

METAL-ORGANIC COMPOUNDS

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Tricarbonyl(η^6 -trimethylphenylsilane)-molybdenum

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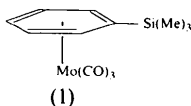
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Abstract

The Mo atom in tricarbonyl(η^6 -trimethylphenylsilane)-molybdenum, $[\text{Mo}(\text{C}_9\text{H}_{14}\text{Si})(\text{CO})_3]$ (1), is situated 1.908 (3) Å above the centre of the arene ring with Mo—C distances in the range 2.351 (5)–2.388 (5) Å. The carbonyl groups are staggered (26° from a fully eclipsed conformation) with respect to the arene-ring C atoms.

Comment

Tricarbonyl(π -arene)molybdenum complexes have been studied quite extensively ever since the isolation of $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ (Fischer, Ofele, Essler, Frohlich, Mortensen & Semmlinger, 1958) and have been used as catalysts in a variety of Friedel–Crafts-type reactions (Davis & Kane-Maguire, 1982). In general, they show dynamic stereochemistry both in solution and in the solid state (Wagner & Hanson, 1987). Variation in the arene ring substituents leads to different conformations of the tricarbonyl moiety with respect to the arene ring (*i.e.* staggered or eclipsed) (Koshland, Myers & Chesick, 1977; Hossain & van der Helm, 1978; Iverson, Junter, Blount, Damewood & Mislow, 1981; Alyea, Ferguson & Somogyvari, 1983; Kerschner, Torres, Fanwick, Rothwell & Huffman, 1989; Braga & Grepioni, 1990; Bürgi, Raselli, Braga & Grepioni, 1992). As a preliminary to multinuclear NMR spectroscopic studies on such molybdenum-carbonyl complexes, we have investigated the structure of $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_3)]$, (1); the results are reported herein.



The isostructural chromium complex (van der Helm, Loghry, Hanlon & Hagen, 1979) is known, but the only tricarbonylmolybdenum-arene complex with a sil-

icon substituent whose structure has been reported is a disiladihydro-anthracene complex (Kirillova, Gusev, Frenkel, Afanasova & Magomedov, 1989). The only examples of tricarbonylmolybdenum-arene compounds with non-carbon-bonded aryl substituents are $[\text{Mo}(\text{Mes}_3\text{Ga})(\text{CO})_3]$ (Mes = mesityl) (Beachley, Royster, Youngs, Zarat & Terrier-Youngs, 1989) and $[\text{Mo}_2\{\text{P}(p\text{-tolyl})_3\}(\text{CO})_8]$ (Alyea, Ferguson & Somogyvari, 1983).

A view of the molecule $[\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_3)(\text{CO})_3]$ together with the atomic numbering scheme is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The Mo—C(carbonyl) [average 1.958 (6) Å] and C—O [average 1.148 (7) Å] distances are similar to those found for other $[\text{Mo}(\eta^6\text{-arene})(\text{CO})_3]$ complexes (Koshland, Myers & Chesick, 1977; Iverson, Junter, Blount, Damewood & Mislow 1981; Braga & Grepioni 1990; Bürgi, Raselli, Braga & Grepioni, 1992). The Mo atom is situated 1.908 (3) Å above the centre of the planar arene ring, which compares with 1.908 Å in $[\text{Mo}(\pi\text{-Mes})(\text{CO})_3]$, 1.923 Å in $[\text{Mo}(\text{hmb})(\text{CO})_3]$ (hmb = hexamethylbenzene) (Koshland, Myers & Chesick, 1977) and 1.897 (8) Å in $[\text{Mo}_2\{\text{P}(p\text{-tolyl})_3\}(\text{CO})_8]$. The Mo—C(arene) distances are in the range 2.351 (5)–2.388 (5) Å [average 2.373 (5) Å], in good agreement with values reported for similar complexes [*e.g.* 2.365 (3) Å for the toluene complex (Braga & Grepioni, 1990)].

