

Ditropylmolybdenum complexes by the sodium reduction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$. X-Ray crystal structure of the ditropyl complex $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta'^6\text{-C}_{14}\text{H}_{14})$

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Abstract

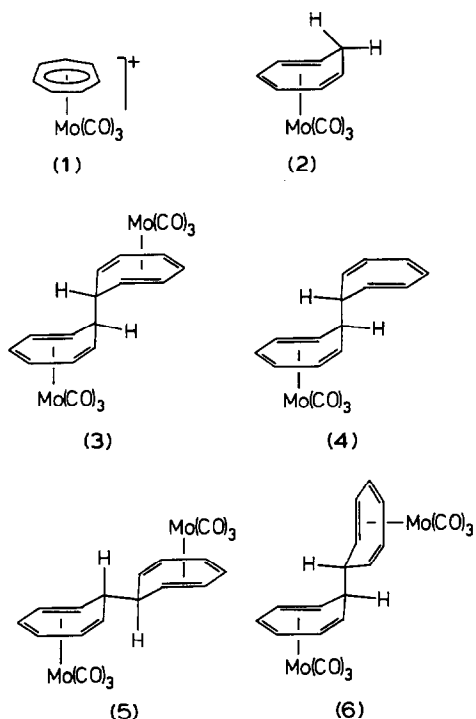
Treatment of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ with either sodium amalgam or sodium naphthalide results in a reductive dimerisation to the ditropyl complex $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta'^6\text{-C}_{14}\text{H}_{14})$. The results of an X-ray crystallographic study confirm that the hydrogen atoms of the linking carbon atoms are both *endo* with respect to molybdenum. The reaction of $\text{Mo}(\text{CO})_6$ with ditropyl, $\text{C}_{14}\text{H}_{14}$, leads to all three possible isomers of $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta'^6\text{-C}_{14}\text{H}_{14})$. The structure of each is assigned by its ^1H NMR spectrum.

Introduction

One of our interests concerns organotransition metal nucleophilic anions and we were interested in a good source of the anion $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]^-$. This anion is in fact known, [1] and is made by reducing $\text{MoX}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)$ with Na/Hg. However, this appears to proceed in rather moderate yield and we were keen to find a high yield route. We speculated that Na/Hg reduction of the cation $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ (1) [2,3] might result in a reductive decarbonylation and formation of the anion. Another possibility would be the formation of $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]^-$. In fact neither path is followed, and this paper addresses these reactions.

Results and discussion

The cation $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ (1) [2,3] is virtually insoluble in THF but a suspension nevertheless undergoes reduction with Na/Hg. The red colour of the salt suspension is discharged resulting in a pale orange solution whose IR spectrum in THF [$\nu(\text{CO})$ (THF) 1979s, 1918s, and 1891s cm^{-1}] is qualitatively very similar to that of the well known $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ (2) [3,4] [$\nu(\text{CO})$ (THF) 1984s, 1914s, and 1887s cm^{-1}]. Separation of the reaction mixture away from the amalgam



followed by workup gives a single product isolated in moderate yield and assigned the structure 3. This complex is air stable and sparingly soluble in organic solvents such as dichloromethane and toluene. Observation of Mo_2 isotope patterns at m/e 542 suggest a dimeric structure with $[\text{Mo(CO)}_3(\text{C}_7\text{H}_7)]_2$ stoichiometry. The similarity between the IR spectrum of 3 and that of the very well known tricarbonyl 2 suggests the hexacarbonyl stoichiometry is likely to arise from two independent tricarbonyl units, and therefore that the two tricarbonyl units are linked through a C-C bond of an organic ligand rather than through a Mo-Mo bond. This is confirmed by the results of an X-ray crystallographic study.

