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Carbonyl-η-hexamethylbenzene complexes of osmium. Carbon-hydrogen activation by (η-C_6Me_6)Os(CO)(H)$_2$

William A. Kiel, Richard G. Ball and William A.G. Graham *
Department of Chemistry, University of Alberta Edmonton, Alberta, T6G 2G2 (Canada)

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Abstract

Reduction of (η-C_6Me_6)Os(CO)Cl_2 (**1**) with zinc/acetic acid/methanol gives (η-C_6Me_6)Os(CO)(Cl)H (**2**), which can be further reduced with Na[$H_2Al(OCH_2CH_2OCH_3)_2$] to (η-C_6Me_6)Os(CO)H_2 (**3**). Photolysis of **3** in hydrocarbons (benzene, cyclohexane, neopentane) results in formation of the carbon–hydrogen bond activation products (η-C_6Me_6Os(CO)(R)(H) (**6a–6c**, R = C_6H_5, C_6H_{11} and $CH_2C(CH_3)_3$, respectively) and free hexamethylbenzene. Independent syntheses of the hydrides **6a–6c** are described as well as syntheses of the complexes (η-C_6Me_6)Os(CO)(R)$_2$ (**4a–4c**) and (η-C_6Me_6)Os(CO)(R)Cl (**5a–5c**). The structure of (η-C_6Me_6)Os(CO)(cyclohexyl)$_2$ (**4b**) determined by single crystal X-ray diffraction is reported.

Introduction

The first reports of alkane activation by soluble metal complexes to form isolable primary activation products involved cyclopentadienyliridium derivatives. One system was (η-C_5Me_5)Ir(PMe_3)(H)$_2$, which lost H_2 upon photolysis [1]; the other was (η-C_5Me_5)Ir(CO)$_2$, which lost CO [2]. The suggestion was that a reactive intermediate, [(η-C_5Me_5)Ir(L)], was formed which was capable of oxidatively adding C–H bonds. In the case of rhodium, alkane activation products were obtained by photolysis of (η-C_5Me_5)Rh(PMe_3)(H)$_2$, but were stable only below −20 °C [3]. These early results established the substantially greater thermal stability of activation products derived from the metal of the third transition series.

In an important theoretical paper [4], it was proposed that other d^8, ML_4 complexes isolobal with (η-C_5R_5)Ir(L) were likely to activate C–H bonds. Indeed, the areneruthenium complexes (η-C_6H_6)Ru{P(i-Pr)$_3$}(H)$_2$ [5] and (η-C_6Me_6)Ru{PH(C_6H_{11})$_2$}(H)$_2$ [6] activate benzene under photolysis. In neither case was intermolecular alkane activation observed; for the isopropyl complex, intramolecular activation supervened [5].

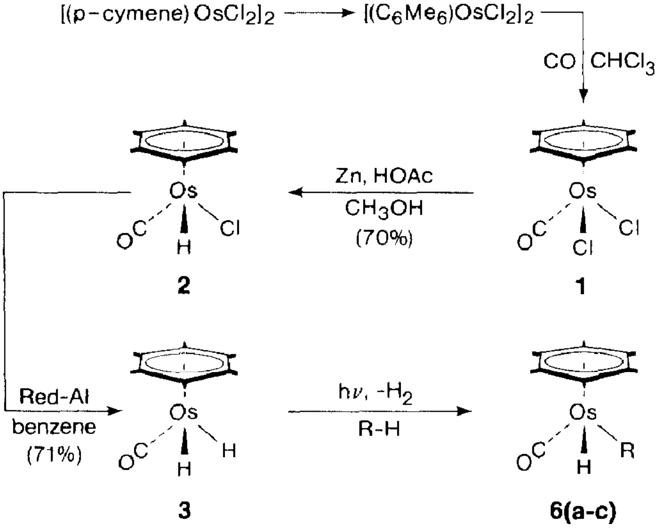
Our interest in the reactivity of C–H bonds towards transition metals prompted us to examine hexamethylbenzene complexes of osmium. Specifically, we wished to synthesize the complex $(\eta\text{-}C_6Me_6)Os(CO)H_2$ (**3**). Our reasons were threefold. First, photo-induced loss of hydrogen would produce an electron-rich, coordinatively unsaturated d^8 ML_4 complex, $[(\eta\text{-}C_6Me_6)Os(CO)]$, conducive to carbon–hydrogen bond activation. Second, we anticipated that the alkyl hydride complexes of osmium, and in particular (η-hexamethylbenzene)osmium, would be more stable than their ruthenium counterparts. Finally, we sought a complex in which the metal center was unlikely to activate one of its own ligands, making CO an attractive choice.

Previous to this work, hexamethylbenzene complexes of osmium had not been reported. In this paper we describe the synthesis of some neutral monocarbonylhexamethylbenzene complexes of the general formulae $(\eta\text{-}C_6Me_6)Os(CO)(R)_2$ and $(\eta\text{-}C_6Me_6)Os(CO)(R)X$ (X = H, Cl; R = H, phenyl, cyclohexyl, neopentyl). In addition, we have found that photolysis of $(\eta\text{-}C_6Me_6)Os(CO)(H)_2$ (**3**), in benzene, cyclohexane and neopentane gives observable carbon–hydrogen bond activation products in each case. Brief reference has previously been made to some of these results [7].

Results and discussion

Preparation of $(\eta\text{-}C_6Me_6)Os(CO)(H)_2$ (3)

The synthesis of **3** is outlined in Scheme 1. Taking into account improved new procedures for preparation of $[(p\text{-cymene})OsCl_2]_2$ [8], the dichloride $(\eta\text{-}C_6Me_6)Os(CO)Cl_2$ (**1**) is available in moderate yield from the inorganic osmium starting materials. We and others have found that treatment of transition metal dihalides with zinc/acetic acid/methanol results in the formation of metal dihydrides [9]. Although small amounts (up to 20%) of dihydride **3** were formed in the zinc/acetic acid/methanol reduction of **1**, the major product of the reaction was, surprisingly, the chlorohydride $(\eta\text{-}C_6Me_6)Os(CO)(Cl)H$ (**2**). Complexes **2** and **3** were



Scheme 1. Synthesis and photolysis of complex 3.

