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Note

Synthesis and characterization of organomolybdenum and organotungsten halides containing the η^5 -pentaphenylcyclopentadienyl ligand η^5 -C₅Ph₅Mo(CO)₃X · *n*CH₂Cl₂ and η^5 -C₅Ph₅W(CO)₃X (X = Cl, Br, I). The X-ray molecular structure of η^5 -C₅Ph₅Mo(CO)₃I · 0.5CH₂Cl₂

Li-Cheng Song ^{a,*}, Qing-Mei Hu ^a, Jin-Song Yang ^a, Xi-Chuan Cao ^a, Ru-Ji Wang ^b, Thomas C.W. Mak ^c

> ^a Department of Chemistry, Nankai University, Tianjin 300071, China ^b Department of Chemistry, Tsinghua University, Beijing 100084, China ^c Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract

Six new organomolybdenum and organotungsten halides with general formulas η^5 -C₅Ph₅Mo(CO)₃X·*n*CH₂Cl₂ and η^5 -C₅Ph₅W(CO)₃X (X = Cl, Br, I) were synthesized through the reaction of η^5 -C₅Ph₅M(CO)₃Li formed from η^5 -C₅Ph₅Li and M(CO)₆ with PCl₃, PBr₃ or I₂ and characterized by elemental analysis, IR, ¹H NMR and MS spectroscopies. The structure of η^5 -C₅Ph₅Mo(CO)₃I·0.5CH₂Cl₂ was determined by single-crystal X-ray diffraction techniques. It crystallized in the triclinic space group PI with cell parameters a = 8.476(2), b = 10.704(2), c = 19.075(4) Å, $\alpha = 84.20(3)$, $\beta = 88.42(3)$, $\gamma = 71.58(3)^\circ$, V = 1633.7(6) Å³; Z = 2 and $D_x = 1.616$ g cm⁻³. The final *R* value was 0.046 for 4161 observed reflections.

Keywords: Molybdenum complexes; Tungsten complexes; Cyclopentadienyl complexes; Carbonyl complexes; Crystal structures

1. Introduction

There has been much interest, since 1982, in the study of η^5 -pentaphenylcyclopentadienyl derivatives of the main group and transition metals, such as Na [1], Li [1], K [2], Mo [2], Sn [3], Co [4] and Rh [4]. The reason for such an interest is probably because derivatives with the η^5 -C₅Ph₅ ligand, in contrast to their counterparts of n^5 -Cp, n^5 -C₅Me₅ and η^5 -C₅Bz₅ ligands, usually possess novel structures and special physical and chemical properties [1-17]. In a previous paper [18], we reported the study of organomolybdenum and organotungsten halides containing the η^5 -C₅Bz₅ ligand. For comparative purposes, we recently initiated a study about organomolybdenum and organotungsten halides containing the π^5 -C₅Ph₅ ligand. Now, we present the results concerning this study, which include the synthesis and properties of Group 6 metal halides containing the η^5 -pentaphenylcyclopentadienyl ligand, η^5 -C₅Ph₅Mo(CO)₃X·nCH₂Cl₂ and η^5 - $C_{s}Ph_{s}W(CO)_{3}X$ (X = Cl, Br, I), as well as the X-ray

structural analysis for one representative example, η^5 -C₅Ph₅Mo(CO)₃I·0.5CH₂Cl₂.

2. Experimental

All reactions were carried out under highly purified tank nitrogen. Tetrahydrofuran (THF) and diglyme were rigorously dried and deoxygenated by distillation from sodium/ benzophenone ketyl. Column chromatography was carried out using silica gel of 300–400 mesh. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Strem Chemical Inc. C₃Ph₅H [4], n-BuLi/hexane [19,20] and C₃Ph₅Li [1] were prepared according to the literature methods. PCl₃, PBr₃ or I₂ were of commercial origin. IR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer. ¹H NMR spectra were recorded on a Jeol FX 90 Q NMR spectrometer. C/H analysis and MS determinations were performed by a Perkin-Elmer model 240C analyzer and an HP 5988A spectrometer, respectively. Melting points were determined on a Yanaco MP-500 apparatus.

^{*} Corresponding author.

