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Photochemical Reaction of $Os_3(CO)_{12}$ with Diphenylacetylene: Synthesis and Structure of Tricarbonyl(η^4-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one)osmium

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*Summary: Photolysis of $Os_3(CO)_{12}$ in the presence of excess diphenylacetylene gives the title compound (η^4-C_4Ph_4CO)$Os(CO)_3$ (**1c**) in moderate yields. Compound **1c** represents the hitherto missing member of the iron-triad (η^4-C_4Ph_4CO)$M(CO)_3$ series. The solid-state structure of **1c** was determined and compared to that of the ruthenium analogue. A triad comparison of the spectroscopic features (^{13}C NMR and CO stretching frequencies) is presented. The order of the ^{13}C coordination shifts, inner diene carbons > outer diene carbons, is the reverse of what is typically seen for (η^4-diene)$M(CO)_3$ complexes. This is explained by polarization of the ketonic carbonyl upon coordination. The "second-row anomaly" of ruthenium is reflected in the spectroscopic data; accordingly, the ruthenium complex is the most reactive in the triad.*

The reaction of alkynes with iron carbonyls has been extensively investigated for almost 40 years.[1] A commonly observed product in these reactions is (cyclopentadienone)-tricarbonyliron type complexes, (η^4-CPD)$Fe(CO)_3$ (**1a**; CPD = substituted cyclopentadienones). Although the analogous ruthenium complexes are rare,[2,3] interest in their chemistry has been heightened by recent reports which showed that tricarbonyl(tetraphenylcyclopentadienone)-ruthenium, (η^4-Ph_4C_4CO)$Ru(CO)_3$ (**1b**), is a useful and versatile catalyst precursor for a variety of chemical transformations[4] and that it displays unusual reactivity.[5] Surprisingly, the preparation of the analogous osmium derivative has hitherto not been reported.

In this paper we describe the synthesis of (η^4-Ph_4C_4CO)$Os(CO)_3$ (**1c**). The solid-state X-ray structure of the complex has also been determined for comparison with the isoelectronic ruthenium relative.[6]

Results and Discussion

Photolysis of $Os_3(CO)_{12}$ in the presence of a large excess of diphenylacetylene leads to the formation of (η^4-Ph_4C_4CO)$Os(CO)_3$ (**1c**) (eq 1). Simple workup allows the isolation of **1c** in moderate yield. The use of a large excess of diphenylacetylene is important; otherwise, a mixture of products is obtained.[7]

$$Os_3(CO)_{12} + \text{excess } PhC{\equiv}CPh \xrightarrow[CH_2Cl_2,\ \text{room temp}]{h\nu,\ \lambda > 370\ \text{nm}} (\eta^4\text{-}Ph_4C_4CO)Os(CO)_3 \quad (1)$$

$$\mathbf{1c}\ (41\%)$$

The spectral characteristics of **1c** are in harmony with its formulation. The mass spectrum of the compound shows a molecular ion, followed by the successive loss of three carbonyl ligands. The spectroscopic data, ^{13}C NMR and IR, on compound **1c** are collected in Table 1. For ease of comparison the same data for the analogous iron (**1a**) and ruthenium (**1b**) derivatives are shown also. The ^{13}C NMR spectrum of **1c** shows the requisite number of signals for the organic fragment, with the bound diene portion exhibiting characteristic upfield coordination shifts.[8] The three carbonyl ligands show a single, averaged signal at 173.6 ppm down to −60 °C, consistent with rapid carbonyl group scrambling,[9] as observed also for **1a** and **1b**. The infrared spectrum of the compound displays three bands in the terminal CO stretching region. Two of these bands are closely spaced (2015 and 1997 cm^{-1}) as a result of their degenerate e-mode origin under local C_{3v} symmetry. As the local symmetry of the $M(CO)_3$ fragment changes to C_s, the band splits; the splitting reflects the degree of distortion from C_{3v} symmetry. The ketonic stretching band of the CPD ligand undergoes a characteristic red shift as the solvent polarity increases and is lowered from 1677 cm^{-1} in cyclohexane to 1646 cm^{-1} in CH_2Cl_2 solution.