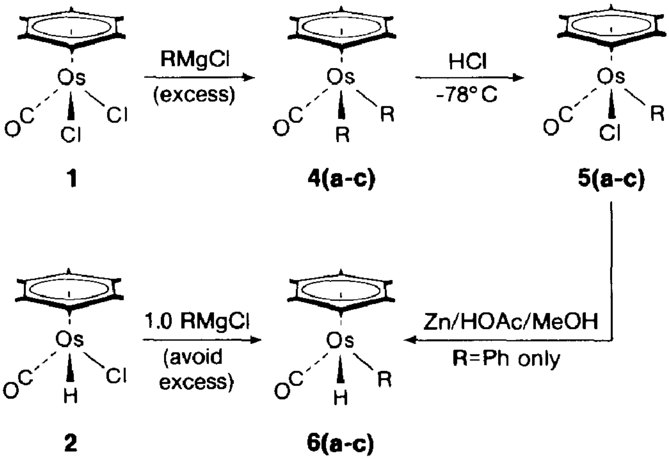
separable by column chromatography on silica gel, after which air-stable, orange-yellow crystals of **2** were obtained in 70% yield. Compound **2** showed a characteristic high field resonance (-11.15, 1H) in the ^1H NMR for the osmium hydride and a doublet (183.3, d, $J(^1H-^{13}C)$ 10.6 Hz) in the proton-coupled ^{13}C NMR spectrum for the carbonyl group, indicating that a single hydrogen was attached to the metal center (Table 1). An osmium-hydrogen stretching absorption was also observed in the IR spectrum of **2** (ν(OsH) 2073w; ν(CO) 1954s) in CH_2Cl_2. Attempts to obtain higher conversions of **1** to **3** with this reduction method by heating and employing longer reaction times failed.

Fortunately, **2** reacted with Red-Al ($Na[H_2Al(OCH_2CH_2OCH_3)_2]$) in benzene to give **3** in 71% yield as an off-white, slightly light-sensitive solid. The ^1H NMR and IR spectra exhibited signals characteristic of hexamethylbenzene, hydride and carbonyl ligands (Table 1). A ^{13}C NMR revealed a triplet for the carbonyl ligand (186.3, t, $J(^1H-^{13}C)$ 9.6 Hz). Reaction of **1** with Red-Al gave decomposition with formation of no dihydride **3**; various other hydride sources ($LiEt_3BH$, $NaBH_4$, $K(sec\text{-}Bu)_3BH$, and $(i\text{-butyl})_2AlH$) also failed in this reaction. In contrast [8b], (p-cymene)$Os(PMe_3)Cl_2$ is smoothly converted to the dihydride by $NaBH_4$ in methanol.

Independent synthesis of alkyl and aryl hydrides

Before investigating the photochemistry of **3** in hydrocarbons we sought an independent synthesis of the aryl and alkyl hydrides (η-C_6Me_6)Os(CO)(R)H, **6a–6c** (R = phenyl, cyclohexyl and neopentyl, respectively) to discover their thermal lability and air sensitivity. Scheme 2 outlines routes to **6a–6c**. A suspension of **1** in benzene reacted with excess RMgCl (R = phenyl, cyclohexyl, neopentyl) to give yellow solutions of the bisaryl or bisalkyl complexes (η-C_6Me_6)$Os(CO)(R)_2$ (**4a–4c**), which were isolable as yellow solids. Spectral data for these complexes are listed in Table 1. Halide metathesis, resulting in the formation of byproduct (η-C_6Me_6)Os(R)Br, is observed if RMgBr is employed in these preparations. The bromides generally appear to be less reactive towards nucleophiles and significant amounts of (η-C_6Me_6)Os(CO)(R)Br can build up in the reaction mixture. We

(*continued on p. 486*)



Scheme 2. Independent synthesis of alkyl and aryl hydrides.

Table 1

Spectroscopic data for complexes **1–6**

Complex	IR (cm^{-1})	^1H NMR [a] (δ, CD_2Cl_2)		^{13}C NMR [b] (δ, CD_2Cl_2)		
		$C_6(CH_3)_6$	Other	$C_6(CH_3)_6$	$C_6(CH_3)_6$	Other
1	ν(CO) 1998 (CH_2Cl_2)	2.20(s)		99.8	15.9	176.7(*C*O)
2	ν(CO) 1972w (hexanes) ν(OsH) 2073wbr ν(CO) 1954s (CH_2Cl_2)	2.30(s, 18H)	−11.15(Os*H*, s, 1H),	100.8	16.9($C_6(CH_3)_6$, q, *J* 128.9 Hz)	183.3(*C*O, d, ^3J(C–H) 10.6 Hz)
3	ν(OsH) 2059wbr ν(CO) 1942s (hexanes)	2.47(s, 18H)	−12.63(Os*H*, s, 2H)	99.2	18.0($C_6(CH_3)_6$, q, *J* 128.3 Hz)	186.3(*C*O, t, ^3J(C–H) 9.6 Hz)
4a	ν(CO) 1950w (hexanes) ν(CO) 1929s (CH_2Cl_2)	2.05(s, 18H)	6.80(*para*, *H*, m, 2H) 6.89(*meta*, *H*, m, 4H) 7.35(*ortho*-*H*, m, 4H)	104.7	16.1	140.8, 140.4, 127.8, 122.1 (phenyl carbons), 186.8(*C*O)
4b	ν(CO) 1922s (hexanes) ν(CO) 1893s (CH_2Cl_2)	2.09(s, 18H)	1.10–1.70(cyclohexyl *H*, mults, 22H)	101.5	16.6	15.5(Os–*C*), 28.3, 32.1, 33.1 40.3, 42.1(cyclohexyl *C*s) 189.4(*C*O)
4c	ν(CO) 1904s (hexanes)	1.99(s, 18H)	0.89(CHH', d, J(H–H′ 11.3 Hz, 2H)	102.6	16.1	24.2(OsCH_2), 34.2($C(CH_3)_3$, 37.0($C(CH_3)_3$,