The structure of 3 is illustrated in Fig. 1 with atomic labelling used in the Tables. The atomic positional parameters are listed in Table 1. Bond lengths and angles

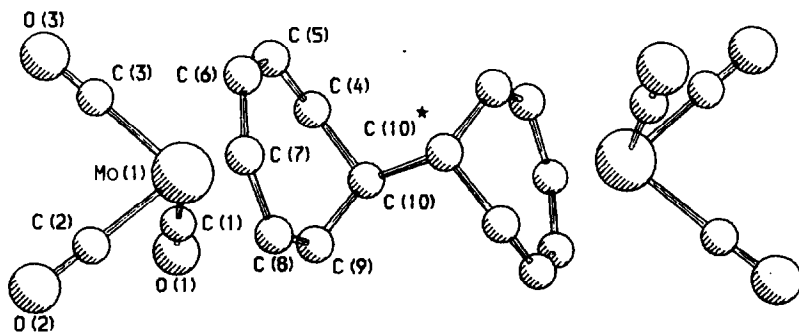


Fig. 1. The molecular structure and atom labelling for $[\{\text{Mo(CO)}_3\}_2(\eta^6, \eta'^6\text{-C}_{14}\text{H}_{14})]$ (3).

Table 1

Atomic positional parameters with estimated standard deviations for $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta^6\text{-C}_{14}\text{H}_{14})^a$

Atom	x/a	y/b	z/c
Mo(1)	0.28342(4)	0.13905(3)	0.11287(6)
O(1)	0.1726(5)	0.2744(3)	0.4103(7)
O(2)	0.5448(4)	0.1319(3)	0.4123(7)
O(3)	0.3939(4)	0.3115(3)	-0.0864(7)
C(1)	0.2131(5)	0.2252(3)	0.3011(8)
C(2)	0.4473(5)	0.1342(3)	0.3030(8)
C(3)	0.3539(5)	0.2476(4)	-0.0176(7)
C(4)	0.0643(4)	0.1190(3)	-0.0749(7)
C(5)	0.1540(5)	0.1102(3)	-0.2040(7)
C(6)	0.2610(5)	0.0488(4)	-0.1861(7)
C(7)	0.3058(5)	-0.0089(3)	-0.0200(8)
C(8)	0.2573(5)	-0.0186(3)	0.1731(7)
C(9)	0.1451(4)	0.0185(3)	0.2207(6)
C(10)	0.0292(4)	0.0431(3)	0.0634(6)
H(4)	0.003(4)	0.164(3)	-0.096(7)
H(5)	0.156(4)	0.149(3)	-0.281(7)
H(6)	0.305(4)	0.052(3)	-0.280(7)
H(7)	0.379(4)	-0.037(3)	-0.012(7)
H(8)	0.324(4)	-0.042(3)	0.287(7)
H(9)	0.127(4)	0.010(3)	0.345(7)
H(10)	-0.024(4)	0.059(3)	0.130(7)

^a Hydrogen atoms are labelled according to the carbon atom to which they are attached.

Table 2

Bond lengths (Å) and bond angles (°) with estimated standard deviations for $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta^6\text{-C}_{14}\text{H}_{14})$

