless).

^1H NMR spectrum. Sharp singlet resonance at τ 7.16 due to the methyl protons of the CH_3CN ligand.

^{19}F NMR spectrum. Resonances at 56.9 and 59.1 ppm upfield from internal CCl_3F of equal relative intensities (dichloromethane solution).

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* High-pressure stainless-steel cylinder (120 atm. service) purchased from Hoke Inc., 1 Tenakill Park, Cresskill, New Jersey (U.S.A.).

Reactions of $(CH_3CN)_3Mo(CO)_3$ with olefins

The $(CH_3CN)_3Mo(CO)_3$ obtained from 2.64 g (10 mmoles) of hexacarbonylmolybdenum was refluxed 14 to 16 h at the boiling point with 2 to 5 ml of the olefin and 75 ml of hexane. The reaction mixture was then filtered hot, washing the residue with a few ml of boiling hexane. Cooling the hexane filtrates overnight at −78° precipitated crystals of the olefin complex which were purified by vacuum sublimation.

A. 1,3-Cyclohexadiene. From 10 mmoles of $(CH_3CN)_3Mo(CO)_3$ and 2.0 ml (1.68 g, 21 mmoles) of 1,3-cyclohexadiene in 75 ml of hexane were obtained 1.06 g (34% yield) of pale yellow $(C_6H_8)_2Mo(CO)_2$ by the general procedure discussed above. Purification of the analytical sample, m.p. 143–147°, was accomplished by sublimation at 90°/0.1 mm. (Found: C, 54.3; H, 5.1; O, 10.2. $C_{14}H_{16}MoO_2$ calcd.: C, 53.8; H, 5.1; O, 10.3%.)

The infrared and proton NMR spectra of $(C_6H_8)_2Mo(CO)_2$ were identical before and after sublimation and were in accord with those published for $(C_6H_8)_2$-$Mo(CO)_2$ rather than $(C_6H_7)(C_6H_9)Mo(CO)_2$. The ultraviolet spectrum exhibited a maximum at 302 mμ (ε 7100) in cyclohexane solution.

B. Cyclooctatetraene. From 10 mmoles of $(CH_3CN)_3Mo(CO)_3$ and 5.0 ml (4.6 g, 44 mmoles) of cyclooctatetraene in 75 ml of hexane were obtained 1.05 g (37% yield) of red $C_8H_8Mo(CO)_3$ by the general procedure discussed above. Purification of this material by vacuum sublimation at 80°/0.1 mm resulted in extensive decomposition, but 20 to 25% of the $C_8H_8Mo(CO)_3$ was recovered as a dark red sublimate.

The NMR spectrum of $C_8H_8Mo(CO)_3$ was similar to that reported by Winstein *et al.*[15], and serves to identify the product. The molybdenum complex $C_8H_8Mo(CO)_3$ was found to be much less stable than its tungsten analogue $C_8H_8W(CO)_3$. Indeed this molybdenum compound decomposed after a few days at −15°. It thus could not be shipped to an analytical laboratory without decomposition.

C. 1,5-Cyclooctadiene. From 10 mmoles of $(CH_3CN)_3Mo(CO)_3$ and 5.0 ml (5.68 g, 52.6 mmoles) of 1,5-cyclooctadiene in 75 ml of hexane were obtained 2.26 g (95% yield based on CO groups) of dirty yellow $C_8H_{12}Mo(CO)_4$ by the general procedure discussed above. The analytical sample, m.p. 115–116° (lit.[10] 119–120°), was obtained by sublimation at ~100°/0.1 mm. (Found: C, 45.7; H, 3.8; O, 20.1. $C_{12}H_{12}MoO_4$ calcd.: C, 45.6; H, 3.8; O, 20.3%.)

The infrared and proton NMR spectra of $C_8H_{12}Mo(CO)_4$ were identical with the published spectra[13].

Attempts to make a dicyclopentadiene complex $C_{10}H_{12}Mo(CO)_4$ by an analogous procedure failed.