To further corroborate the structure and to provide precise metrical comparison with the catalytically active ruthenium analogue, the X-ray molecular structure of **1c** was determined. A view of the molecule, with numbering scheme, is shown in Figure 1. Table 2 provides a list of pertinent bond distances and angles, and for ease of comparison, the corresponding data for **1b** are also given. The structure clearly reveals the now-classical geometry and bonding of (η^4-diene)$M(CO)_3$ type complexes.[10] The geometry around osmium is best described as tetragonal

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Table 1. Spectroscopic Data for (η^4-C_4Ph_4CO)$M(CO)_3$ (M = Fe, Ru, Os) Complexes

	^{13}C chem shifts (δ, ppm)[a]						CO stretching freq (ν_{CO}, cm^{-1})[b]			
Me	inner	outer	C=O	M(CO)	Δ(inner)	Δ(outer)	M(CO)			C=O
Fe	104.7	83.0	170.6	209.2	50.4	42.8	2060	2015	1988	1642
Ru	108.4	82.6	174.7	195.0	46.7	43.2	2081	2026	2005	1657
Os	104.5	79.0	175.4	174.7	50.6	46.8	2079	2015	1997	1677

[a] Chemical shifts are relative to TMS in CD_2Cl_2. "Inner" and "outer" refer to the carbon atoms that belong to the closed and open ends of the 1,3-dienes, respectively. Δ refers to the difference between free and complexed ligands; a positive number indicates an upfield coordination shift. The ^{13}C chemical shifts of the free ligand and those of the Fe and Ru complexes have been reported: Knothe, L.; Prinzbach, H.; Fritz, H. *Justus Liebigs Ann. Chem.* **1977**, 687. Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140. For the sake of consistency the ^{13}C NMR spectra of all three compounds and that of the free ligand (δ_{inner} 155.1, δ_{outer} 125.8, $\delta_{C=O}$ 200.7) were recorded in CD_2Cl_2 at room temperature. The listed values are in satisfactory agreement with previous values (maximum difference 1.0 ppm). [b] Solvent cyclohexane.

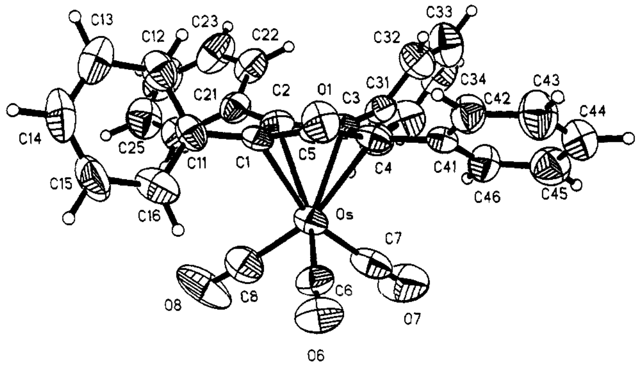

Figure 1. ORTEP view of the solid-state structure of **1c**·1.5C_6H_{12}. Probability ellipsoids at the 50% level are shown for non-hydrogen atoms. Cyclohexane molecules of solvation have been omitted for clarity.