	ν(CO) 1879s (CH_2Cl_2)		0.93(C(CH_3, s, 18H), 1.58(CHH', d, 2H)			190.3(CO),
5a	ν(CO) 1961s (CH_2Cl_2)	2.08(s, 18H)	6.90(*para*-H, m, 1H), 6.98(*meta*-H, m, 2H), 7.13(*ortho*-H, m, 2H),	102.7	15.9	123.3, 128.1, 139.2, 141.0, (phenyl carbons) 182.6(CO)
5b	ν(CO) 1959s (hexanes)	2.11(s, 18H)	1.24–1.76(cyclohexyl H's, mults, 10H), 2.57(H_α, tt, $^3J_{\alpha\text{-}\beta}$ 11.6 Hz and 3.5 Hz)	101.4	16.0	21.0, 27.9, 32.3, 32.7, 40.3, 41.8 (cyclohexyl Cs), 183.7(CO)
5c	ν(CO) 1949s (hexanes)	2.08(s, 18H)	0.95(C($CH_3)_2$, s, 9H), 1.77(CHH′, d, J(H–H′) 10.2 Hz, 1H), 2.07(CHH', d, 1H)	101.4	15.5	26.8(Os$C$$H_2$), 32.8 (C($C$$H_3)_3$), 36.1($C$($CH_3)_3$, 185.5($C$O),
6a	ν(OsH) 2064br ν(CO) 1949s (hexanes)	2.25(s, 18H)	−11.44(OsH, s, 1H) 6.80 and 7.28 (C_6H_5, m, 3H+2H)	101.5	17.0	122.0, 127.7, 139.1, 143.9, (phenyl carbons) 187.8(CO)
6b	ν(OsH) 2076wbr ν(CO) 1929s (hexanes)	2.26(s, 18H)	−12.51(OsH, s, 1H), 1.10–1.80(cyclo- hexyl H, mults, 11H)	99.7	16.8	15.3, 27.8, 33.1, 33.2 45.0, 48.8, (cyclohexyl carbons), 190.0(CO)
6c	ν(OsH) 2094w ν(CO) 1933s (hexanes)	2.22(s, 18H)	−11.55(OsH, s, 1H), 0.83(C(C$H_3)_3$), s, 9H), 0.89(CHH′, d, J(H–H′) 11.0 Hz, 1H), 1.58 (CHH', d, 1H)	99.4	16.7	13.7($C$$H_2$), 33.3(C($C$$H_3)_3$) 35.7($C$($CH_3)_3$), 188.6($C$O)

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[a] Chemical shifts relative to solvent (CHDCl_2, δ 5.32). [b] Chemical shifts relative to solvent ($C$$D_2Cl_2$, δ 53.8).

therefore limited our use of Grignards to those derived from the organic chlorides. Complexes **4a**–**4c** react with hydrogen chloride gas in dichloromethane at −78 °C to give the phenyl and alkyl chlorides (η-C_6H_6)Os(CO)(R)Cl, **5a**–**5c**. Loss of both alkyl groups is observed if the reaction is conducted at room temperature or if a large excess of acid is employed. The biscyclohexyl complex **4b** appeared to be the most sensitive and the bisphenyl complex **4a** the least sensitive to cleavage of the second metal carbon bond.

*X-ray structure of (η-C_6Me_6)Os(CO)(C_6H_{11})$_2$ (**4b**)*

The bis(cyclohexyl) complex **4b** was chosen as representative for X-ray crystallographic study. Crystals were obtained from methanol. The cell chosen initially turned out to be doubled along *b* as a result of twinning of the crystal. Since no other crystals were available of sufficient quality for data collection, it was decided to re-index the collected data based on the new cell parameters and proceed with the refinement *. Relevant experimental conditions and parameters are given in Table 2.

A three dimensional Patterson map was solved for the Os atom position with subsequent atoms located by successive cycles of least-squares refinement and difference Fourier map calculation. Initial solutions were tried for two independent molecules in $P\bar{1}$ but when these failed the cell parameters and data were changed as indicated above and solution proceeded normally.

The structure determined for **4b** is shown in Figs. 1 and 2, atomic coordinates in Table 3, and selected bond lengths and angles in Table 4. One of the cyclohexyl rings is disordered with respect to a rotation about its Os–C bond. This was modelled by setting the appropriate atoms to occupancies of 0.5 but otherwise refining them as normal, isotropic atoms.

The C_6Me_6 ring deviates from planarity in a way that appears to be dictated by the large steric requirements of the cyclohexyl ligands. Methyl carbons C8, C9, C11 and C12 lie above the best plane through C2–C7 by an average of 0.26 Å; C10 and C13, which do not lie over the cyclohexyl groups, are an average 0.10 Å below this plane. In fact, the central six-membered ring C2–C7 is rather far from planar, and can be regarded as folded along the C4 to C7 vector; the angle between planes comprising C2, C3, C4, C7 and C7, C4, C5, C6 is 11.8°.

As expected, the bulky metal center is in an equatorial position of the cyclohexane ring; this is consistent with the large vicinal coupling constant (*J* 11.6 Hz) between the α and β axial protons of the cyclohexyl ring in **5b**.