Mo(1)–C(1)	1.962(5)	O(1)–C(1)	1.130(7)	C(4)–H(4)	0.91(4)
Mo(1)–C(2)	1.949(5)	O(2)–C(2)	1.148(6)	C(5)–H(5)	0.75(5)
Mo(1)–C(3)	1.975(5)	O(3)–C(3)	1.133(7)	C(6)–H(6)	0.82(5)
Mo(1)–C(4)	2.439(4)	C(10)–C(4)	1.496(6)	C(7)–H(7)	0.86(5)
Mo(1)–C(5)	2.313(5)	C(4)–C(5)	1.357(6)	C(8)–H(8)	0.99(5)
Mo(1)–C(6)	2.313(5)	C(5)–C(6)	1.417(7)	C(9)–H(9)	0.87(5)
Mo(1)–C(7)	2.326(5)	C(6)–C(7)	1.383(7)	C(10)–H(10)	0.79(5)
Mo(1)–C(8)	2.330(5)	C(7)–C(8)	1.428(7)		
Mo(1)–C(9)	2.433(4)	C(8)–C(9)	1.368(6)		
Mo(1)–C(10)	2.971(4)	C(9)–C(10)	1.500(6)		
		C(10)–C(10)*	1.561(6)		
C(1)–Mo(1)–C(2)	90.5(2)	C(10)–C(4)–H(4)	112(3)		
C(1)–Mo(1)–C(3)	88.0(2)	C(5)–C(4)–H(4)	121(3)		
C(2)–Mo(1)–C(3)	87.1(2)	C(4)–C(5)–H(5)	116(3)		
Mo(1)–C(1)–O(1)	179.6(5)	C(6)–C(5)–H(5)	114(3)		
Mo(1)–C(2)–O(2)	178.8(4)	C(5)–C(6)–H(6)	116(3)		
Mo(1)–C(3)–O(3)	177.6(5)	C(7)–C(6)–H(6)	117(3)		
C(10)–C(4)–C(5)	123.9(4)	C(6)–C(7)–H(7)	121(3)		
C(4)–C(5)–C(6)	128.5(5)	C(8)–C(7)–H(7)	110(3)		
C(5)–C(6)–C(7)	127.4(5)	C(7)–C(8)–H(8)	112(3)		
C(6)–C(7)–C(8)	128.0(5)	C(9)–C(8)–H(8)	120(3)		
C(7)–C(8)–C(9)	126.4(4)	C(8)–C(9)–H(9)	119(3)		
C(8)–C(9)–C(10)	124.8(4)	C(10)–C(9)–H(9)	113(3)		
C(9)–C(10)–C(4)	109.4(3)	C(9)–C(10)–H(10)	105(3)		
C(9)–C(10)–C(10)*	112.1(3)	C(4)–C(10)–H(10)	112(3)		
C(4)–C(10)–C(10)*	112.4(3)	C(10)*–C(10)–H(10)	106(3)		

^a Atom C(10)* is symmetry related to atom C(10) through the inversion centre at (0,0,0).

Table 3

Details of planar fragments of $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta^6\text{-C}_{14}\text{H}_{14})$. The equation of a plane is of the form: $pX + qY + rZ = d$, where p , q , and r are direction cosines referred to orthogonal crystal axes a , b , and c^* . Deviations (\AA) of atoms from the mean planes are given in parentheses

<i>Plane A</i> C(5)–C(8), r.m.s. deviation 0.005 \AA		
0.5516	0.7297	0.4041 1.6371
(C(5) –0.003, C(6) 0.006, C(7) –0.006, C(8) 0.003, Mo(1) 1.690, C(4) –0.166, C(9) –0.158, C(10) –0.887, H(5) 0.26, H(6) 0.11, H(7) 0.14, H(8) 0.37)		
<i>Plane B</i> C(4), C(5), C(8), C(9), r.m.s. deviation 0.001 \AA		
0.4484	0.7667	0.4595 1.4324
(C(4) –0.001, C(5) 0.001, C(8) –0.001, C(9) 0.001, Mo(1) 1.715, C(6) –0.130, C(7) –0.146, C(10) –0.661, H(4) 0.15, H(5) 0.25, H(8) 0.33, H(9) 0.13)		
<i>Plane C</i> C(4), C(9), C(10)		
–0.3719	0.6817	0.6301 0.5897
(Mo(1) 0.172, C(5) –1.005, C(6) –1.945, C(7) –1.955, C(8) –1.011, H(4) 0.58, H(9) 0.54, H(10) 0.66)		
<i>Angles between planes</i> ($^\circ$)	A–B	7.0
	B–C	49.8
	A–C	56.8

(together with estimated standard deviations) and details of planar fragments are given in Tables 2 and 3.

