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TRICARBONYL (TRIQUINACENE)-MOLYBDENUM AND -TUNGSTEN

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Summary

Triquinacene reacts with hexacarbonylmolybdenum to give tricarbonyl(triquinacene)molybdenum, and with tris(acetonitrile)tricarbonyltungsten to give tricarbonyl(triquinacene)tungsten, whereas efforts to synthesize the corresponding chromium complex, tricarbonyl(triquinacene)chromium, were unsuccessful. The molybdenum complex was characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectra, and a single crystal X-ray structure determination. The tungsten complex is thermally less stable and more susceptible to oxidation than its molybdenum analogue and was characterized by the mass spectrum and the ^{1}H NMR spectrum. The crystal structure of the tricarbonyl(triquinacene)molybdenum is compared to that for the free ligand. Besides the expected lengthening of the C=C bonds, the complex shows a deepening of the triquinacene "basket", presumably to give better overlap of the C=C bonds with molybdenum orbitals.

Introduction

Tricyclo[5.2.1.1^{4,10}]deca-2,5,8-triene, more commonly called triquinacene (I), was first synthesized by Woodward and co-workers in 1964 [1]. These authors conceived of triquinacene as a precursor, through dimerization, of the symmetrical hydrocarbon dodecahedrane (II). Two recent reviews on dodecahedrane chemistry have appeared [2,3] and the synthesis of the 1,16-dimethyl analogue has been recently announced [4].

All attempts to dimerize triquinacene per se have failed, most probably because the transition state is sterically hindered and also statistically improbable. For these reasons, Jacobson suggested bringing two molecules of triquinacene together in the correct orientation for subsequent dimerization via a

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transition metal complex III [5]. In a first step towards the synthesis of such complexes (III), we have sought to establish bonding criteria for the prospective transition metal. It is clear that the ultimate choice of metal will depend on its coordination number since at least one ligand bond should remain uncomplexed. Also, the metal will have to be removed prior to the complete linking of the two triquinacene units.

Group VI metals (Cr, Mo, W) were first investigated for optimum size since there is much precedent for the relatively easy formation of stable half-sandwich compounds (IV). Although relatively air-stable crystals of a bright yellow complex resulted from the direct reaction of triquinacene with hexacarbonylmolybdenum, hexacarbonyltungsten was too unreactive and had to be converted into the tris(acetonitrile)tricarbonyl compound before exchange with triquinacene to form a yellow green complex. No complex could be isolated from the reaction of triquinacene with hexacarbonylchromium. The molybdenum complex has been characterized by X-ray diffraction and by ^{1}H and ^{13}C NMR spectroscopy *.

Results and discussion

Complexes with conjugated cyclic ligands are numerous in the organometallic literature. The ^{13}C NMR spectra of the compounds tricarbonyl(cycloheptatriene)molybdenum and tricarbonyl(cycloheptatriene)chromium, for example, were measured by Kreiter and Lang [6]. Their data show that the terminal carbons, C(1) and C(6), of the conjugated system experience a much larger coordination shift than the internal carbons, C(2) to C(5); a review article on this subject has appeared [7].

On the other hand, relatively few data are available for isolated double bonds, such as in triquinacene, coordinated to a metal carbonyl fragment. Moreover, the symmetry of triquinacene (I) and its complexes greatly simplifies the ^{13}C and the ^{1}H NMR spectra, so that conclusive assignments can be made. The NMR data are summarized in Tables 1 and 2.

The molecular structure of tricarbonyl(triquinacene)molybdenum is shown in Fig. 1. The Mo atom is coordinated so that each carbonyl is *trans* to a double bond. Although the geometry of the molecule is not constrained by crystal symmetry, it has approximate C_{3v} symmetry. Each of the three five-membered rings is planar within the error of the experiment. The six carbons that define the rim of the basket lie in a plane perpendicular to the axis of the tricarbonylmolybdenum moiety with an average Mo—C distance of 2.555(7) Å. The distance from the Mo atom to the centre of the double bond is 2.465(5) Å.

The crystal structure of the free ligand at 90 K has been reported [8]. The free ligand has a crystallographic 3-fold axis through the apical carbon atom but shows no significant deviation from the C_{3v} symmetry expected in the gas phase. The dimensions of the tricarbonylmolybdenum complex and the free ligand are compared in Table 3. Both have been averaged to C_{3v} symmetry.