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* During review a referee suggested, based on a cell reduction calculation with a sufficiently large allowed discrepancy, that the correct space group should be *C*2/*m* with the molecule lying on a mirror plane. Transformation of the coordinates into this space group reveals that the molecule is not positioned such that it may be translated to lie on a mirror plane. The possibility that the molecule is in a general position in *C*2, *Cm* or *Cc* was also considered but examination of the reflection data after transformation to a *C*-centered monoclinic system shows no absences consistent with *Cc* nor any solutions for *C*2 or *Cm* in Patterson maps calculated with the transformed data. Indeed averaging of the equivalent forms generated by the transformation shows extremely poor agreement, R_{int} 28% vs. 2.2% for the triclinic data.

Our conclusion remains that the correct space group is $P\bar{1}$ despite the problems with the structure which we ascribe to poor quality data collected from a twinned crystal.

Table 2

Crystal data and details of data collection and refinement

(A) Crystal parameters at 25 °C

Formula $C_{25}H_{40}OOs$ Formula weight: 546.80

Crystal dimensions: 0.30×0.33×0.36 mm

Triclinic Space group: $P\bar{1}$

a, 8.555(1); b, 16.339(4); c, 8.449(3) Å

α 101.64(2)°, β 94.39(1)°, γ 100.79(2)°

V 1128.2 $Å^3$ $Z = 2$ D_{calcd} 1.609 g cm^{-3} μ 56.69 cm^{-1}

(B) Data collection

Diffractometer: Enraf–Nonius CAD-4

Radiation: Mo-K_α (λ 0.71073 Å)

Monochromator: Incident beam, graphite crystal

Take-off angle: 3.0°

Detector aperture: 2.40 mm horizontal, 4.0 mm vertical

Crystal to detector distance: 205 mm

Scan type: ω–2θ, Scan rate: 10.1–1.1° min^{-1}, Scan width: 0.70+0.35 tan θ°

Data collection 2θ limit: 54.00°

Reflections measured: h, ± k, ± l; 4904 unique, 4378 with $I > 3\sigma(I)$

Corrections applied: absorption correction [a]. Maximum and minimum correction coefficients applied to F_o were 1.6348 and 0.6375, respectively.

Refinement method: full matrix, using F magnitudes with weight of $1/\sigma^2(I)$

Atom refinement: hydrogen atoms not included, remaining atoms anisotropic except carbon atoms of disordered ring.

Parameters in final cycle: 226, Final R and R_w: 0.052, 0.075

[a] An empirical correction based on the absorption surface method was used: N. Walker and D. Stuart, Acta Crystallogr., A, 39 (1983) 158.

Conversion of aryl and alkyl chlorides to hydrides

Preparation of the aryl and alkyl hydrides from chlorides **5a**–**5c** proved to be a problem. Reaction of **5a**–**5c** with hydride sources such as $NaBH_4$, $LiEt_3BH$, diisobuylaluminium hydride, and Red-Al gave either decomposition or very low

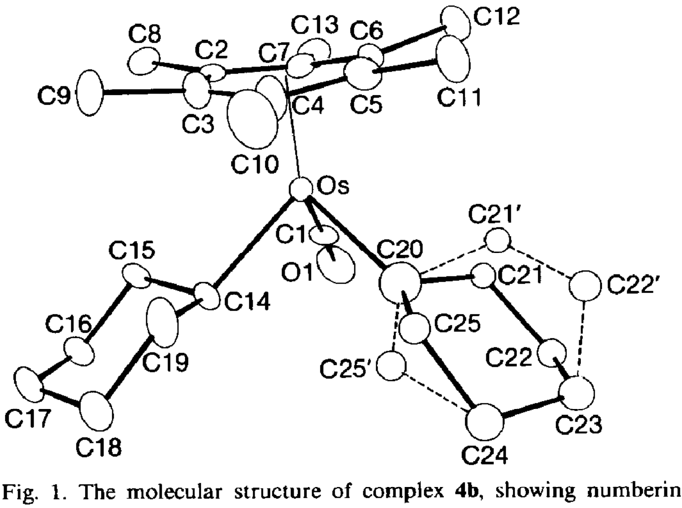

Fig. 1. The molecular structure of complex **4b**, showing numbering of atoms. One of the cyclohexyl ligands is disordered.

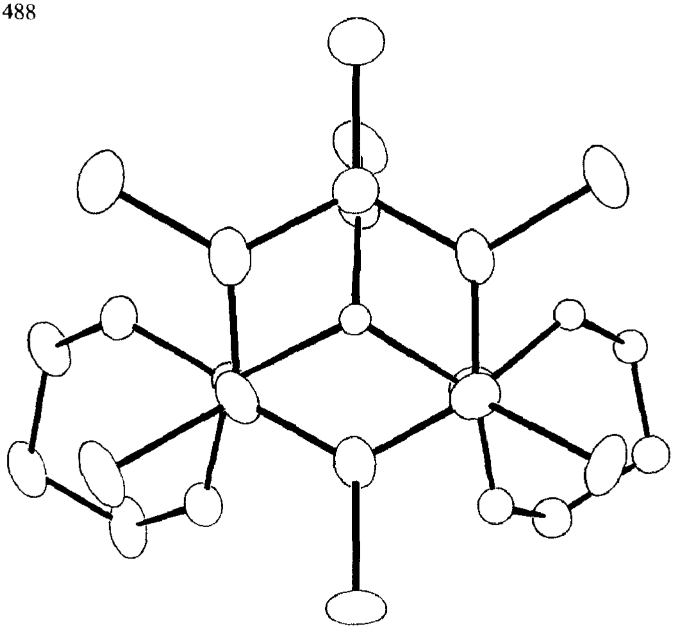

Fig. 2. Complex **4b** viewed approximately normal to the (η-C_6Me_6) ring, showing orientation of other ligands.