Table 2. Selected Bond Distances (Å) for (η^4-C_4Ph_4CO)$M(CO)_3$ (M = Os (1c), Ru (1b)) and Angles (deg) for 1c

Bond Distances

	1c	1b[a]
M-C(1)	2.230(11)[b]	2.240(3)
M-C(2)	2.231(12)	2.209(3)
M-C(3)	2.199(12)	2.216(3)
M-C(4)	2.265(11)	2.216(3)
M-C(6)	1.919(14)	1.953(4)
M-C(7)	1.961(15)	1.911(3)
M-C(8)	1.929(15)	1.926(4)
C(1)-C(2)	1.480(18)	1.438(4)
C(2)-C(3)	1.428(15)	1.437(4)
C(3)-C(4)	1.456(17)	1.455(4)
C(1)-C(5)	1.509(16)	1.491(4)
C(4)-C(5)	1.546(15)	1.485(4)
C(5)-O(1)	1.207(15)	1.224(4)
C(6)-O(6)	1.142(18)	1.119(4)
C(7)-O(7)	1.109(19)	1.138(4)
C(8)-O(8)	1.147(19)	1.132(4)

Bond Angles

C(6)-Os-C(7)	96.2(6)	C(1)-C(2)-C(3)	107.1(10)
C(6)-Os-C(8)	93.9(6)	C(2)-C(3)-C(4)	111.6(10)
C(7)-Os-C(8)	91.1(6)	C(3)-C(4)-C(5)	105.1(9)
Os-C(6)-O(6)	175.5(12)	C(4)-C(5)-C(1)	103.5(9)
Os-C(7)-O(7)	175.4(16)	C(5)-C(1)-C(2)	107.4(9)
Os-C(8)-O(8)	175.7(13)	C(1)-C(5)-O(1)	127.8(10)
		C(4)-C(5)-O(1)	128.5(10)

[a] From ref 6. [b] Esd's are given in parentheses.

pyramidal with two terminal carbonyl groups and the midpoints of the η^4-bonded CPD double bonds providing the basis of the pyramid while the apical coordination position is occupied by the carbonyl ligand, C(6)O(6). The latter is directed toward the "open" end of the bound diene and approximately eclipses the CPD carbonyl group. The dihedral angle between C(6)O(6) and C(5)O(1) is 9.4°, compared to 7.0° in **1b**. Not unexpectedly, comparison between **1c** and **1b** reveals that the respective bond distances, with some minor variations, are rather similar. The values of both M–C and C–C distances are close, as is the nonbonding interaction between the respective metals and the ketonic carbon C(5) (2.563(10) Å in the present case and 2.530(3) Å in **1b**). The C–C distances of the diene portion in **1c** range from 1.438(15) to 1.480(18) Å (in **1b** the range is 1.437(4)–1.455(4) Å). There is perhaps a somewhat more regular long–short–long bond alternation of the bound diene system in **1c**, which implies a stronger Os-to-CPD back-donation in this compound. Another measure of this interaction is the deviation of the ring from planarity and the lengthening of the C–C distances involving the CPD–carbonyl group upon coordination. The bending of the ring carbonyl from the 1,3-diene portion in **1c** is 20.4°, slightly larger than the 18.7° observed in **1b**. Similarly, the C–C distances involving C(5) in **1c** (1.509(16) and 1.546(15) Å) appear to be longer than in **1b** (1.491(4) and 1.485(4) Å), with a concomitant shortening of the C(5)–O(1) ketonic carbonyl bond (1.207(15) Å in **1c** and 1.224(4) Å in **1b**). It is interesting to note that although all the above criteria indicate a somewhat stronger metal-to-CPD back-donation in **1c** relative to the analogous ruthenium complex, there is no evidence for a corresponding weakening of the back-donation to the carbonyl ligands. In particular, there is no lengthening of the apical Os–C(6) bond relative to the other osmium–carbonyl distances. Such lengthening is a documented distortion in the analogous ruthenium complex **1b** and was used to support the required greater lability of one of the carbonyl ligands in **1b** to initiate its catalytic activity.

Since it is well recognized that IR and NMR features are much more sensitive to subtle changes in bonding than X-ray-determined distances, a closer examination of the spectral data is warranted. Furthermore, the availability of all three iron-triad derivatives offers an opportunity to gauge how the metal-dependent spectral changes reflect conventional bonding arguments.