Reactions of $(CH_3CN)_3Cr(CO)_3$ with olefins

A. 1,3-Cyclohexadiene. The $(CH_3CN)_3Cr(CO)_3$ obtained from 2.2 g (10 mmoles) of hexacarbonylchromium was refluxed 16 h at the boiling point with 2.0 ml (1.68 g, 21 mmoles) of 1,3-cyclohexadiene and 75 ml of hexane. The resulting reaction mixture was filtered hot and the residue washed with ~30 ml of boiling hexane in two portions. The filtrate was cooled ~24 h in a −78° bath. The resulting mixture of white and yellow crystals was filtered and dried. This solid was sublimed 20 h at 65°/0.1 mm. Some $Cr(CO)_6$ sublimed beyond the water cooled probe into the vacuum system. A yellow sublimate of $C_6H_6Cr(CO)_3$ (0.13 g, 6.1% yield) collected on the probe. This product was identified by its infrared spectrum, melting point, and analyses for carbon, hydrogen, and oxygen.

B. Cyclooctatetraene. The $(CH_3CN)_3Cr(CO)_3$ obtained from 2.2 g (10 mmoles) of hexacarbonylchromium was refluxed 20 h at the boiling point with 2.0 ml (1.84 g, 17.7 mmoles) of cyclooctatetraene and 75 ml of hexane. The resulting deep red solution was filtered hot under nitrogen, washing the residue with a few milliliters of boiling hexane. The filtrate was cooled overnight in a −78° bath. The red crystals which separated were filtered and dried. They were sublimed at ~80–100°/0.3 mm for 5 h. Some $Cr(CO)_6$ sublimed beyond the probe into the vacuum system. A total of 0.212 g (8.8% yield) of deep red crystalline $C_8H_8Cr(CO)_3$ was collected on the probe.

The red crystals of $C_8H_8Cr(CO)_3$ were very unstable decomposing to a black pyrophoric material upon standing overnight at −15°. The analyses cited below were very approximate. More satisfactory confirmation of the molecular formula of this new compound was obtained by mass spectroscopy. (Found: C, 51.3; H, 3.2; O, 19.4. $C_{11}H_8CrO_3$ calcd.: C, 55.0; H, 3.3; O, 20.0%.)

Mass spectrum: The following ions with m/e > 100 were observed at 70 e.v.: $C_8H_8Cr(CO)_3^+$ (m/e 240, rel. int. 15), $C_6H_6Cr(CO)_3^+$ (m/e 214, rel. int. 3), $C_8H_8Cr(CO)_2^+$ (m/e 212, rel. int. 1), $C_{16}H_{15}^+$ (m/e 207, rel. int. 17), $C_8H_8CrCO^+$ (m/e 184, rel. int. 47), $C_8H_8Cr^+$ (m/e 156, rel. int. 14), $C_6H_6Cr^+$ (m/e 130, rel. int. 80), $C_8H_8^+$ (m/e 104, rel. int. 1210), and $C_8H_7^+$ (m/e 103, rel. int. 880).

Infrared spectrum: ν(CH) at 2950 (w) cm^{-1}; ν(CO) (metal) at 1970 (vs) and 1855 (vs) cm^{-1}; ν(C=C) at 1665 (w) cm^{-1}; other bands at 1490 (w), 1460 (w), 1382 (w), 1333 (w), 1261 (vw), 1235 (vw), 1184 (w), 1154 (m), 965 (w), 896 (w), 847 (vw), 823 (vw), 813 (m), 778 (m), and 738 (w) cm^{-1}.

Reactions of $Cr(CO)_6$ with olefins in acetonitrile solution

A. Cycloheptatriene. A mixture of 4.4 g (20 mmoles) of hexacarbonylchromium, 5.0 ml (4.03 g, 44 mmoles) of technical 91% cycloheptatriene, and ~50 ml of acetonitrile was refluxed at the boiling point 24 h. After cooling to room temperature, solvent was removed from the red reaction mixture at 40°/30 mm. The red residue was extracted with 75 ml of boiling hexane in four portions and the extracts filtered hot by gravity. The filtrate was cooled ~24 h in a −78° bath. The resulting red crystals were filtered and dried to give 1.00 g (22% yield) of cycloheptatrienetricarbonylchromium, m.p. 128–130° (lit.[6] 128–130°). Further purification (with 84% recovery) could be accomplished by sublimation at ~100°/0.2 mm.