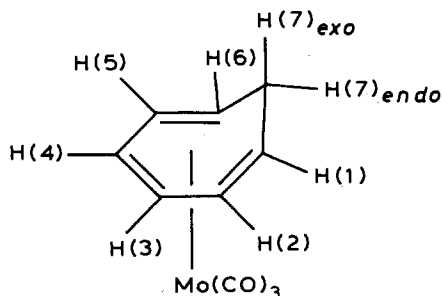
The molecule is a centrosymmetric dimer comprising a bis-cycloheptatrienyl (ditropy) ligand, each ring of which is attached to a $\text{Mo}(\text{CO})_3$ unit. The four carbon atoms of the cycloheptatrienyl ring which are remote from the centre of symmetry [C(5)–C(8)] are closely coplanar (r.m.s. deviation 0.0047 \AA). The immediately adjacent atoms [C(4) and C(9)] and C(10) deviate progressively further from this mean plane (Table 2). The deviations of the hydrogen atoms are realistic and consistent with the imperfect coplanarity of the hexatrienyl fragment. Ring bond-length alternation, molybdenum–carbon distances and hydrogen atom out-of-plane deviations, together with the orientation of the $\text{Mo}(\text{CO})_3$ fragment, all show almost perfect (but not crystallographically imposed) C_s symmetry for each half of the dimer giving overall approximate C_{2h} molecular symmetry. The hydrogen atom on C(10) is orientated *endo* with respect to the metal. The basic framework of the $\text{Mo}(\text{CO})_3$ unit and its bonding to the C_7 ring system is, as expected, very similar to that reported for the cycloheptatriene complex **2** [5].

The ^1H NMR spectrum is quite complex but is readily related to that of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ (**2**). There are four complex multiplets (Table 4) with relative intensities 4/4/4/2 as expected of the symmetrical structure **3**. The three four-proton multiplets are observed at very similar shifts to the three two-proton multiplets of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ (**2**) as might be expected. The *endo*-hydrogen of **3** is manifested by the multiplet at δ 1.72, which compares with the corresponding *endo* proton signal of **2** which is at δ 3.15 [6].

The same compound **3** is produced by reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with sodium naphthalide ($\text{NaC}_{10}\text{H}_8$) [7] and in comparable yield. In both the amalgam

Table 4

^1H NMR spectra of the complexes. All spectra were recorded in CDCl_3 at ambient temperature. All values on the δ (ppm) scale. Data for **2** are included for comparison. Data for **3**, **5**, and **6** were recorded at 400 MHz, the others at 220 MHz. Observed splittings are given in parentheses in Hz. Hydrogen labels refer to the following diagram:



Complex	H(3,4)	H(2,5)	H(1,6)	H(7) _{exo}	H(7) _{endo}
3	5.99 (4.5, 3.0)	4.91 (8.0, 4.5, 3.0)	3.59 (8.0, 5.0, 2.5)		1.72 (multiplet)
5	6.08 (4.5, 3.0)	5.02 (8.5, 4.5, 3.0)	3.20 (8.5)	2.49 (br, s)	
6	5.93 (4.5, 3.0)	4.93 (8.0, 4.5, 3.0)	3.11 (8.5, 3.0)	0.95 (11.0)	
	5.87 (4.5, 3.0)	4.83 (8.0, 4.5, 3.0)	3.99 (8.5, 8.5, 2.5)		3.42 (11.0, 8.0, 8.0)
4	5.93 (4, 3)	4.93 (8, 4, 3)	3.98 (8, 8)		3.28 (11, 8, 8)
	6.55 (4, 3)	6.13 (8, 3, 3)	5.04 (8, 6)		0.81 (11, 6, 6)
2	6.07 (4, 3)	4.93 (8, 4, 3)	3.61 (8, 8, 3)	2.45 (14)	3.15 (14, 8, 8)
ditropyl	6.68 (4, 3)	6.27 (9, 4, 3)	5.30 (9+ unresol- ved small)	1.97 (broad singlet)	

and naphthalide reductions, we attribute the rather moderate yields to a tendency for **3** to undergo decomplexation of ditropyl, this tendency was alluded to for chromium systems in other work [8].