Table 3

Positional ($\times 10^3$) and thermal ($\times 10^2$) parameters

Atom	x	y	z	U (Å^2) [b]
Os	40.15(3)	229.27(2)	239.67(3)	3.183(8) [a]
O1	181(1)	157.4(7)	−52(1)	9.6(3) [a]
C1	121.8(9)	183.8(7)	59(1)	4.8(3) [a]
C2	−151.0(8)	123.9(6)	311(1)	4.9(3) [a]
C3	−100(1)	193.0(7)	454(1)	6.2(3) [a]
C4	−98(1)	277.5(7)	451(1)	7.0(3) [a]
C5	−172(1)	298.3(6)	313(1)	5.6(3) [a]
C6	−226.0(9)	233.2(6)	168(1)	4.8(3) [a]
C7	−199(1)	150.4(6)	162(1)	4.9(3) [a]
C8	−162(1)	31.7(7)	314(2)	6.9(4) [a]
C9	−59(1)	166.8(8)	618(1)	8.4(4) [a]
C10	−47(2)	345.4(8)	605(1)	9.1(5) [a]
C11	−207(1)	384.8(6)	316(2)	7.8(4) [a]
C12	−323(1)	250.9(8)	21(1)	7.6(4) [a]
C13	−250(1)	81.0(8)	1(2)	7.3(4) [a]
C14	267(1)	212.6(6)	357(1)	5.1(3) [a]
C15	260.4(9)	118.8(6)	358(1)	5.2(3) [a]
C16	426(1)	103.7(8)	420(1)	7.6(4) [a]
C17	475(1)	160.5(9)	595(1)	9.1(4) [a]
C18	482(2)	250.6(9)	595(2)	11.4(5) [a]
C19	311(2)	264.9(8)	531(1)	9.4(5) [a]
C20	179(2)	347(1)	200(2)	9.3(4)
C21′	73(2)	380(1)	68(2)	3.3(3)
C21	143(2)	360(1)	26(2)	3.5(3)
C22	262(2)	433(1)	−26(2)	4.4(4)
C22′	126(2)	472(1)	58(2)	4.7(4)
C23	309(1)	508.8(7)	103(1)	5.7(2)
C24	374(1)	489.9(7)	261(1)	6.2(3)
C25	242(2)	425(1)	324(2)	4.5(4)
C25′	323(2)	382(1)	249(2)	4.4(4)

[a] Indicates an atom refined anisotropically. [b] The equivalent isotropic thermal parameter is given by $U = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$.

Table 4

Selected bond length (Å) and angles (°) for **4b**

Atoms	Distance	Atoms	Distance
Bonds			
Os–C1	1.808(6)	Os–C20	2.17(1)
Os–C2	2.348(5)	C1–O1	1.147(7)
Os–C3	2.356(6)	C2–C3	1.45(1)
Os–C4	2.306(6)	C3–C4	1.38(1)
Os–C5	2.368(5)	C4–C5	1.419(9)
Os–C6	2.327(5)	C5–C6	1.432(9)
Os–C7	2.181(5)	C6–C7	1.405(8)
Os–C14	2.197(5)		
Mean C–CH_3 distance in C_6Me_6 ring			1.527(34)
Mean C–C distance in non-disordered cyclohexyl ring			1.536(44)
Angles			
Os–C1–O1	176.5(6)	C6–Os–C1	108.6(2)
Os–C14–C15	110.7(3)	C6–Os–C14	165.7(2)
Os–C14–C19	113.5(5)	C6–Os–C20	105.3(3)
C1–Os–C14	81.5(2)	C7–Os–C1	94.2(2)
C1–Os–C20	82.4(3)	C7–Os–C14	135.8(2)
C14–Os–C20	85.7(3)	C7–Os–C20	137.7(3)
C4–Os–C1	172.2(3)	C2–Os–C1	109.9(3)
C4–Os–C14	104.9(3)	C2–Os–C14	102.9(2)
C4–Os–C20	102.3(4)	C2–Os–C20	165.8(3)
C5–Os–C1	139.6(2)	C3–Os–C1	142.8(3)
C5–Os–C14	137.8(2)	C3–Os–C14	91.8(2)
C5–Os–C20	90.6(3)	C3–Os–C20	133.9(3)
Mean C–C–C in non-disordered cyclohexyl ring			109.5(19)

yields of the aryl or alkyl hydride. Complexes **5a**–**5c** did not react with zinc/acetic acid/methanol at room temperature. Elevated temperatures led to decomposition for **5b** and **5c** presumably via cleavage of the osmium-alkyl bond by the acid. However the phenyl chloride, **5a**, which was more stable toward acid, was smoothly reduced by zinc/acetic acid/methanol at reflux giving (η-C_6Me_6)Os(CO)(C_6H_5)H (**6a**) as an off-white solid. The identity of **6a** as the phenyl hydride was confirmed by its ^1H NMR spectrum which contained a metal hydride resonance at -11.44 (s, 1H), two phenyl multiplets at 6.80 and 7.28 (3H and 2H), and the hexamethylbenzene ligand at 2.25 (s, 18H). The IR spectrum exhibited a carbonyl stretching band at 1949 cm^{-1} and a weak osmium hydride stretch at 2064 cm^{-1}. Alkyl hydrides **6b** and **6c** were synthesized in moderate yield by treating **2** with cyclohexyl- or neopentyl-magnesium chloride (Scheme 2). This method also works well for the preparation of **6a**. Use of excess Grignard reagent led to formation of the bisaryl or bisalkyl complexes **4a**–**4c** which were difficult to separate from their corresponding hydrides. As a consequence, the progress of the reactions was monitored by infrared to avoid addition of excess Grignard. That both **6b** and **6c** were osmium hydrides was evident from high field resonances (-12.51 and -11.55, respectively) in their ^1H NMR spectra and weak broad osmium-hydride stretches (ν(OsH 2076 and 2094) in their IR spectra (Table 1). All of the hydrides **6a**–**6c** were thermally stable white solids at room temperature, exhibiting little sensitivity to air.

One feature of the NMR spectra of the alkyl complexes merits comment. Geminal methylene protons of the neopentyl compounds **4c**, **5c**, and **6c** exhibit different chemical shifts because of their attachment to the OsXYZ moiety. A less familiar instance of "diastereotopic" character is clear in the ^{13}C NMR spectra of the cyclohexyl groups in **4b**, **5b**, and **6b**, where six different resonances are observed (Table 1).