The tricarbonyl moiety is only 4° from a fully staggered orientation (which corresponds to a 26° rotation from a fully eclipsed conformation); the corresponding values in the toluene complex are 2 and 28° , respectively. In the phenyl ring, the bond lengths fall into two types: those that intersect with the projection of the Mo—C—O bonds have an average value of 1.429 (9) Å, while the other three have an average value of 1.391 (8) Å. A similar situation was found for the isostructural chromium complex and also in other tricarbonylmolybdenum-arene complexes.

The Si atom is in a slightly distorted tetrahedral configuration with the mean C(arene)—Si—C(methyl) angle $[108.4(3)^\circ]$ less than the mean C(methyl)—Si—C(methyl) angle of $110.5(4)^\circ$. Unlike the chromium analogue (in which the Si atom is located 0.020 Å from the aromatic ring plane in the direction of the Cr atom), the Si atom is not displaced significantly from the aromatic ring plane in the present case $[0.008(8) \text{ Å}]$. The Si—C(ring) distance of 1.881 (5) Å is significantly longer than the Si—C(methyl) distances [average 1.848 (8) Å] found in all other trimethylsilicon-arene complexes. The angles around the arene atom C11 sum to $360.0(4)^\circ$ but the internal C12—C11—C16 angle $[116.6(5)^\circ]$ is considerably smaller than the two exocyclic Si—C11—C(arene) angles [mean $121.7(4)^\circ$]. The intermolecular distances correspond to normal van der Waals contacts.

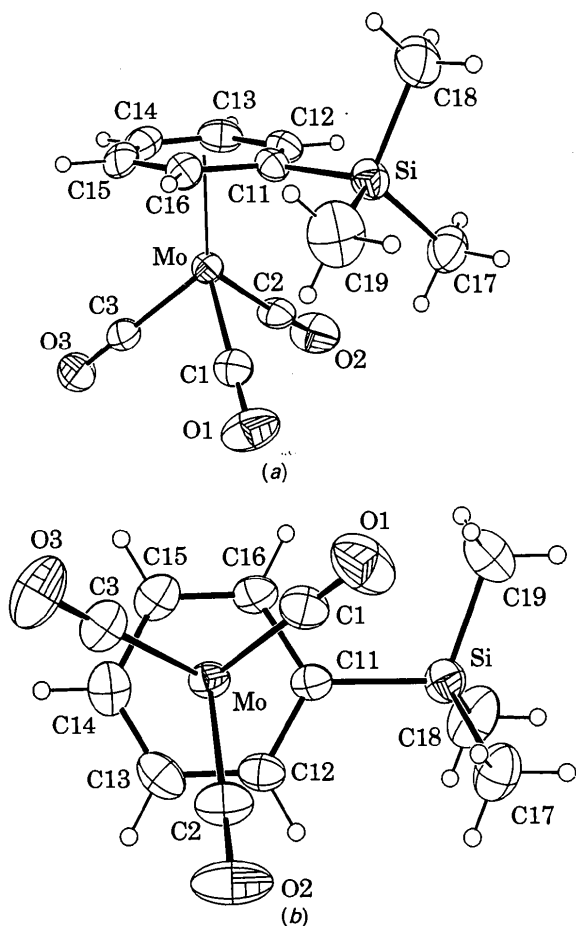


Fig. 1. ORTEP plots of (1) showing the crystallographic numbering scheme: (a) a general view and (b) a view normal to the aromatic ring plane. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level while, for clarity, H atoms are drawn as small spheres of arbitrary size.