The reaction of $\text{Mo}(\text{CO})_6$ with ditropyl was discussed some time ago [4]. The two isolated products were assigned the formulae $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_{14}\text{H}_{14})$ and $\{\text{Mo}(\text{CO})_3\}_2(\eta^6, \eta'^6\text{-C}_{14}\text{H}_{14})$. It was not clear from our IR data for **3** and the published data for the latter compound whether their identities are similar. To test this, we also reacted ditropyl with $\text{Mo}(\text{CO})_6$. Under the published reaction conditions (heptane at reflux) we find that a dark red crystalline material does indeed result on cooling the reaction mixture. Its colour is clearly much darker than that of **3**. The reason for this is immediately apparent from the ^1H NMR spectrum at 400 MHz. The dark red material from the ditropyl reaction is a mixture of three isomers in roughly equal quantities. These isomers are not separable by conventional

chromatography on alumina but adequate quantities for ^1H NMR spectra of each are resolvable by high performance liquid chromatography which in appropriate cases is a valuable method in organotransition metal chemistry [9].

As expected, it is also possible to arrange for a single metal to bind to ditropyl [4] by altering the reaction stoichiometry. When ditropyl is in excess, formation of **4** is favoured, although in our hands the isolated yield is very low owing to the necessary repeated chromatography employed in order to achieve a pure material. Only the *endo*-hydrogen isomer was isolated, which is not to say that the *exo*-hydrogen species is not formed in the reaction.

The identity of each of the three compounds containing two molybdenums is clearly established from their NMR spectra as **3**, **5**, and **6**, that is, all three possible isomers. The assignments of the spectra are indicated in Table 4. For comparison, the NMR spectra of ditropyl, **2** and **4** are included. The spectrum of one isomer is identical to that of the material analysed by X-ray crystallography, confirming its identity. The other isomer with an NMR intensity pattern of 4/4/4/2 is therefore assigned the *exo-exo* symmetrical structure **5**. The other complex is the *endo-exo* isomer **6** and has the expected pattern of signals with intensity pattern 2/2/2/2/2/2/2/1/1. The assignment of signals in the spectra of **4** and **6** is aided by double irradiation experiments at 220 MHz which clearly show which signals arise from each ring. In addition, the shift positions of the alkenyl protons of the metal-free ring are virtually identical to those of ditropyl.

The criteria in the ^1H NMR spectra for assigning the structures of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7\text{R})$ as having *endo* or *exo* hydrogen on the CHR group rest on the shift of the CHR proton, its coupling constants to the adjacent CH groups, and the chemical shifts of the adjacent CH groups. The complexes **3**, **5**, and **6** can be regarded as $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7\text{R})$ ($\text{R} = \text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7)$) and their ^1H NMR spectra so interpreted.

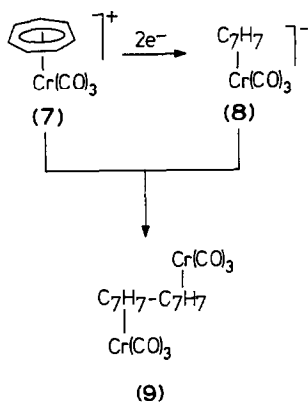
When the CHR hydrogen is *endo* to the metal the adjacent CH signal lies at higher frequency [10] than when the CHR hydrogen is *exo* to the metal. This is clearly the case when comparing the observed shifts for **3** and **5**. The spectrum of **6** is interpreted assuming this to be the case. For hydrogen atoms *exo* to the metal, there are only very small coupling constants to the H(1,6) hydrogen atoms, the corresponding values for *endo* hydrogen atoms are around 8 Hz.

Normally the shift of the CHR proton is to lower frequency when it is *exo* with respect to the metal. This is not the case for **3** and **5**. Inspection of Fig. 1 and molecular models shows that the *endo*-hydrogens in **3** lie over the adjacent C_7 unit and we assume that this positioning of the *endo*-hydrogens results in the apparent reversal of expected chemical shifts. Again, the spectrum of **6** is assigned with those of **3** and **5** in mind and is consistent with the geometry illustrated for structure **5**.

The reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with $[\text{Na}][\text{SnPh}_3]$ was reported some time ago [11], a single product was isolated in 1% yield and assigned the formula $\text{Mo}_2(\text{CO})_6(\text{C}_{14}\text{H}_{14})$. It is likely to be **3** or one of its isomers.

It is certain that the reductive coupling experiments give predominantly only the one isomer **3**. We have not detected any of the possible second or third isomers **5** or **6**. It is not clear to us why the reduction reactions using $\text{NaC}_{10}\text{H}_8$ or Na/Hg should be so selective.

There are two possibilities for the reductive formation of **3**. One electron reduction of the cation would lead to radicals $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7)]^\cdot$; dimerisation



of two such radicals would form 3. Another possibility is indicated by electrochemical studies on analogous chromium systems [12,13]. Electrochemical reduction of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ (7) (in MeCN) proceeds by a two-electron reduction to the corresponding anion (8), which subsequently couples with another molecule of the cation 7 to form 9. Perhaps an analogous process is also followed during reduction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ by Na/Hg or $\text{NaC}_{10}\text{H}_8$.

Finally, we note that continued reduction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with excess Na/Hg gives an uncharacterised pale green anionic species which has low frequency IR carbonyl stretching bands [$\nu(\text{CO})(\text{THF})$; 1898s, 1812s, 1794sh, 1770w, and 1736 cm^{-1}]. These values and the appearance of the spectrum are very similar in appearance to the IR spectra of other $[\text{Na}][\text{Mo}(\text{CO})_3(\eta^5\text{-dienyl})]$ salts, such as $[\text{Na}][\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ [14] [$\nu(\text{CO})(\text{THF})$; 1901s, 1796s, and 1746s cm^{-1}]. The shoulder and weak bands are reproducible in repeated experiments and may be a consequence of an ion-pairing phenomenon. We feel this material probably has the empirical formula $[\text{Mo}_2(\text{CO})_6(\text{C}_{14}\text{H}_{14})]^{2-}$ and may be a diradical. We have not yet succeeded in isolating products from any of its reactions other than that with air. This proceeds with the colour change pale green to orange, during which time the IR spectrum reverts back to that of 3. Complex 3 is the only product subsequently isolated.

Experimental

Infrared spectra were measured using a Perkin-Elmer 257 instrument and calibrated using the 1601.4 cm^{-1} absorption of polystyrene film or on a Perkin-Elmer 1710 Fourier Transform instrument linked to a Perkin-Elmer 4600 Data Station.

Proton NMR spectra were recorded using Perkin-Elmer R34 (220 MHz), or Bruker WH-400 (400.13 MHz) spectrometers.

Mass spectra were recorded with a Kratos MS25 spectrometer operating at low resolution using the electron impact mode.

All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate agent, THF from sodium-benzophe-

none and light petroleum (b.p. 40–60 °C throughout) from LiAlH₄. Alumina was Brockmann Activity I and deactivated with water (5% w/w throughout) or Brockmann Activity II used as supplied. The compounds Mo(CO)₃(η⁶-C₇H₈) [2], [Mo(CO)₃(η-C₇H₇)] [BF₄] [1], and ditropyl [15] were prepared according to literature methods.

Reaction of [Mo(CO)₃(η-C₇H₇)] [BF₄] with Na / Hg

Sodium amalgam (Hg, 3 cm³; Na, 0.065 g, 2.8 mmol) was treated with a suspension of [Mo(CO)₃(η-C₇H₇)] [BF₄] (0.50 g, 1.4 mmol) in THF (40 cm³). The suspension dissolved over a period of about 30 min, according to the stirring rate, giving a solution whose IR spectrum (1979s, 1918s, and 1891s cm⁻¹) was very similar in appearance to that of Mo(CO)₃(η⁶-C₇H₈). Removal of THF and chromatography on alumina (5 × 2 cm) gave a single orange fraction containing **3** (0.088 g, 23%), m.p. 185–190 °C (Found: C, 43.8; H, 2.7%; M⁺, 542. C₁₇H₁₄MoO₃ calc: C, 44.3; H, 2.6%; M⁺, 542); ν(CO) (CH₂Cl₂) 1981s, 1915s, and 1891s cm⁻¹.