Photochemical C–H activation using 3

With authentic samples of the phenyl and alkyl hydrides available we proceeded to investigate the photolysis of **3** in hydrocarbons. Following ultraviolet irradiation of a 2.62 m*M* solution of **3** in C_6D_6 for 2 h in a 5 mm NMR tube, the ^1H NMR spectrum showed free hexamethylbenzene and a new hexamethylbenzene resonance. No other hexamethylbenzene resonances besides starting material were apparent. The photolysis was then carried out in a quartz photolysis tube employing C_6H_6 as solvent. After removal of the benzene under reduced pressure, the residue was extracted into CD_2Cl_2. Again the ^1H NMR showed the presence of only three hexamethylbenzene resonances; **3** (δ 2.47), free hexamethylbenzene (δ 2.20), and 2.25 in a 70/10/20 ratio (integration of $C_6(CH_3)$ resonances). Further examination of the ^1H NMR spectrum revealed two multiplets in the aromatic region (6.80 and 7.28) and a new high field proton resonance (−11.44). Comparison with an authentic sample of **6a** showed the new hydride to be in fact (η-C_6Me_6)Os(CO)(C_6H_5)H resulting from carbon-hydrogen bond activation of benzene. The yield of **6a** based on dihydride **3** consumed was 67%.

The dihydridoosmium complex was also found to activate cyclohexane and neopentane. Photolysis of a cyclohexane solution of **3** as above was followed by infrared spectroscopy. After 2 h photolysis a new complex had formed as evidenced by the appearance of a new carbonyl absorbance at 1928 cm^{-1}. Comparing the IR spectrum of **6b** to the spectrum of the photolysis mixture suggested that (η-C_6Me_6)Os(CO)(C_6H_{11})H was forming. The ^1H NMR of the reaction showed that **3**, free hexamethylbenzene, and **6b** were present in a 68/12/20 ratio, implying that the yield of **6b** based on reacted **3** was 63%.

In a competition experiment, a solution of **3** in an equimolar benzene/cyclohexane mixture was irradiated for 1 h, after which 40% of **3** had been consumed. A ratio of phenyl hydride **6a** to cyclohexyl hydride **6b** of 1/1 was observed, indicating a twofold preference for an aromatic carbon–hydrogen bond over a secondary aliphatic carbon–hydrogen bond. The presumed intermediate here is [(η-C_5Me_5)Os(CO)], which should be high in energy, highly reactive, and therefore rather unselective in its reactions. The slight kinetic preference for benzene over cyclohexane activation is reminiscent of (η-C_5Me_5)Ir(PMe_3)$(H)_2$ [1] and (η-C_5Me_5)Ir$(CO)_2$ [2], where the preferences (per C–H bond) are 4.0/1 and 2.5/1, respectively. On the basis of studies of (η-C_5Me_5)Ir(PMe_3)(R)H systems [10], there is little doubt that **6a** would have been the exclusive product if the competition reaction had been thermodynamically controlled.

When a neopentane solution of **3** was irradiated it was again apparent from the ^1H NMR and IR spectra of the photolysis mixture that a new osmium hydride species had formed. Neopentyl hydride (η-C_6Me_6)Os(CO)($CH_2C(CH_3)_3$)H (**6c**) was formed in 36% yield along with 64% free hexamethylbenzene after 35% conversion of **3**. In all of the irradiations described, continued photolysis lead to further decomposition of the hexamethylbenzene osmium complexes and production of more free hexamethylbenzene. The osmium-containing products resulting from hexamethylbenzene ring loss have not been characterized. Generally, with the low conversions of **3** to aryl and alkyl hydrides, we did not attempt to isolate **6a**–**6c** from the photolysis mixtures.

Conclusions

Osmium is surrounded by other metals of the third transition series which are capable of intermolecular C-H activation: tungsten [11], rhenium [12], iridium [1,2] and platinum [13]. In fact osmium, together with ruthenium, provided the first examples of intermolecular C–H activation with the formation of $(dmpe)_2M(H)(2\text{-naphthyl})$ (M = Ru, Os; dmpe = bis(dimethylphosphino)ethane) when $(dmpe)_2MCl_2$ was reduced with $NaC_{10}H_8$ in THF [14]. A related activation of aromatic C–H bonds occurs when $(Me_3P)_2[P(OMe)_3]_2MCl_2$ (M = Ru, Os) is reduced in benzene or toluene with sodium amalgam [15].

Intermolecular carbon–hydrogen activations by osmium complexes which do not involve use of an alkali metal to generate the reactive intermediate have also been reported. Reaction of (*p*-cymene)$Os(PMe_3)(C_2H_4)$ in benzene solution with excess Me_3P forms $(Me_3P)_4Os(H)(C_6H_5)$ [16], and the same product is formed with loss of neopentane when $(Me_3P)_4Os(H)(CH_2CMe_3)$ is heated in benzene to 70 °C [17]. More recently, this hydridoneopentyl complex has been found to activate methane, but not other alkanes or cycloalkanes, apparently for steric reasons [18]. We are also aware of investigations in the laboratory of M.A. Bennett directed towards C–H activation and based on derivatives of the $[(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Os(PR_3)]$ moiety [19].

In the present work, we have demonstrated that photolysis of the complex $(\eta\text{-}C_6Me_6)Os(CO)(H)_2$ (**3**) offers a photochemical activation route for C–H bonds in both saturated and aromatic hydrocarbons, with little selectivity. To our knowledge, these reactions are the first photochemically initiated hydrocarbon activations by osmium complexes with one intriguing exception: flash photolysis of $Os(CO)_5$ in C_6D_6 solution produced a transient species formulated as $Os(CO)_4 \cdot C_6D_6$ [20], which we interpret as an $\eta^2\text{-}C_6D_6$ complex. The transient decayed to $Os(CO)_5$ and $Os_2(CO)_9$, with no evidence under the experimental conditions for conversion to the product of "full" oxidative addition $(OC)_4Os(H)(C_6H_5)$.