B. Cyclooctatetraene. A mixture of 2.2 g (10 mmoles) of hexacarbonylchromium, 5.0 ml (4.6 g, 44 mmoles) of cyclooctatetraene, and 75 ml of acetonitrile gave 0.12 g (5% yield) of dark red $C_8H_8Cr(CO)_3$ after sublimation at 70–100°/0.1 mm. In general the reaction procedure and product isolation followed entirely the procedure described above for the reaction between hexacarbonylchromium and cycloheptatriene in acetonitrile solution.

C. Isolation of $CH_3CNCr(CO)_5$. Similar reactions of $Cr(CO)_6$ with 1,3-cyclohexadiene and with 1,5-cyclooctadiene in acetonitrile solution gave small amounts of a yellow solid subliming readily at ~60°/0.1 mm. Analyses of the material from the reaction between $Cr(CO)_6$ and 1,3-cyclohexadiene in acetonitrile solution indicated it to be the known[20] acetonitrile complex $CH_3CNCr(CO)_5$. (Found: C, 35.4; H, 1.2; N, 5.9. $C_7H_3CrNO_5$ calcd.: C, 36.0; H, 1.3; N, 6.0%.)

DISCUSSION

A. Molybdenum complexes

The reaction between $(CH_3CN)_3Mo(CO)_3$ and methyl vinyl ketone has been reported[18] to give a solid of composition $[(CH_3COCH{=}CH_2)_2Mo(CO)_2]_n$. However, the discovery[3,4] of the yellow air-stable tungsten complex $(CH_3COCH{=}CH_2)_3W$ from the reaction of $(CH_3CN)_3W(CO)_3$ with methyl vinyl ketone prompted a re-investigation of the corresponding reaction of $(CH_3CN)_3Mo(CO)_3$.

The major product of the reaction between $(CH_3CN)_3Mo(CO)_3$ and methyl vinyl ketone was a brown hexane-insoluble non-volatile solid which was not investigated in detail but which appears to be the previously reported[19] $[(CH_3COCH{=}CH_2)_2Mo(CO)_2]_n$. However, the hexane solution from the reaction mixture yielded traces of a yellow air-stable volatile solid. By working in more dilute solution than customary for reactions of $(CH_3CN)_3M(CO)_3$ compounds enough of this rare yellow solid could be obtained for characterization.

Analyses of this yellow solid indicated it to be the sought $(CH_3COCH{=}CH_2)_3Mo$. The infrared spectrum showed no metal or ketonic carbonyl stretching frequencies in the normal regions. It was similar, but not identical, to that of $(CH_3COCH{=}CH_2)_3W$. The proton NMR spectrum indicated all three methyl vinyl ketone ligands to be equivalent and the vinyl groups to be π-complexed to the metal atom. These spectra thus correspond entirely to those found for the tungsten compound $(CH_3COCH{=}CH_2)_3W$ (I: $M = W$) and indicate $(CH_3COCH{=}CH_2)_3Mo$ to have the analogous structure (I) ($M = Mo$).

Like its tungsten analogue, the molybdenum compound $(CH_3COCH{=}CH_2)_3Mo$ exhibits the ions $(CH_3COCH{=}CH_2)_3Mo^+$ (m/e 306) and $(CH_3COCH{=}CH_2)_2Mo^+$ (m/e 236) as major constituents of its mass spectrum. The mass spectrum of the sample of $(CH_3COCH{=}CH_2)_3Mo$ also exhibited ions arising from a $(CH_3COCH{=}CH_2)_3W$ impurity too small to have been detected by analyses and the NMR spectrum. Since tungsten complexes have previously not been detected in products obtained from $Mo(CO)_6$ of the same commercial source, it appears reasonable to conclude that the formation of $(CH_3COCH{=}CH_2)_3M$ complexes enriches tungsten relative to molybdenum and thus concentrates trace tungsten impurities. The much greater ease of formation of $(CH_3COCH{=}CH_2)_3W$ relative to $(CH_3COCH{=}CH_2)_3Mo$ makes this a likely possibility.

Even under optimum conditions, the yield of $(CH_3COCH{=}CH_2)_3Mo$ remained under 2%. However, once formed, $(CH_3COCH{=}CH_2)_3Mo$ appears to be stable to air oxidation and approximately as stable thermally as its tungsten analogue. The very low yield of $(CH_3COCH{=}CH_2)_3Mo$ even under optimum conditions apparently accounts for its being overlooked in the previous studies[19] of the reaction between $(CH_3CN)_3Mo(CO)_3$ and methyl vinyl ketone.