2.1. Preparation of η^5 -C₅Ph₅Mo(CO)₃X · nCH₂Cl₂ (X = Cl, Br, I) (I–III)

A 100 ml two-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 0.892 g (2 mmol) of C₅Ph₅H and 20 ml of THF. The mixture was stirred and cooled to 0°C. Then, a 2.5 mmol solution of n-BuLi/hexane was added and the solution turned blue-green. After 5 h stirring, 0.528 g (2 mmol) of $Mo(CO)_6$ was added and the reaction mixture was refluxed for 22 h. The yellow-brown solution of the salt η^{5} -C₅Ph₅Mo(CO)₃Li was formed and then cooled to room temperature. To this salt a given amount of PCl₃, PBr₃ or I₂ was added and the mixture turned red-brown immediately. The reaction mixture was stirred for about 4 h. Solvent was removed at reduced pressure and the residue was extracted with CH₂Cl₂. The extracts were subjected to column chromatography. A red band was eluted with 1:3 (vol./vol.) CH_2Cl_2 /petroleum ether to give the corresponding crude product. All crude products were recrystallized from about 1:1 (vol./vol.) CH₂Cl₂/petroleum ether for m.p., C/H analysis, IR, ¹H NMR and MS determination. When 0.21 ml (2.4 mmol) of PCl₃ was added, 0.181 g of η^{5} - $C_5Ph_5Mo(CO)_3Cl \cdot 0.14CH_2Cl_2$ (I) was obtained in 14% yield; m.p. 168 °C (dec.), Anal. Found: C, 68.06; H, 3.74. Calc. for C₃₈H₂₅ClMoO₃ · 0.14CH₂Cl₂: C, 68.07; H, 3.79%. IR (KBr disc) (cm⁻¹): ν (C=O) 2048.8(s), 1983.2(vs), 1942.2(s). ¹H NMR (CDCl₃, δ (ppm)): 5.24 (s, 0.28H, 0.14CH₂Cl₂), 6.78–7.18 (m, 25H, 5C₆H₅). MS (EI, ⁹⁸Mo), m/z (relative intensity): 578 ($(M-3CO)^+$, 2.1), 445 $(C_5Ph_5^+, 4.7), 77 (Ph^+, 2.7), 28 (CO^+, 100).$

When 0.3 ml (2.4 mmol) of PBr₃ was added, 0.385 g η^5 -C₅Ph₅Mo(CO)₃Br (II) was obtained in 28% yield; m.p. 196 °C (dec.). Anal. Found: C, 64.47; H, 3.76. Calc. for C₃₈H₂₅BrMoO₃: C, 64.70; H, 3.57%. IR (KBr disc) (cm⁻¹): ν (C=O) 2038.4(vs), 1959.5(vs). ¹H NMR (CDCl₃, δ (ppm)): 6.80–7.20 (m, 25H, 5C₆H₅). MS (EI, ⁹⁸Mo), m/z (relative intensity): 651 ($(M - 2CO)^+$, 3.3), 445 (C₅Ph₅⁺, 100), 178 (MoBr⁺, 13.5), 98 (Mo⁺, 1.4), 80 (Br⁺, 2.3), 77 (Ph⁺, 18.3), 28 (CO⁺, 13.3).

When 0.584 g (2.3 mmol) of I₂ was added, 0.730 g of η^5 -C₅Ph₅Mo(CO)₃I·0.52CH₂Cl₂ (**III**) was obtained in 46% yield; m.p. 77 °C (dec.). *Anal.* Found: C, 58.37; H, 3.37. Calc. for C₃₈H₂₅IMoO₃·0.52CH₂Cl₂: C, 58.07; H, 3.30%. IR (KBr disc) (cm⁻¹): ν (C \equiv O) 2024.2(vs), 1959.6(vs), 1918.6(s). ¹H NMR (CDCl₃, δ (ppm)): 5.25 (s, 1.04H, 0.52CH₂Cl₂), 6.80–7.21 (m, 25H, 5C₆H₅). MS (EI, ⁹⁸Mo), *m/z* (relative intensity): 670 ((*M*-3CO)⁺, 0.9), 127 (I⁺, 0.3), 98 (Mo⁺, 0.6), 28 (CO⁺, 100).