As mentioned already and shown in Table 1, the bound diene portion of the CPD ligand exhibits upfield coordination shifts. The magnitude of the coordination shift for the inner carbon atoms is similar to those observed in typical (η^4-diene)$M(CO)_3$ (M = Fe, Ru, Os) complexes.[11] However, the shielding of the outer carbon atoms is considerably less.[11] Indeed, the order Δ(inner) > Δ(outer) observed with (η^4-CPD)$M(CO)_3$ complexes is the reverse of what is typically seen in (η^4-diene)$M(CO)_3$ derivatives. The difference between the two classes of compounds is the presence of the conjugated ketonic carbonyl group;

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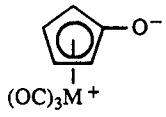
[11] Zobl-Ruh, S.; von Philipsborn, W. *Helv. Chim. Acta* **1980**, *63*, 773. The coordination shifts in (η^4-butadiene)$M(CO)_3$ are as follows: Δ(inner) *ca.* 50 ppm; Δ(outer) 76.5 (Fe), 85.5 (Ru), and 92.8 ppm (Os).

polarization of this functionality upon coordination is the most plausible reason for the substantive reduction of the coordination shift of the outer carbon atoms in compounds **1**. Polarization of the ketonic carbonyl group in **1a** and **1b** was noted by Shvo.[6] It is evidenced in compound **1c** by the *ca.* 30 ppm upfield shift of the ketonic carbon atom and the significant shift of the ketonic infrared stretching to lower wavenumbers relative to the free ligand, tetraphenylcyclopentadienone ($\nu_{C=O}$ 1712 cm^{-1}).



The polarization argument and the resulting contribution from the charge-separated structure to the bonding also account for the higher metal–carbonyl stretching frequencies observed in compounds **1** compared to typical (η^4-diene)M(CO)$_3$ molecules.[12]

The infrared stretching frequency and the ^{13}C chemical shift of the ketonic carbonyl group both increase in the order Fe < Ru < Os. A similar trend has been seen by Shvo in a series of substituted (η^4-CPD)Ru(CO)$_3$ complexes and has been attributed to a reduction in the polarization of the coordinated CPD ring within the series. An anticipated result of the decreased polarization is an increase in the diene–M interaction. This expectation is corroborated by the increased shielding of the outer carbons of the coordinated CPD ligand from Fe to Os (Table 1), a trend which is consistent with increasing rehybridization of the carbon atoms toward sp^3 and mirrored by the X-ray results, which show increasing bending of the ring carbonyl (Fe ≈ Ru < Os). It must be noted that the ^{13}C coordination shift of the inner carbons does not follow the above trend. Indeed, the change on going from Fe to Os is minimal, and the coordination shift of the Ru complex is in fact *smaller* than that for either Fe or Os compounds. Similar observations were made by von Philipsborn[11] for a series of (η^4-diene)M(CO)$_3$ (M = Fe, Ru, Os) complexes, the Ru complex again being the anomaly.

The anomalous behavior of Ru is also seen in the carbonyl stretching data; the order of increasing stretching frequencies Fe < Os < Ru is not regular. This trend is not unique to the present series and has been seen in (η^4-diene)M(CO)$_3$ complexes[12] and the parent pentacarbonyls.[13]

Although there is no universal agreement as to how to account for the nonregular triad variations in ^{13}C chemical shifts of olefinic ligands and the stretching frequencies of coordinated CO ligands in terms of the relative importance of the σ/π components of M–olefin and M–CO bonds,[14] the observed second-row anomaly is now firmly established. Thus, theoretical calculations[15] on binary metal carbonyls have shown that the M–CO bond strength varies in the order second-row < third-row < first-row transition metal. This is in accord with the experimental observation that, in general, second-row organotransition-metal complexes are the most substitutionally labile in a given triad[16] and that they are the most active in homogeneous catalytic processes.[17] The Ru complex (η^4-C$_4$Ph$_4$CO)Ru(CO)$_3$ is no exception in this regard.[18]