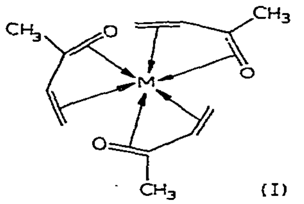
In contrast to the molybdenum analogue of $(CH_3COCH{=}CH_2)_3W$ the molybdenum analogue of $[(CF_3)_2C_2]_3WNCCH_3$ was easily obtained in comparable yields to the tungsten analogue. White air-stable volatile crystalline $[(CF_3)_2C_2]_3MoNCCH_3$ exhibited proton and ^{19}F NMR spectra similar to its tungsten analogue and thus must have a similar structure. It is thus related to the (alkyne)$_3$MoCO compounds which are known[21] but which have not received as much attention as their tungsten analogues.

A characteristic feature of $(CH_3CN)_3W(CO)_3$ is its reaction with certain non-conjugated dienes, notably 1,5-cyclooctadiene and bicyclo[2.2.1]heptadiene, to give the tetracarbonyls (diene)$W(CO)_4$. Despite the fact that in the formation of these (diene)$W(CO)_4$ complexes an "extra" carbonyl group must come from decomposition of some of the $(CH_3CN)_3W(CO)_3$, the yields of the complexes from 1,5-cyclooctadiene and bicyclo[2.2.1]heptadiene are remarkably good (~75%).

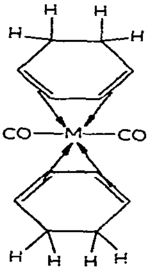
The molybdenum complex $(CH_3CN)_3Mo(CO)_3$ likewise reacts with 1,5-cyclooctadiene to form the known[9,10] tetracarbonyl $C_8H_{12}Mo(CO)_4$ in good yield. Again the only source of the "extra" carbonyl group is decomposition of some of the $(CH_3CN)_3Mo(CO)_3$. Attempts to synthesize the unknown dicyclopentadiene complex $C_{10}H_{12}Mo(CO)_4$ from dicyclopentadiene and $(CH_3CN)_3Mo(CO)_3$ failed even when an attempt was made to introduce the "extra" mole of carbon monoxide by carrying out the reaction in an atmosphere of carbon monoxide rather than the usual atmosphere of nitrogen.

Fischer and Fröhlich[17] reported 1,3-cyclohexadiene to react with $Mo(CO)_6$ at ~100° to give a low yield of yellow crystals originally reported to be the complex $(C_6H_8)_2Mo(CO)_2$ (II: M=Mo). Later work by Fritz, Keller, and Fischer[16] showed this material to be $(C_6H_7)(C_6H_9)Mo(CO)_2$ (III: M = Mo). However, the true $(C_6H_8)_2Mo(CO)_2$ (II: M = Mo) was obtained by these workers[16] by the ultraviolet irradiation of mesitylenetricarbonylmolybdenum and 1,3-cyclohexadiene.

The product from $(CH_3CN)_3Mo(CO)_3$ and 1,3-cyclohexadiene of composition $(C_6H_8)_2Mo(CO)_2$ likewise appears to be the true diene complex (II) (M = Mo). This material can be purified by sublimation at 90°/0.1 mm *without* rearrangement to the isomer $(C_6H_7)(C_6H_9)Mo(CO)_2$ (III: M = Mo).



(I)



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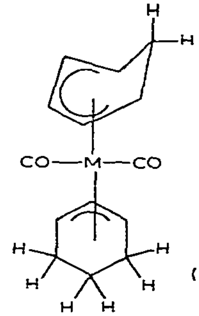

(III)

The synthesis of $(C_6H_8)_2Mo(CO)_2$ from $(CH_3CN)_3Mo(CO)_3$ and 1,3-cyclohexadiene appears to be more convenient than the syntheses of Fischer *et al.*, especially for larger scale preparations. Attempts to abstract hydride ion from $(C_6H_8)_2Mo(CO)_2$ with triphenylmethyl hexafluorophosphate to form a salt were not successful: little reaction to occur when the reagents were mixed in dichloromethane solution. Other 1,3-cyclohexadiene complexes such as $C_6H_8Fe(CO)_3$[22], $C_5H_5CoC_6H_8$[23], or C_6H_6-RuC_6H_8[24] form the π-cyclohexadienyl or π-benzene cations $[C_6H_7Fe(CO)_3]^+$, $[C_5H_5CoC_6H_6]^{++}$, or $[(C_6H_6)_2Ru]^{++}$, respectively, when reacted with triphenylmethyl salts under similar conditions.