2.2. Preparation of η^5 -C₅Ph₅W(CO)₃X (X = Cl, Br, I) (IV-VI)

A 100 ml two-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 0.904 g (2 mmol) of C_5Ph_5Li , 0.704 g (2 mmol) of W(CO)₆ and 20 ml of diglyme. The mixture was refluxed for 6 h. To this mixture, a given amount of PCl₃, PBr₃ or I₂ was added at 60 or 80 °C, and the mixture was stirred for 3 h. The work-up was the same as that in the preparation of **I–III**. When 0.21 ml (2.4 mmol) of PCl₃ was added and the reaction mixture was stirred at 60 °C, 0.042 g of η^5 -C₅Ph₅W(CO)₃Cl (**IV**) was obtained in 3% yield; m.p. 181 °C (dec.). Anal. Found: C, 61.09; H, 3.35. Calc. for C₃₈H₂₅ClO₃W: C, 60.94; H, 3.36%. IR (KBr disc) (cm⁻¹): ν (C \equiv O) 2040.6(s), 1958.6(vs), 1917.6(s). ¹H NMR (CDCl₃, δ (ppm)): 6.86–7.37 (m, 25H, 5C₆H₅). MS (EI, ¹⁸⁴W), *m/z* (relative intensity): 694 ((*M*-2CO)⁺, 1.4), 666 ((*M*-3CO)⁺, 1), 445 (C₅Ph₅⁺, 20.1), 219 (WCl⁺, 0.8), 77 (Ph⁺, 100), 28 (CO⁺, 50.6).

When 0.3 ml (2.4 mmol) of PBr₃ was added and the reaction mixture was stirred at 80 °C, 0.305 g of η^5 -C₅Ph₅W(CO)₃Br (V) was obtained in 19% yield; m.p. 105 °C (dec.). *Anal.* Found: C, 57.59; H, 3.43. Calc. for C₃₈H₂₅BrO₃W: C, 57.52; H, 3.18%. IR (KBr disc) (cm⁻¹): ν (C \equiv O) 2032.4(vs), 1958.6(vs), 1917.6(s). ¹H NMR (CDCl₃, δ (ppm)): 6.98–7.31 (m, 25H, 5C₆H₅). MS (EI, ¹⁸⁵W), *m*/*z* (relative intensity): 710 ((*M* – 3CO)⁺, 1), 445 (C₅Ph₅⁺, 1), 80 (Br⁺, 0.9), 77 (Ph⁺, 5.3), 28 (CO⁺, 100).

When 0.584 g (2.3 mmol) of I₂ was added and the reaction mixture was stirred at 80 °C, 0.623 g of η^5 -C₅Ph₅W(CO)₃I (**VI**) was obtained in 37% yield; m.p. 191 °C (dec.). Anal. Found; C, 54.19; H, 3.00. Calc. for C₃₈H₂₅IO₃W: C, 54.31; H, 3.00%. IR (KBr disc) (cm⁻¹): ν (C=O) 2024.2(s), 1942.2(vs), 1925.8(s). ¹H NMR (CDCl₃, δ (ppm)): 6.82– 7.16 (m, 25H, 5C₆H₅). MS (EI, ¹⁸⁴W), m/z (relative intensity): 812 ((M-CO)⁺, 22.1), 756 ((M-3CO)⁺, 62.9), 445 (C₅Ph₅⁺, 8.4), 311 (WI⁺, 26), 127 (I⁺, 0.6), 77 (Ph⁺, 13.2).

2.3. Single-crystal structure determination of η^5 -C₅Ph₅Mo(CO)₃I \cdot 0.5CH₂Cl₂ (**III**)

Crystals suitable for X-ray diffraction were obtained by recrystallization from 1:1 (vol./vol.) CH₂Cl₂/petroleum ether in a refrigerator. An orange-red crystal measuring $0.30 \times 0.30 \times 0.40$ mm was mounted on a glass fiber and placed on a Siemens P4/PC four-circle diffractometer. A total of 5740 independent reflections was collected at room temperature with Mo K α (λ =0.71073 Å) radiation by ω -2 θ scan in the range of $4 \le 2\theta \le 50^{\circ}$, of which 4161 reflections with $I \ge 3\sigma(I)$ were considered to be observed. Data were corrected for Lp factors and empirical absorption corrections were applied using Ψ -scan data. The crystal is triclinic, space group $P\overline{1}$, with a=8.476(2), b=10.704(2), c=19.075(4) Å, α =84.20(3), β =88.42(3), γ =71.58(3)°, V= 1633.7(6) Å³; Z=2; D_x =1.616 g cm⁻³; F(000)=786.

Patterson superposition yielded the positions of all nonhydrogen atoms, which were subjected to anisotropic refinement. All hydrogen atoms of the organic ligand were generated geometrically (C-H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms. They were assigned to the same isotropic temperature factors (U=0.08Å²) and included in the structure-factor calculations. There was a disordered solvent molecule of CH₂Cl₂ in the cell, which was represented by C(39) and Cl(1) with the site occupancy factor of 0.5. The final refinement was carried out by the full-matrix least-squares method for the coordinates and anisotropic thermal parameters of non-hydrogen atoms and converged to give unweighted and weighted *R* factors of 0.046 and 0.044. The highest peak on the final difference Fourier map had a height of 0.75 e Å⁻³. Computations were performed using the SHELXTL PC program package on a PC 486 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [21].