Table 3. Crystallographic Data for [η^4-(C$_6$H$_5$)$_4$C$_4$CO]Os(CO)$_3$·1.5C$_6$H$_{12}$ (1c·1.5C$_6$H$_{12}$)

formula	$C_{32}H_{20}O_4Os\cdot1.5C_6H_{12}$
fw	784.91
color, habit	colorless, parallelepiped
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	15.300(3)
b, Å	10.618(2)
c, Å	21.666(4)
β, deg	101.10(2)
V, Å^3	3454(1)
Z	4
ρ_{calc}, g cm^{-3}	1.509
temp, °C	20
μ, mm^{-1}	3.73
transmission coeff	0.65–1.00
radiation	Mo Kα
$R(F_o)^a$	0.055
$R_w(F_o)^a$	0.064

[a] The R values are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The function minimized is $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$ for counterweights $\sigma(F) = [[\sigma(F_o)]^2 + (p|F_o|)^2]^{1/2}$, where the "ignorance factor", p, has the value 0.03.

Experimental Section

All experimental procedures were performed under an atmosphere of purified nitrogen or argon using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agent and distilled prior to use. Diphenylacetylene (minimum 95%) was purchased from Aldrich Chemical Co. and used as received. Os$_3$(CO)$_{12}$ was prepared from OsO$_4$ by a published procedure.[19]

Photoreactions were performed in an immersion well apparatus using a high-pressure mercury lamp (Philips HPK 125 W) surrounded by a GWV (Glasswerk Wertheim) cutoff filter tube (λ ≥ 370 nm).

Spectra were recorded on the following instruments: NMR, Bruker WH-200; IR Bomem MB-100 FT; MS, AEI MS-12 operating under EI mode. The elemental analysis was determined by the Microanalytic Laboratory of this department.

Preparation of Tricarbonyl(η^4-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one)osmium (1c). The immersion well was charged with 115 mg of Os$_3$(CO)$_{12}$ (0.13 mmol), 535 mg of diphenylacetylene (3.0 mmol), and 80 mL of CH$_2$Cl$_2$. The resulting slurry was purged with argon for 15 min and then irradiated until the IR bands of Os$_3$(CO)$_{12}$ disappeared (*ca.* 3.5 h). The yellow solution was transferred to a flask, and the solvent was removed *in vacuo*. After sublimation of excess diphenylacetylene to a dry-ice-cooled probe (room temperature, 0.005 mmHg), the beige residue was washed with a small amount of cyclohexane and was recrystallized from the same solvent. More of the compound precipitated after concentration of the mother liquor: combined yield of **1c** 106 mg (0.16 mmol, 41%); white solid. It is recommended that for large scale preparation (500 mg of Os$_3$(CO)$_{12}$) benzene, instead of CH$_2$Cl$_2$, be used as solvent. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2083 (s), 2018 (s), 2005 (s), 1646 (m). IR

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[12] The carbonyl stretching frequencies of (η^4-butadiene)M(CO)$_3$ in hydrocarbon solution are as follows: (ν_{CO}, cm^{-1}): Fe, 2056, 1990, 1980; Ru, 2069, 2006, 1995; Os, 2070, 1995, 1985. Fe: Warren, J. D.; Clark, R. J. *Inorg. Chem.* **1970**, *9*, 373. Ru: Ruh, S.; von Philipsborn, W. *J. Organomet. Chem.* **1972**, *127*, C59. Os: Reference 11.