There are only two significant changes in the dimensions of triquinacene

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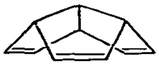
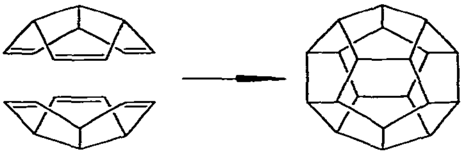
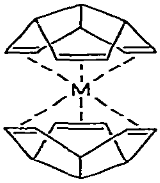
* R.B. King and K.C. Nainan at the University of Georgia have also prepared the molybdenum complex (private communication 1981).



(I)



(II)



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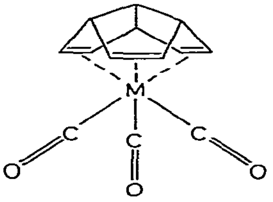


(IV)

upon formation of the complex. The double bond lengthens from 1.319 to 1.341 Å and the external angle at the allylic carbon (C(1)—C(2)—C(1″)) is reduced from 113.8 to 107.6°. These changes correlate with the NMR results. Carbon C(1) and its associated proton H(1), are both shifted upfield by coordination to tricarbonylmolybdenum by 52.8 and 1.48 ppm, respectively. This suggests that the main effect of complex formation is the donation of electron

TABLE 1

TRIQUINACENEMETAL TRICARBONYLS: ^{1}H NMR CHEMICAL SHIFTS [a] AND COUPLING CONSTANTS

M	H(1)	H(2)	H(3)	J_{12} (Hz)	J_{23} (Hz)
Mo	4.10	4.34	3.52	1.2	7.8
	−1.48 [b]	+0.66	−0.16		
W	3.79	5.12	3.52	1.2	8.0
	−1.79 [b]	+1.44	−0.16		

[a] In ppm downfield from internal TMS at ambient temperature in chloroform-*d*. [b] Coordination shifts.

TABLE 2

TRICARBONYL(TRIQUINACENE)MOLYBDENUM: ^{13}C NMR CHEMICAL SHIFTS [a] AND COORDINATION SHIFTS

Compound	C(1)	C(2)	C(3)
triquinacene	132.9	57.7	48.0
IV, M = Mo	80.1	53.8	46.4
Coordination shift	—52.8	—3.9	—1.6

[a] In ppm downfield from internal TMS at —60°C in chloroform-*d*.

density into the antibonding orbitals of the ligand. In this connection, ν_1(CO) decreases from 2117 in the hexacarbonyl to 1942 cm^{-1} in the complex.

Reduction of the angle at C(2) draws up the edges of the basket so that the diameter decreases and the distance from the plane of the three double bonds to the allylic carbon increases from 0.82 Å in the free ligand to 0.89 Å in the tricarbonylmolybdenum complex. The distance from that plane to the apical carbon is also increased from 1.41 to 1.49 Å. This geometry seems likely to improve the overlap between the orbitals of Mo and the ligand. The line between the Mo atom and the midpoint of the double bond makes an angle of 6.9° with the direction of the π orbitals on carbon. However, it is not clear how this change in geometry is correlated with the downfield shift of the proton

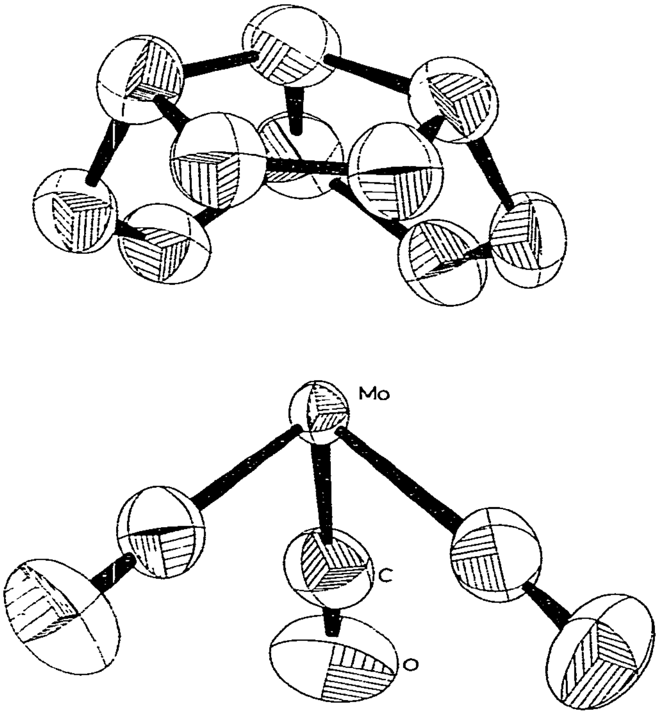
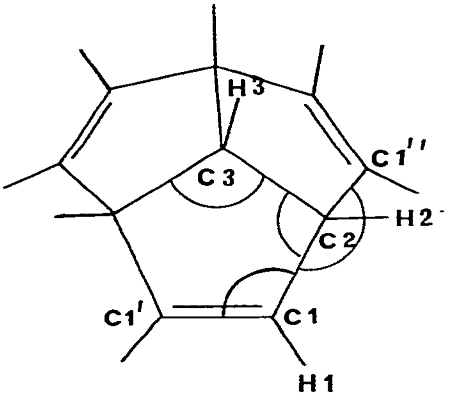