3. Results and discussion

3.1. Synthesis and characterization

We found that when an equimolar amount of $M(CO)_6$ (M=Mo, W) was added to a THF or diglyme solution of (pentaphenylcyclopentadienyl)lithium, prepared from pentaphenylcyclopentadiene and n-BuLi/hexane, the salts of η^5 - $C_5Ph_5M(CO)_3Li$ (M=Mo, W) could be formed. Further treatment of such intermediate salts with halogenating agents such as PCl₃, PBr₃ and I₂ afforded, after recrystallization of the crude products from a mixed solvent of CH₂Cl₂ and petroleum ether, the respective pure organomolybdenum or organotungsten halides η^5 -C₅Ph₅Mo(CO)₃X · *n*CH₂Cl₂ (I-III) and η^5 -C₅Ph₅W(CO)₃X (IV-VI), as shown in Scheme 1.

These new products were characterized by combustion analysis, IR, ¹H NMR and mass spectroscopies, whose data are consistent with the structures shown in Scheme 1. In the IR spectra of I–VI there are two to three absorption bands in the range 1917–2049 cm⁻¹, indicating the terminal carbonyls present in these molecules. The maximum ν (C=O) values of I–VI, like those of the counterparts containing the η^5 -C_sBz_s ligand [18], exhibit a decreasing tendency in the order:





chloride > bromide > ide for the molybdenum and tungsten series, respectively. This is presumably due to the decreasing electronegativity of the halogens in the same order and in turn the increasing π -backbonding between metal and terminal carbonyls [22]. The ¹H NMR spectra of I and III show a singlet for the solvent CH₂Cl₂ at 5.24 ppm besides a multiplet for the Ph₅C₅ ligand between 6.78 and 7.30 ppm, whereas each spectrum of II and IV-VI only exhibits a multiplet for the Ph₅C₅ ligand between 6.82 and 7.37 ppm. So, molybdenum halides I and III, in contrast to their analogs II and IV-VI and their counterparts containing the η^5 -Bz₅C₅ ligand [18], are inclined to be combined with solvent molecules such as CH_2Cl_2 . It is noteworthy that the molecules of CH₂Cl₂ in halides I and III are too difficult to be removed completely by evacuation under high vacuum but can be replaced easily by other polar solvents, such as acetone, through recrystallization of I and III from acetone. Examples of the ¹H NMR spectra for such solvates are given in Fig. 1.

Although the mass spectra of I-VI do not show their respective parent ion, they do show their corresponding fragment ions of $M^+ - nCO$ (usually n = 2 or 3), and the other ions such as the ligand ions $C_5Ph_5^+$ and CO^+ . It is noteworthy that the overall yields of I-VI, just like in the case of η^5 - $C_5Bz_5M(CO)_3X$ [18], are quite low (3-28%) for the chlo-



Fig. 1. ¹H NMR spectra for some solvates.

rides and bromides I–II and IV–V. However, the overall yields of iodides III and VI, in contrast to the case of η^5 -C₅Bz₅M(CO)₃X [18], are much improved (46 and 37%, respectively).

3.2. Crystal structure

In order to further confirm the structure of I–VI and to compare them with their counterparts η^5 -C₅Bz₅M(CO)₃X structurally, an X-ray single-crystal diffraction study of III was undertaken. The atomic coordinates and equivalent iso-

Table 1

Atomic coordinates ($\times10^5$ for Mo and I; 10^4 for others) and equivalent isotropic temperature factors a ($\times10^4$ for Mo and I; 10^3 for others) for III