Data collection

Enraf-Nonius CAD-4
diffractometer
 $\theta/2\theta$ scans
Absorption correction:
empirical
 $T_{\min} = 0.588$, $T_{\max} = 0.692$
3094 measured reflections
3094 independent reflections

2729 observed reflections
[$I_{\text{net}} > 3.0\sigma(I_{\text{net}})$]
 $\theta_{\max} = 27.00^\circ$
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 8$
 $l = -21 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity variation: 2.5%

Refinement

Refinement on F
 $R = 0.053$
 $wR = 0.075$
 $S = 1.92$
2729 reflections
154 parameters
 $w = 1/[\sigma^2(F) + 0.0012F^2]$

$\Delta\rho_{\max} = 1.63 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.38 \text{ e } \text{\AA}^{-3}$
($\Delta\rho_{\min}$, $\Delta\rho_{\max}$ adjacent to the Mo atom)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

| | x | y | z | U_{eq} |
|-----|--------------|--------------|---------------|-----------------|
| Mo | 0.25429 (5) | 0.45886 (5) | 0.165675 (23) | 0.0435 (3) |
| Si | 0.2732 (3) | 0.69730 (24) | 0.36376 (9) | 0.0585 (8) |
| O1 | -0.0303 (10) | 0.2590 (9) | 0.2983 (4) | 0.104 (4) |
| O2 | 0.6127 (8) | 0.0638 (7) | 0.1683 (4) | 0.107 (4) |
| O3 | 0.0545 (11) | 0.2677 (8) | 0.0448 (3) | 0.098 (4) |
| C1 | 0.0738 (9) | 0.3329 (8) | 0.2489 (4) | 0.060 (3) |
| C2 | 0.4750 (9) | 0.2057 (8) | 0.1681 (4) | 0.064 (3) |
| C3 | 0.1288 (10) | 0.3394 (8) | 0.0892 (4) | 0.062 (3) |
| C11 | 0.2892 (7) | 0.7103 (7) | 0.2499 (3) | 0.0471 (23) |
| C12 | 0.4871 (8) | 0.6417 (8) | 0.1987 (4) | 0.056 (3) |
| C13 | 0.5047 (10) | 0.6525 (9) | 0.1126 (4) | 0.067 (3) |
| C14 | 0.3231 (12) | 0.7271 (9) | 0.0769 (4) | 0.069 (4) |
| C15 | 0.1202 (10) | 0.8013 (7) | 0.1263 (4) | 0.060 (3) |
| C16 | 0.1037 (8) | 0.7926 (7) | 0.2103 (3) | 0.053 (3) |
| C17 | 0.4317 (13) | 0.4468 (10) | 0.3937 (4) | 0.083 (4) |
| C18 | 0.3862 (17) | 0.9008 (12) | 0.3909 (6) | 0.101 (6) |
| C19 | -0.0099 (14) | 0.7413 (18) | 0.4123 (5) | 0.111 (6) |

Experimental

The title compound was synthesized by the reaction of [Mo(py)₃(CO)₃] with Me₃SiPh in the presence of 3 equivalents of BF₃·Et₂O in diethyl ether and was recrystallized from a diethylether-hexane (1:5 v/v) mixture at 273 K.

Crystal data

[Mo(C₉H₁₄Si)(CO)₃]

$M_r = 330.26$

Triclinic

$P\bar{1}$

$a = 6.5051 (11) \text{ \AA}$

$b = 6.8828 (18) \text{ \AA}$

$c = 16.681 (3) \text{ \AA}$

$\alpha = 86.036 (16)^\circ$

$\beta = 79.892 (18)^\circ$

$\gamma = 75.458 (18)^\circ$

$V = 711.5 (3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.542 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 20.50\text{--}27.00^\circ$