Dihydride **3** is not as effective in photochemically induced hydrocarbon activation as the $(\eta\text{-}C_5Me_5)Ir(L)$ systems [1,2]. Yields of activation products are reduced by loss of C_6Me_6 ligand; yields of free C_6Me_6 range from 33% in benzene activation to 64% in neopentane. The lability of arene ligands relative to cyclopentadienyl is a pervasive feature of organometallic chemistry.

Nevertheless, expectations based on the isolobal analogy [21] have been amply confirmed. The lability of the arene ligand in the various osmium(II) compounds reported here may offer synthetic opportunities, which we have not explored at this stage.

Experimental

Solvents were dried (benzene, hexane and cyclohexane by refluxing over potassium; CH_2Cl_2 and $CHCl_3$ over P_2O_5) when necessary and distilled immediately

Table 5

Analytical and mass spectral data for complexes **1**–**6**

Complex	Elemental Formula	Analysis (Found (calcd) (%))		Ions observed [a]
		C	H	
1	$C_{13}H_{18}Cl_2OOs$	34.59 (34.83)	4.02 (4.01)	M^+, $M^+ - CO$, $M^+ - CO - Cl$
2	$C_{13}H_{19}ClOOs$	37.45 (37.33)	4.59 (4.58)	M^+, $M^+ - CO$
3	$C_{13}H_{20}OOs$	40.82 (40.85)	5.27 (5.48)	M^+, $M^+ - 2$, 350 [b]
4a	$C_{25}H_{28}OOs$	56.16 (56.02)	5.28 (5.28)	M^+, $M^+ - CO$, $M^+ - 2(C_6H_5)$
4b	$C_{25}H_{40}OOs$	54.92 (54.77)	7.37 (7.43)	M^+, $M^+ - C_6H_{11}$, $M^+ - C_6H_{11} - C_6H_{10}$
4c	$C_{23}H_{40}OOs$	52.84 (52.74)	7.71 (7.62)	M^+, $M^+ - C_5H_{11}$, $M^+ - C_5H_{11} - C_4H_9$, $M^+ - 2(C_5H_{11})$
5a	$C_{19}H_{23}ClOOs$	46.29 (46.20)	4.70 (4.74)	M^+, $M^+ - CO$, $M^+ - CO - C_6H_5$
5b	$C_{19}H_{29}ClOOs$	45.73 (45.68)	5.68 (5.85)	M^+, $M^+ - HCl$, $M^+ - C_6H_{11}$, $M^+ - C_6H_{11} - CO$
5c	$C_{18}H_{29}ClOOs$	44.39 (44.13)	6.00 (5.96)	M^+, $M^+ - C_5H_{11}$, $M^+ - C_5H_{11} - CO$
6a	$C_{19}H_{24}OOs$	49.76 (49.84)	5.27 (5.37)	M^+, $M^+ - CO$, $M^+ - C_6H_6$
6b	$C_{19}H_{30}OOs$	49.11 (50.05)	6.51 (6.75)	M^+, $M^+ - C_6H_{12}$
6c	$C_{18}H_{30}OOs$	47.76 (47.90)	6.68 (6.67)	M^+, $M^+ - C_5H_{12}$

[a] Operating at 16 eV. [b] m/e for ^{192}Os; unassigned.

prior to use. All reactions were performed under an argon atmosphere. Osmium tetroxide (Johnson Matthey Chemicals Ltd.), $R(-)$-α-phellandrene (Fluka), and hexamethylbenzene (Aldrich) were used as received. Phenyl- and cyclohexyl-magnesium chloride were prepared by standard techniques. Neopentylmagnesium chloride was prepared by the method of Schrock and Fellman [22]. Chlorobenzene (BDH), chlorocyclohexane (Aldrich) and neopentylchloride (Strem) were all distilled from anhydrous calcium chloride prior to use in Grignard reactions. Red-Al (Aldrich, $Na[H_2Al(OCH_2CH_2OCH_3)_2]$) was generally diluted with benzene before use to facilitate transfer of small amounts of the hydride.

Infrared spectra were recorded on a Nicolet MX-1 Fourier transform instrument. ^1H and ^{13}C NMR spectra were recorded on either a Bruker WH-200 or WH-400 instrument. Infrared and NMR data for all numbered compounds are given in Table 1. Mass spectra were obtained using an AEI-MS-12 spectrometer and microanalyses were performed by the Microanalytical Laboratory of this department. Melting points were taken on a hot stage and are uncorrected. Analytical and mass spectral data for all numbered compounds are given in Table 5.