Atom	x	у	Z	U _{eq} ^a
Mo(1)	1241(6)	20943(5)	20919(3)	368(2)
I(1)	-29164(6)	29760(5)	28601(3)	790(2)
O(1)	-2387(6)	4117(4)	1017(3)	89(1)
O(2)	-847(5)	-462(4)	2549(3)	91(1)
0(3)	478(5)	610(4)	749(2)	69(1)
C(1)	-1560(7)	3412(6)	1398(3)	63(1)
C(2)	-565(6)	492(5)	2397(3)	59(1)
C(3)	344(6)	1160(5)	1250(3)	49(1)
C(4)	2086(5)	1884(4)	2998(3)	37(1)
C(5)	2903(5)	1172(4)	2422(3)	34(1)
C(6)	2813(5)	2117(4)	1818(3)	32(1)
C(7)	1964(5)	3408(4)	2027(3)	36(1)
C(8)	1562(5)	3265(4)	2757(3)	36(1)
C(9)	2172(6)	1293(5)	3750(3)	40(1)
C(10)	1651(7)	201(5)	3959(3)	58(1)
C(11)	1853(7)	-365(6)	4646(3)	71(1)
C(12)	2564(7)	148(6)	5138(3)	69(1)
C(13)	3101(7)	1221(6)	4955(3)	63(1)
C(14)	2910(6)	1798(5)	4250(3)	49(1)
C(15)	3910(5)	-271(4)	2498(3)	35(1)
C(16)	5304(6)	-643(5)	2940(3)	52(1)
C(17)	6316(6)	- 1933(5)	3027(3)	63(1)
C(18)	5974(7)	-2878(5)	2683(3)	62(1)
C(19)	4626(7)	-2536(5)	2238(3)	60(1)
C(20)	3582(6)	-1231(5)	2142(3)	47(1)
C(21)	3715(6)	1836(5)	1139(3)	39(1)
C(22)	2981(6)	2372(5)	487(3)	41(1)
C(23)	3907(6)	2171(5)	-128(3)	52(1)
C(24)	5549(6)	1408(5)	-94(3)	55(1)
C(25)	6295(6)	869(5)	550(3)	52(1)
C(26)	5381(6)	1088(5)	1170(3)	41(1)
C(27)	1726(6)	4693(5)	1587(3)	41(1)
C(28)	3033(6)	4898(5)	1192(3)	49(1)
C(29)	2840(7)	6085(5)	793(3)	64(1)
C(30)	1352(8)	7092(5)	789(3)	76(1)
C(31)	72(7)	6915(5)	1193(3)	70(1)
C(32)	225(7)	5723(5)	1586(3)	56(1)
C(33)	1036(6)	4394(5)	3209(3)	41(1)
C(34)	- 191(6)	4505(5)	3726(3)	51(1)
C(35)	-531(7)	5537(6)	4149(3)	64(1)
C(36)	326(7)	6438(5)	4068(3)	67(1)
C(37)	1544(7)	6320(5)	3572(3)	66(1)
C(38)	1899(7)	5307(5)	3142(3)	56(1)
Cl(1)	5524(5)	3707(4)	4910(3)	262(1)
C(39)	4713(10)	4760(9)	5516(7)	145(1)

^a U_{eq} defined as one third of the trace of the orthogonalized U tensor.

tropic temperature factors are given in Table 1. Selected bond lengths and angles are listed in Table 2 and Table 3, respectively. Fig. 2 presents an ORTEP drawing of the structure of III.

As seen from Fig. 2 this molecule is very similar to its η^{5} - $C_5Bz_5Mo(CO)_3I$ counterpart [18], which, if all the phenyl substituents attached to the cyclopentadienyl ring are ignored, is like a four-legged piano-stool. The bond length of Mo-I in this molecule is 2.866(1) Å, almost the same as that of η^{5} - $C_{5}Bz_{5}Mo(CO)_{3}I(2.8501(8) \text{ Å})$ [18]. The Mo-cyclopentadienyl centroid distance in this molecule is 2.042(6) Å, also almost the same as that of η^5 -C₅Bz₅Mo(CO)₃I (2.022) Å) [18]. However, in contrast to the distribution of the five benzyl groups being above and below the cyclopentadienyl plane of η^5 -C₅Bz₅Mo(CO)₃I [18], the five phenyl substituents of **III** are all bisected by the parent cyclopentadienyl plane and arranged in a propeller orientation. This orientation was also encountered in the cobalt compound containing the pentaphenylcyclopentadienylligand η^5 -C₅Ph₅Co(CO)₂[4]. The five phenyl substituents in III are canted relative to the cyclopentadienyl ring by an angle of 45.5-65.4°, whereas