Reaction of Mo(CO)₆ and ditropyl (method A)

A solution of ditropyl (0.91 g, 5 mmol) and Mo(CO)₆ (3.0 g, 11.4 mmol) in heptane (50 cm³) was heated at reflux under an N₂ atmosphere for 40 h, during which time the solution turned deep red. After cooling, deep red crystals dropped out of solution, these were collected, washed with light petroleum, and dried under vacuum. This product (2.13 g, 79% based on C₁₄H₁₄), m.p. 232–234 °C (dec.) analyses correctly for Mo₂(CO)₆(C₁₄H₁₄) (Found: C, 44.1; H, 2.6; M⁺, 542. C₂₀H₁₄Mo₂O₆ calc: C, 44.3; H, 2.6; M⁺, 542); ν(CO) (CH₂Cl₂) 1983s, 1917s, and 1891s cm⁻¹. The ¹H NMR spectrum indicates the product to contain three components, these were separated by HPLC on silica (14 μ grade, 25 cm × 12 mm), ethyl acetate/light petroleum (60–80 °C) (30/70), 5.0 cm³ min⁻¹, monitoring by refractive index or UV (254 nm) to give adequate quantities of each for ¹H NMR spectra (400 MHz).

Reaction of Mo(CO)₆ and ditropyl (method B)

A solution of ditropyl (2.52 g, 14 mmol) and Mo(CO)₆ (0.82 g, 3.5 mmol) in light petroleum (120–160 °C fraction) (50 cm³) was heated at reflux under an N₂ atmosphere for 2.5 h, during which time the solution turned deep red. Some Mo₂(CO)₆(C₁₄H₁₄) crystallised out of the solution. Removal of solvent and chromatography gave unreacted Mo(CO)₆ followed by ditropyl on elution with light petroleum. Continued elution with dichloromethane/light petroleum 10/90 changing to 90/10 provided crude Mo(CO)₃(η⁶-C₁₄H₁₄) followed by Mo₂(CO)₆(C₁₄H₁₄). The fraction containing Mo(CO)₃(η⁶-C₁₄H₁₄) was repeatedly rechromatographed and crystallised from light petroleum to give pure red Mo(CO)₃(C₁₄H₁₄) (**4**) (0.036 g, 3%), m.p. 117–119 °C (Found: C, 56.7; H, 4.2%; M⁺, 364. C₁₇H₁₄MoO₃ calc: C, 56.4; H, 3.9%; M⁺, 364); ν(CO) (light petroleum) 1997s, 1935s, and 1910s cm⁻¹.

Crystal data

{Mo(CO)₃}₂(η⁶,η⁶-C₁₄H₁₄); C₂₀H₁₄Mo₂O₆, M = 542.12; crystallises from toluene as red bricks, crystal dimensions 0.35 × 0.16 × 0.10 mm, monoclinic, a 10.463(4), b 14.418(7), c 6.476(3) Å, β 99.01(3)°, U 964.8(8) Å³, Z = 2, D_m 1.82, D_c 1.866 g cm⁻³, space group P2₁/n (non-standard setting of P2₁/c, No. 14); Mo-K_α radiation (λ 0.71069 Å), μ(Mo-K_α) 13.02 cm⁻¹, F(000) = 532.

Three dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet/Syntex R3 diffractometer by the ω -scan method. The 1350 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least-squares. Hydrogen atoms were detected close to calculated positions (C-H 0.95 Å) and their positions refined (B 2.0 Å²). Refinement converged at R 0.0266 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum. Table 1 lists the atomic positional parameters of all atoms with estimated standard deviations. Tables of anisotropic thermal vibrational parameters with estimated standard deviations and of observed structure amplitudes and calculated structure factors are available from the authors. Scattering factors were taken from Ref. 16; computer programs formed part of the Sheffield X-ray system.

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