$\mu = 0.98 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Needle

$0.15 \times 0.15 \times 0.50 \text{ mm}$

Yellow

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------|------------|-------------|------------|
| Mo—C1 | 1.957 (6) | O2—C2 | 1.148 (7) |
| Mo—C2 | 1.963 (5) | O3—C3 | 1.150 (7) |
| Mo—C3 | 1.954 (6) | C11—C12 | 1.405 (7) |
| Si—C11 | 1.881 (5) | C11—C16 | 1.448 (7) |
| Si—C17 | 1.859 (7) | C12—C13 | 1.419 (9) |
| Si—C18 | 1.851 (8) | C13—C14 | 1.383 (10) |
| Si—C19 | 1.835 (8) | C14—C15 | 1.421 (9) |
| O1—C1 | 1.147 (8) | C15—C16 | 1.386 (8) |
| C1—Mo—C2 | 86.21 (24) | Mo—C2—O2 | 176.1 (5) |
| C1—Mo—C3 | 84.27 (25) | Mo—C3—O3 | 179.3 (5) |
| C2—Mo—C3 | 88.62 (25) | Si—C11—C12 | 120.5 (4) |
| C11—Si—C17 | 108.7 (3) | Si—C11—C16 | 122.9 (4) |
| C11—Si—C18 | 107.1 (3) | C12—C11—C16 | 116.6 (5) |
| C11—Si—C19 | 109.3 (3) | C11—C12—C13 | 121.8 (5) |
| C17—Si—C18 | 111.2 (4) | C12—C13—C14 | 120.0 (5) |
| C17—Si—C19 | 111.3 (5) | C13—C14—C15 | 120.1 (5) |
| C18—Si—C19 | 109.1 (5) | C14—C15—C16 | 119.8 (5) |
| Mo—C1—O1 | 179.2 (6) | C11—C16—C15 | 121.7 (5) |

Compound (1) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and this was confirmed by the successful refinement. All H atoms were clearly visible in difference maps; they

were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. Examination of the structure with *PLATON* (Spek, 1992) showed that there were no solvent-accessible voids in the crystal lattice. Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX* Patterson map. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*; *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* and *WP6.0*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71736 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1152]

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[Me₃PhN]₂[WCl₆] und [PPh₄]₂[W₂Cl₆O₂(μ-N)(μ-Cl₂PO₂)], ein μ-N-Nitrido-wolfram mit Dichlorophosphatbrücke

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Abstract

Trimethylphenylammonium hexachlorotungstate(IV), [C₉H₁₄N]₂[WCl₆], consists of octahedral anions that alternate with the cations in layers parallel to (100). In bis(tetraphenylphosphonium) μ-dichlorophosphinato-O:O'-μ-nitrido-bis[trichloro(oxo)tungstate], [C₂₄H₂₀P]₂[W₂Cl₆O₂(μ-N)(μ-Cl₂PO₂)], the anion contains two W atoms linked symmetrically by an N atom, forming a slightly bent W=N=W group with short bonds; in addition, the W atoms are bridged by a dichlorophosphate group, resulting in a six-membered ring.

Kommentar

Bei der Reaktion des Wolfram(VI)imidokomplexes [Cl₄-WNC(Cl)=C(H)CN]₂ (Wollert, 1992) mit Trimethylphenylammonium-chlorid in Acetonitril haben wir das Hexachlorowolfram(IV) [Me₃PhN]₂[WCl₆] (I) erhalten. Aus dem gleichen Imidokomplex entstand mit Tetraphenylphosphonium-chlorid im Beisein von POCl₃ und Spuren von Wasser das Ion [W₂Cl₆O₂(μ-N)(μ-Cl₂PO₂)]²⁻.

Im IR-Spektrum zeigt das WCl₆²⁻-Ion die beiden Absorptionsbanden der Rasse *F*_{1u}, die für ein oktaedrisches Ion zu erwarten sind, und zwar bei 285 cm⁻¹ (ν_{as}) und 158 cm⁻¹ (δ). Entsprechend der höheren negativen Ionenladung liegen diese Werte unter denen von WCl₆ (ν_{as} 367 cm⁻¹) und WCl₆⁻ (332 cm⁻¹). Im Kristall finden wir WCl₆²⁻-Ionen, die kaum nennenswert von der Oktaedersymmetrie abweichen. Die W—Cl-Bindungen sind im Mittel 2,375(1) Å lang (Tabelle 2), so wie bei anderen WCl₆²⁻-Salzen (Roesky, Mainz, Noltemeyer & Sheldrick, 1988); sie sind damit länger als im WCl₆⁻-Ion (2,25–2,33 Å; Eichler & Seifert 1977; El-Kholi & Müller, 1989; Uhl, Hey, Becker, Weller & Dehnicke, 1983). Kationen und Anionen wechseln sich schichtweise in Richtung [100] ab (Fig. 1).