The synthesis of the cyclooctatetraene complex $C_8H_8Mo(CO)_3$ from cyclooctatetraene and the acetonitrile complex $(CH_3CN)_3Mo(CO)_3$ appears to proceed about as well as the reported[15] synthesis of $C_8H_8Mo(CO)_3$ from cyclooctatetraene and the diglyme[14] complex (diglyme)Mo$(CO)_3$. Since the acetonitrile complex $(CH_3CN)_3Mo(CO)_3$ can be prepared and handled so readily *in situ* as described in the Experimental section, it appears to be a more easily handled intermediate than the likewise air-sensitive diglyme complex[14] (diglyme)Mo$(CO)_3$. The cyclooctatetraene complex $C_8H_8Mo(CO)_3$ had the properties reported by Winstein *et al.*[15]. It decomposed after a few days at −15° and appeared to be much less stable than the tungsten analogue[2,4] $C_8H_8W(CO)_3$.

B. Chromium complexes

Reactions between the chromium compound $(CH_3CN)_3Cr(CO)_3$ and olefins proceed less satisfactorily than corresponding reactions of the molybdenum and tungsten compounds $(CH_3CN)_3M(CO)_3$ (M = Mo and W). This may possibly be a consequence of the greater air-sensitivity of $(CH_3CN)_3Cr(CO)_3$[18] leading to greater losses through oxidation during its handling. However, the mechanistic possibilities for reactions of $(CH_3CN)_3Cr(CO)_3$ may be somewhat more limited than for reactions of its molybdenum and tungsten analogues. Comparative kinetic studies by Angelici and Graham[25] on the similar hexacoordinate derivatives (bipy)M$(CO)_4$ (M = Cr, Mo, and W) (bipy = 2,2-bipyridine) suggest that the molybdenum and tungsten compounds undergo both unimolecular and bimolecular substitution reactions, whereas compounds with the smaller chromium atom undergo only unimolecular substitution reactions.

The reaction between $(CH_3CN)_3Cr(CO)_3$ and 1,3-cyclohexadiene followed a different course than the corresponding reactions of $(CH_3CN)_3Mo(CO)_3$ and $(CH_3CN)_3W(CO)_3$. The known[26] compound $(C_6H_8)_2Cr(CO)_2$ was not obtained. Instead the product was the benzene complex $C_6H_6Cr(CO)_3$ previously prepared from benzene and hexacarbonylchromium[27]. Hexacarbonylchromium has previously been reported to dehydrogenate 1,3-cyclohexadiene derivatives to give arenechromium tricarbonyls[28]. Furthermore, dibenzenechromium is formed in a similar dehydrogenation reaction when a mixture of chromium(III) chloride and 1,3-cyclohexadiene is treated with isopropylmagnesium bromide[29].

The previously unreported cyclooctatetraene complex $C_8H_8Cr(CO)_3$ (IV: M = Cr) may be obtained in fairly low yield from $(CH_3CN)_3Cr(CO)_3$ and cyclooctatetraene. This dark red volatile solid began to decompose within a few hours at −15° and thus did not survive shipment to the microanalyst. Confirmation of the formula $C_8H_8Cr(CO)_3$ was obtained from the mass spectrum of a freshly prepared sample. This spectrum exhibited all of the ions $C_8H_8Cr(CO)_n^+$ ($0 < n < 3$). The other predominant feature of the mass spectrum was the series of ions $C_6H_6Cr(CO)_n^+$ ($n = 0$, 2, and 3), possibly fragments containing a π-bonded benzene ligand. A π-cyclooctatetraene C_8H_8 ligand such as in (IV) can be converted to a π-benzene C_6H_6 ligand with little disturbance of the metal–ring bonding by loss of the two carbon atoms not π-bonded to the metal atom as an acetylene fragment followed by joining of the broken ends.