Fig. 1. A perspective drawing of tricarbonyl(triquinacene)molybdenum showing carbonyls *trans* to the double bonds of the triquinacene moiety.

TABLE 3

DIMENSIONS OF TRICARBONYL(TRIQUINACENE)MOLYBDENUM AVERAGED TO C_{3v} SYMMETRY



There are 3 unique distances and 4 unique angles in the triquinacene ligand. The figure in brackets is the standard deviation of the mean for symmetrically equivalent dimensions.

Complex		Free ligand [8]
C(1)—C(1)′	1.341(13) Å	1.319 Å
C(1)—C(2)	1.519(8) Å	1.512 Å
C(2)—C(3)	1.559(4) Å	1.558 Å
Mo—C	1.922(10) Å	
C—O	1.183(4) Å	
C(1′)—C—C(2)	112.5(5)°	112.8°
C(1)—C(2)—C(3)	104.1(3)°	103.8°
C(1)—C(2)—C(1″)	107.6(5)°	113.8°
C(2)—C(2)—C(2′)	106.8(9)°	106.5°
Mo—C—O	117(1)°	

H(2) on formation of the complex. The shift is even more pronounced in the case of the tungsten compound.

The fact that no complex was formed with hexacarbonylchromium may be related to the size of the metal. The distance between the centers of the isolated double bonds in the free ligand is 3.192(3) Å. Thus triquinacene is considerably broader than, say, benzene for which the tricarbonylchromium complex is known. It may be that chromium is too small to span the wider distance. A similar explanation has been advanced in the case of *cis,cis,cis*-1,4,7-cyclononatriene [9] which forms complexes Mo and W but not with Cr.

Experimental

Infrared measurements were conducted on a Perkin—Elmer 467 grating spectrometer, ^{1}H NMR measurements on a Varian HA 100, and ^{13}C NMR measurements on a Bruker WH 90 FT spectrometer.

All organometallic syntheses were performed under nitrogen, which was purified over deoxo catalyst R3-11 (BASF) at 160°C and over molecular sieve 4A. Hexacarbonylmolybdenum was purchased from Chemical Procurement Laboratories and hexacarbonyltungsten from Alfa Inorganics. Thiele's acid

[10] and triquinacene [11] were prepared according to published procedures. In the synthesis of Thiele's acid a second isomer was sometimes isolated; this isomer could be converted into Thiele's acid by heating the solid in refluxing 0.1 *M* sulfuric acid.

Tricarbonyl(triquinacene)molybdenum (IV, M = Mo)

A solution of hexacarbonylmolybdenum (0.400 g; 1.53 mmol) and triquinacene (0.105 g; 0.81 mmol) in 30 ml of spectrograde isooctane was heated for 20 h at 110—115°C. After the solution had cooled, a green solid product was filtered, which was recrystallized from methylene chloride/cyclohexane, yield: 28 mg (11%), decomposes on heating.

Infrared (KBr): ν(CO) at 1942 and 1828 cm^{-1}. Mass spectrum based on ^{98}Mo (70 eV): *m/e* 312 (5, *M*), 284 (2, *M* — CO), 256 (3, *M* — 2 CO), 228 (12, *M* — 3 CO), 130 (100), 28 (54). Found: C, 50.0; H, 3.1. $C_{13}H_{10}MoO_3$ calcd.: C, 50.3; H, 3.2%.