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Table 4. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline [(η^4-$(C_6H_5)_4C_4CO)Os(CO)_3$]·$1.5C_6H_{12}$[a]

atom type[b]	fractional coordinates			equiv isotropic thermal param, B, Å^2 × 10[c]
	10^4x	10^4y	10^4z	
Complex				
Os	1534(1)	2031(1)	2407(1)	35(1)
O(1)	902(6)	5220(8)	2567(4)	44(3)
O(6)	345(7)	2249(10)	3386(5)	55(3)
O(7)	2984(8)	314(12)	3141(7)	83(5)
O(8)	527(9)	–196(11)	1691(7)	82(5)
C(1)	951(8)	3598(10)	1774(6)	33(3)
C(2)	1732(8)	3077(12)	1551(5)	35(3)
C(3)	2486(7)	3247(10)	2046(5)	32(3)
C(4)	2247(7)	3904(11)	2580(6)	33(3)
C(5)	1299(7)	4421(10)	2336(5)	30(3)
C(6)	786(8)	2115(13)	3022(6)	41(3)
C(7)	2439(10)	925(15)	2894(8)	54(5)
C(8)	914(10)	604(15)	1978(8)	50(5)
C(11)	59(7)	3819(12)	1417(6)	35(3)
C(12)	–62(8)	4660(13)	913(7)	45(4)
C(13)	–893(10)	4963(17)	587(7)	57(5)
C(14)	–1648(10)	4434(16)	769(8)	58(5)
C(15)	–1527(9)	3621(16)	1263(9)	61(5)
C(16)	–684(9)	3305(13)	1581(8)	53(5)
C(21)	1709(9)	2589(12)	911(6)	38(3)
C(22)	2408(9)	2803(14)	601(6)	46(4)
C(23)	2397(11)	2338(18)	15(7)	60(5)
C(24)	1690(14)	1636(16)	–292(7)	65(6)
C(25)	988(11)	1432(15)	–2(8)	59(5)
C(26)	996(9)	1866(12)	597(7)	46(4)
C(31)	3450(7)	2986(14)	2009(5)	36(3)
C(32)	4031(9)	3968(17)	2059(7)	51(4)
C(33)	4889(9)	3783(19)	2000(8)	60(5)
C(34)	5197(11)	2648(20)	1891(7)	66(6)
C(35)	4607(11)	1637(17)	1837(8)	63(6)
C(36)	3751(9)	1797(12)	1897(7)	45(4)
C(41)	2834(8)	4325(12)	3154(5)	33(3)
C(42)	2675(9)	5463(13)	3426(6)	45(4)
C(43)	3209(10)	5890(16)	3974(7)	60(5)
C(44)	3935(11)	5214(16)	4252(8)	58(5)
C(45)	4098(10)	4035(16)	3995(7)	56(5)
C(46)	3543(9)	3651(14)	3442(6)	43(4)
Cyclohexane Solvent Molecule 1				
C(1s)	3412(15)	7979(32)	1431(14)	130(13)
C(2s)	2706(20)	7532(34)	1748(11)	144(15)
C(3s)	2016(18)	6932(28)	1356(13)	124(12)
C(4s)	1618(15)	7606(29)	779(12)	108(11)
C(5s)	2288(21)	8148(27)	461(12)	126(12)
C(6s)	3012(19)	8702(30)	852(13)	133(12)
Cyclohexane Solvent Molecule 2[d]				
C(7s)	4428(16)	5893(25)	–242(17)	178(17)
C(8s)	4219(16)	4928(30)	156(17)	306(17)
C(9s)	4678(18)	3872(21)	7(22)	360(43)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] For all atoms except C(8s) (which could not be refined satisfactorily as an anisotropic atom), this is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] The second cyclohexane moleucle is sufficiently disordered about the crystallographic inversion center at ($^1/_2$, $^1/_2$, 0) that its atoms could not be satisfactorily refined as independent atoms. They were therefore constrained to have a common C–C bond length, which was refined to a final value of 1.368(15) Å. The C···C separation between alternate carbon atoms in the ring was constrained to be 1.633 times the constrained C–C bond length.