The proton NMR spectrum of $C_8H_8Cr(CO)_3$ exhibited a single resonance at room temperature or above but a more complex pattern at lower temperatures*.

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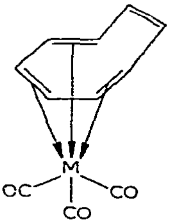
* For details of this NMR spectrum see ref. 1.

** *Note added in proof.* After this manuscript was submitted for publication, an indepent synthesis of $C_8H_8Cr(CO)_3$ from $(NH_3)_3Cr(CO)_3$ and cyclooctatetraene was reported[30].

The infrared spectrum of $C_8H_8Cr(CO)_3$ exhibited not only the expected very strong metal carbonyl stretching frequencies but also a weak band at 1665 cm^{-1} due to the carbon–carbon stretching frequency of the uncomplexed carbon–carbon double bond.



(IV)

The low yields obtained in reactions of $(CH_3CN)_3Cr(CO)_3$ with 1,3-cyclohexadiene, cyclooctatetraene, and other olefins prompted a search for other methods for preparing olefin–chromium carbonyl complexes. One possibility, described here, is the reaction of hexacarbonylchromium with olefins in acetonitrile solution hoping that the possibility for formation of $(CH_3CN)_3Cr(CO)_3$ as an intermediate would aid the reaction.

In this connection hexacarbonylchromium and excess cycloheptatriene reacted in boiling acetonitrile to give a mediocre ($\sim$22%) yield of the known[5,6] cycloheptatriene complex $C_7H_8Cr(CO)_3$. Qualitative observations (yellow, hexane-insoluble pyrophoric solid) suggested that much of the remaining chromium was converted to $(CH_3CN)_3Cr(CO)_3$ and remained in that form. Unreacted $Cr(CO)_6$ was also generally present. Another material sometimes present in these systems was acetonitrilepentacarbonylchromium[20], $CH_3CNCr(CO)_5$, isolated and analyzed from the reaction between hexacarbonylchromium and 1,3-cyclohexadiene in acetonitrile.

The cyclooctatetraene complex $C_8H_8Cr(CO)_3$ could be obtained by a similar method using $Cr(CO)_6$ and cyclooctatetraene in acetonitrile solution, but this synthesis was not better than the one from pre-formed $(CH_3CN)_3Cr(CO)_3$ and cyclooctatetraene in hexane. The molybdenum and tungsten cycloheptatriene complexes $C_7H_8M(CO)_3$ ($M = Mo$ or W) were *not* obtained from the corresponding metal hexacarbonyl and cycloheptatriene in boiling acetonitrile. Instead, essentially all of the metal appeared to be converted to the corresponding $(CH_3CN)_3M(CO)_3$ ($M = Mo$ or W) derivative. This indicates some differences in the relative stabilities of metal olefin complexes and metal acetonitrile complexes in the series chromium, molybdenum and tungsten.

Attempts to prepare the tris(methyl vinyl ketone) complex $(CH_3COCH{=}CH_2)_3$-Cr from $(CH_3CN)_3Cr(CO)_3$ and methyl vinyl ketone in boiling hexane and from Cr-$(CO)_6$ and methyl vinyl ketone in boiling acetonitrile were uniformly unsuccessful. An insoluble green solid resembling Cr_2O_3 was instead obtained. The complex $(CH_3COCH{=}CH_2)_3Cr$ thus might be unstable with respect to chromium oxides and organic material.

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SUMMARY

Yellow, volatile tris(methyl vinyl ketone)molybdenum, $(CH_3COCH{=}CH_2)_3$-Mo, has been isolated in low yield from the reaction between $(CH_3CN)_3Mo(CO)_3$ and methyl vinyl ketone in hexane solution. Hexafluoro-2-butyne reacts with $(CH_3CN)_3Mo(CO)_3$to give white volatile crystalline $[(CF_3)_2C_2]_3MoNCCH_3$. Reactions of cyclooctatetraene, 1,3-cyclohexadiene, and other similar olefins with the acetonitrile complexes $(CH_3CN)_3M(CO)_3$ (M = Cr or Mo) are also described.

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