Table 2					
Selected	bond	lengths	(Å)	for	ш

Mo(1)-I(1)	2.866(1)	Mo(1)-C(1)	2.057(5)
Mo(1)-C(2)	2.009(6)	Mo(1)-C(3)	1.951(6)
Mo(1)-C(4)	2.376(5)	Mo(1)-C(5)	2.325(4)
Mo(1)-C(6)	2.331(5)	Mo(1)-C(7)	2.401(5)
Mo(1)-C(8)	2.457(6)	Mo(1)–Cp ^a	2.042(6)
C(4) - C(5)	1.434(7)	C(4)-C(8)	1.432(6)
C(4)-C(9)	1.502(7)	C(5)-C(6)	1.441(7)
C(5)-C(15)	1.505(6)	C(6)-C(7)	1.433(6)
C(6)-C(21)	1.493(7)	C(7)-C(8)	1.430(7)
C(7)–C(27)	1.495(7)	C(8)-C(33)	1.500(7)
O(1)-C(1)	1.083(7)	O(2)-C(2)	1.129(8)
O(3)-C(3)	1.157(8)	Cl(1)-C(39)	1.68(1)
C(39)-Cl(1a)	1.71(1)		

^a Cp is the center of the five-membered ring composed of the C(4)-C(8) atoms. Symmetry transformation: a = (1 - x, 1 - y, 1 - z).

 Table 3

 Selected bond angles (°) for III

I(1)-Mo(1)-C(1)	74.1(2)	I(1)-Mo(1)-C(2)	72.8(1)
C(1)-Mo(1)-C(2)	111.8(2)	I(1)-Mo(1)-C(3)	123.5(2)
C(1)-Mo(1)-C(3)	76.4(2)	C(2)-Mo(1)-C(3)	75.2(3)
I(1)-Mo(1)-Cp *	121.9(2)	C(1)-Mo(1)-Cp	123.7(2)
C(2)-Mo(1)-Cp	124.5(2)	C(3)-Mo(1)-Cp	114.6(2)
C(5)-C(4)-C(8)	107.7(4)	C(5)-C(4)-C(9)	124.2(4)
C(8)-C(4)-C(9)	126.4(4)	C(4) - C(5) - C(6)	108.0(4)
C(4)-C(5)-C(15)	123.9(4)	C(6)-C(5)-C(15)	127.4(4)
C(5)-C(6)-C(7)	107.8(4)	C(5)-C(6)-C(21)	125.9(4)
C(7)-C(6)-C(21)	125.3(4)	C(6)-C(7)-C(8)	107.9(4)
C(6)-C(7)-C(27)	126.2(4)	C(8)-C(7)-C(27)	125.5(4)
C(4)-C(8)-C(7)	108.5(4)	C(4)-C(8)-C(33)	126.5(4)
C(7)-C(8)-C(33)	123.7(4)	Mo(1)-C(1)-O(1)	176.7(6)
Mo(1)-C(2)-O(2)	175.0(4)	Mo(1)-C(3)-O(3)	179.7(5)
Cl(1)-C(39)-Cl(1a)	104.7(7)		

^a Cp is the center of five-membered ring composed of C(4)-C(8) atoms. Symmetry transformation: a = (1-x, 1-y, 1-z).



Fig. 2. ORTEP drawing of **III** showing the atomic-labeling scheme and thermal motion ellipsoids (35%).



Fig. 3. Molecular packing of III viewed along the a axis.

those of η^5 -C₅Ph₅Co(CO)₂ are canted by an angle of 50.4– 68.2° [4]. Both sets of the twist angles for such two compounds are close, but much larger than those of η^3 -C₃Ph₃Co(CO)₃ ranging from 2.9 to 23.5° [23] and $(\eta^4$ -C₄Ph₄) (η^5 -C₅H₅)Co ranging from 31.6 to 41.7° [24]. Obviously, the increase of the twist angles in the order of η^3 -C₃Ph₃Co(CO)₃ < (η^4 -C₄Ph₄) (η^5 -C₅H₅)Co < III and η^5 -C₃Ph₅Co(CO)₂ is due to increasing the steric crowding in the same order. Also similar to η^5 -C₅Ph₅Co(CO)₂, the phenyl *ipso* carbons in III are above the cyclopentadienyl plane and away from the molybdenum atom by an average of 0.27 Å, ranging from 0.10 to 0.34 Å, while ranging from 0.02 to 0.19 Å for η^5 -C₅Ph₅Co(CO)₂ [4].

Finally, it should be pointed out that the crystal of III consists of discrete molecules of η^5 -Ph₅C₅Mo(CO)₃I and disordered solvent molecules, CH₂Cl₂, in the ratio of 2:1. They are separated by normal van der Waals distances, as shown in Fig. 3.

4. Supplementary material

Complete lists of bond lengths and angles, anisotropic thermal parameters of the non-hydrogen atoms, and structure factors for **III** are available from the authors.

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