(C_6H_{12}, cm^{-1}): ν_{CO} 2079 (s), 2015 (s), 1997 (s), 1677 (m). ^{1}H NMR (25 °C, 200.00 MHz, δ in $CDCl_3$): 7.24 (m, phenyl). ^{13}C NMR (–60 °C, 50.323 MHz, δ in $CDCl_3$): 173.9 (keto CO), 173.6 (Os–CO), 129.5 (M, phenyl), 102.0 (inner diene), 78.4 (outer diene). MS (150 °C, 70 eV, ^{192}Os): *m/e* 660 (M$^+$), 632 (M$^+$ – CO), 604 (M$^+$ – 2CO), 576 (M$^+$ – 3CO). Anal. Calcd for $C_{32}H_{20}O_4Os$: C, 58.35; H, 3.06. Found: C, 58.35; H, 3.26.

X-ray Crystal Structure of Analysis of [η^4-$(C_6H_5)_4C_4CO$]-$Os(CO)_3$·$1.5C_6H_{12}$. A colorless, rectangular, parallelepiped-shaped crystal of the cyclohexane solvate of **1c** was sealed under argon in a thin-walled glass capillary and mounted on the goniometer of a computer-controlled four-circle Nicolet (Siemens) Autodiffractometer. Lattice constants determined from alignment data for 15 reflections having 2θ(Mo K$\bar{\alpha}$) > 17° are given with other relevant crystallographic data in Table 3. A total of 6328 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 50.8° (the equivalent of 0.8 limiting Cu K$\bar{\alpha}$ spheres) were collected in three concentric shells of increasing 2θ using full (0.90°-wide) ω scans and scan rates of 4 or 2°/min with graphite-monochromated Mo K$\bar{\alpha}$ radiation. The intensities of 6 standard reflections measured every 300 reflections did not vary during data collection. The intensity data were corrected empirically for variable absorption effects using ψ scans for 6 reflections having 2θ between 6.01 and 21.76°; the relative transmission factors varied from 0.65 to 1.00.

The structure was solved using the "heavy atom" technique, and the resulting structural parameters have been refined to convergence ($R(F_o)$ = 0.055 for 3720 independent absorption-corrected reflections having 2θ(Mo K$\bar{\alpha}$) < 50.8° and $I > 3\sigma(I)$) using counterweighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms (except disordered solvent carbon atom C_{8s}) and isotropic thermal parameters for carbon atom C_{8s} and all hydrogen atoms. Hydrogen atoms were fixed at idealized sp^2- or sp^3-hybridized positions with a C–H bond length of 0.96 Å; their isotropic thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

The second cyclohexane molecule is sufficiently disordered about the crystallogrpahic inversion center at ($^1/_2$, $^1/_2$, 0) that its atoms could not be satisfactorily refined as independent atoms. They were therefore constrained to have a common C–C bond length, which was refined to a final value of 1.368(15) Å. The C···C separation between alternate carbon atoms in the ring was constrained to be 1.633 times the constrained C–C bond length.

All structure factor calculations employed recent tabulations of atomic form factors[20] and anomalous dispersion corrections[20] to the scattering factors of the Os atom. The final cycles of refinement utilized a least-squares-refineable extinction coefficient[21] which was refined to a final value of 0.000 43(5). All calculations were performed on a Data General Eclipse S-200 or S-230 computer using versions of the Nicolet E-XTL or SHELXTL interactive crystallographic software package or on a DEC Micro Vax II computer using versions of the SHELXTL-PLUS software package.

Final positional and equivalent isotropic thermal parameters for non-hydrogen atoms of **1c**·$1.5C_6H_{12}$ are given with estimated standard deviations in Table 4.

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Supplementary Material Available: A full structural report on **1c**·$1.5C_6H_{12}$, containing tables of crystal data and data collection and refinement details, anisotropic thermal parameters, hydrogen atom parameters, and all bond lengths and bond angles (15 pages). Ordering information is given on any current masthead page.

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