Tricarbonyl(triquinacene)tungsten (IV, M = W)

A suspension of hexacarbonyltungsten (0.450 g; 1.28 mmol) in 60 ml of acetonitrile was heated for 44 h at reflux [12]. After the excess acetonitrile had been removed under reduced pressure, 50 ml of hexane were added to the solid residue. Triquinacene (0.100 g; 0.77 mmol) was added and the solution was refluxed for another 16 h. Subsequently the solution was cooled and concentrated to about half of its initial volume; a yellow-green product was filtered, yield 50 mg (16%).

Infrared (KBr): ν(CO) at 1934 and 1824 cm^{-1}. Mass spectrum based on ^{186}W (79 eV): 186 (1), 130 (100). This sample may be contaminated with hexacarbonyltungsten since a few colorless crystals seem to be present.

Crystal structure determination

The sample chosen for analysis was a rectangular parallelopiped of dimensions 0.10 × 0.10 × 0.18 mm. Since the compound is air sensitive both in solution and in the solid state, the crystal was coated with expoxy resin.

Crystal data: $MoC_{13}H_{10}O_3$, mol. wt. 310.16 *a* 8.0322(8), *b* 12.5029(11), *c* 11.1766(11) Å, α 88.639(8), β 91.457(8), γ 85.927(8)°, *V* 1118.5 $Å^3$ C_1, $Z = 4$. $F(000) = 616$, ρ_{calc} 1.79 g cm^{-3}. $\mu(Mo\text{-}K_\alpha)$ 11.14 cm^{-1}.

Diffraction data were collected at room temperature with a CAD-4 diffractometer equipped with a graphite monochromator and operated in the $\omega/2\theta$ scan mode with a nominal scan rate of 7 deg min^{-1} and a scan width of $\Delta\omega = 1.5$ $(0.40 + 0.35 \tan\theta)$. A total of 2436 independent reflections were measured to a θ_{max} of 27.0°. Three standard reflections were monitored every 1800 sec of exposure. These showed a decline in intensity of about 2 percent during the course of data collection. No correction was made for absorption.

The structure was solved by standard Patterson and Fourier techniques and refined by full matrix least squares minimizations of $\Sigma w(|F_0| - |F_c|)^2$ to a final *R*-value of 0.031 for the 1935 contributing reflections ($R_w = 0.040$).

The weighting scheme was $w = (\sigma^2(F) + 0.002\,F^2)^{-1}$ where $\sigma^2(F)$ was evaluated from counting statistics. Reflections with $I \leqslant 3\sigma(I)$ were included in the refinement if $F_c >$ threshold. The final value of $(\Sigma w\Delta^2/m - n)^{1/2} = 1.273$. The maximum

TABLE 4

TRICARBONYL(TRIQUINACENE) MOLYBDENUM ATOMIC COORDINATES ($\times 10^5$ for Mo; $\times 10^4$ for others)

	x/a	y/b	z/c	U_{equ}
Mo	42520(6)	10632(4)	24889(4)	258
O(1)	1292(6)	347(4)	1030(4)	763
O(2)	5012(6)	−1336(4)	3293(4)	803
O(3)	1675(6)	1066(4)	4616(4)	929
C(1)	2436(7)	638(4)	1596(5)	505
C(2)	4753(7)	−414(4)	3026(5)	550
C(3)	2688(8)	1096(4)	3874(5)	574
C(4)	3850(7)	2860(4)	1463(5)	562
C(5)	3994(7)	3116(5)	2617(5)	583
C(6)	5819(7)	3101(4)	3051(5)	553
C(7)	6134(7)	2151(5)	3907(5)	585
C(8)	7139(7)	1372(5)	3473(5)	592
C(9)	7702(7)	1646(5)	2233(5)	580
C(10)	6899(7)	900(4)	1362(5)	572
C(11)	5720(7)	1433(4)	643(5)	532
C(12)	5526(7)	2625(4)	888(5)	555
C(13)	6822(7)	2770(4)	1921(5)	569

shift/error was 0.03. Hydrogen atoms were located in difference maps and included in the model as fixed contributions. Scattering curves were those tabulated in Cromer and Mann [13] with dispersion terms from International Tables for Crystallography Vol. IV [14]. Atomic coordinates are listed in Table 4.

Tables of structure factors and anisotropic thermal parameters can be obtained from the authors upon request.

Acknowledgements

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