Preparation of [(cymene)OsCl$_2$]$_2$

This procedure is a modification of a previously reported synthesis [23]; note that Na_2OsCl_6 or $OsCl_3 \cdot 3H_2O$ [8] have been used as starting materials to obtain this complex in improved yield (> 80%). A mixture of 2.00 g (7.90 mmol) of OsO_4 and 40 ml of concentrated HCl was heated to 110 °C for 48 h. Slow warming was necessary to avoid excessive loss of OsO_4. Removal of the HCl from the bright red solution was accomplished by distillation under reduced pressure. This left a red-black oil which was dissolved in 40 ml of water. The water was subsequently removed by distillation. Repetition of the water distillation (twice) followed by two ethanol distillations (40 ml each) left a black oil, presumably containing crude H_2OsCl_6 [24]. Dissolution of the oil in 40 ml of 95% ethanol followed by a reflux with 11 ml (67.7 mmol) of R(−)-α-phellandrene for 18 h gave a dark brown solution. Ethanol was removed by rotary evaporation and the residue was washed with hexane (3 × 50 ml). Hot methanol extraction of the remaining solid, followed by filtration (to remove a small amount of insoluble black material), concentration and cooling gave 1.52 g (1.92 mmol, 49%) of $[(\text{cymene})OsCl_2]_2$ as orange needles, m.p. 235 °C. ^1H NMR (δ, CD_2Cl_2): 6.13 (arene H, d, J 5.0 Hz, 2H), 5.98 (arene H′, d, J 5.0 Hz, 2H), 2.72 ($C\mathit{H}(CH_3)_2$, sept, J 7.0 Hz, 1H), 2.18 (p-CH_3, s, 3H), 1.28 ($CH(C\mathit{H}_3)_2$, d, J 7.0 Hz, 6H); ^{13}C NMR (δ, CD_2Cl_2: 92.7, 89.4 (quaternary arene-C), 74.4, 73.0 (CH arene), 31.8 ($\mathit{C}H(CH_3)_2$), 22.6 ($CH(\mathit{C}H_3)_2$), 19.6 (p-CH_3); MS (14 eV, 185 °C, m/e): M^+, $M^+/2$, $(\frac{1}{2}M - Cl)^+$. Anal. Found: C, 30.64; H, 3.63. $C_{20}H_{28}Cl_4Os_2$ calcd.: C, 30.38; H, 3.57%.

Preparation of $[(\eta\text{-}C_6Me_6)OsCl_2]_2$

This procedure is similar to that used in the analogous ligand exchange for ruthenium complexes [25]. A mixture of 1.20 g (1.50 mmol) of $[(\text{cymene})OsCl_2]_2$ and 6.0 g (37 mmol) of hexamethylbenzene was placed in two Pyrex tubes (1.5 × 10 cm) equipped with magnetic stir bars. The tubes were sealed under vacuum and heated, with stirring, to 185 °C for 22 h. After allowing the tubes to cool to room temperature they were broken open and their contents extracted with CH_2Cl_2 and filtered. Removal of the CH_2Cl_2 from the extracts by rotary evaporation left a solid which was washed with 4 × 50 ml of hexanes to remove organics. The remaining powder was washed with 3 × 10 ml of hot ethanol leaving 1.00 g (1.18 mmol, 78%) of the product as an orange solid which decomposed before melting at 280 °C. ^1H NMR (δ, CD_2Cl_2) 1.92(s); ^{13}C NMR (δ, CD_2Cl_2) 82.6 ($\mathit{C}_6(CH_3)_6$), 16.9 ($C_6(\mathit{C}H_3)_6$). MS (16 eV): $\frac{1}{2}M^+$, $(\frac{1}{2}M - Cl)^+$, 362 (unassigned). Anal. Found: C, 34.04; H, 4.29. $C_{24}H_{36}Cl_4Os$ calcd.: C, 33.84; H, 4.20%.

Preparation of $(\eta\text{-}C_6Me_6)Os(CO)Cl_2$ (1)

Carbon monoxide was bubbled into a suspension of 0.220 g (0.260 mmol) $[(\eta\text{-}C_6Me_6)OsCl_2]_2$ in 30 ml of $CHCl_3$ for 0.5 h. Chloroform was removed by rotary evaporation and the residue dissolved in CH_2Cl_2. Addition of hexanes followed by concentration gave 0.223 g (0.494 mmol, 95%) of **1** as an orange powder which decomposed without melting at 280 °C.

Preparation of $(\eta\text{-}C_6Me_6)Os(CO)(Cl)H$ (2)

A suspension of 0.500 g (1.11 mmol) of **1** in 100 ml of methanol was stirred with 4.50 g (68.8 mmol) of zinc dust and 3.5 ml (61.2 mmol) of glacial acetic acid for 2 h at room temperature. After the reaction mixture was filtered to remove excess zinc dust, the methanol was removed by rotary evaporation. The residue was extracted with 100 ml CH_2Cl_2 and the resulting yellow CH_2Cl_2 solution was washed with

2 × 100 ml of water. The CH_2Cl_2 layer was dried over anhydrous magnesium sulphate, filtered, concentrated to 10 ml, and then filtered through a plug of silica gel on a sintered glass disk. The IR of this filtrate showed that **2** and small amounts of **3** (up to 20%, varying from reaction to reaction) were present. Pure **3** was obtained by column chromatography (20 × 2.5 cm silica gel column; CH_2Cl_2 as eluent). Collection of the yellow fraction and recrystallization from methanol gave 0.330 g (0.780 mmol, 70%) of **2** as yellow-orange needles, m.p. 135 °C (dec).

Preparation of (η-C_6Me_6)Os(CO)H_2 (3)

Red-Al in benzene was added dropwise to a solution of 0.200 g (0.480 mmol) of **2** in 40 ml of benzene until the solution was pale yellow and an IR of the reaction mixture indicated no **2** remained. Excess Red-Al was destroyed by the addition of 0.1 ml of water. The reaction mixture was dried over anhydrous magnesium sulfate and filtered. Rotary evaporation to remove benzene left a dark residue which was dissolved in CH_2Cl_2 and filtered through a silica gel plug. Removal of the CH_2Cl_2 and extraction of the remaining light brown solid with hexanes followed by column chromatography (15 × 4 cm silica gel column, CH_2Cl_2 eluent) gave after recrystallization from hexanes 0.130 g (0.340 mmol, 71%) of **3** as off-white needles, m.p. 110 °C (dec).

Preparation of (η-C_6Me_6)Os(CO)$(C_6H_5)_2$ (4a)

A suspension of 0.400 g (0.886 mmol) of **1** in 150 ml of benzene was treated with 2.0 ml (2.00 mmol) of phenyl magnesium chloride (1.0 *M* in THF). After stirring for 1 h at room temperature 2.0 ml of water was added to the resulting yellow solution. The reaction mixture was dried over anhydrous magnesium sulphate and filtered. Removal of the solvent by rotary evaporation left a yellow oil which was chromatographed on a silica gel column (12 × 4.5 cm, CH_2Cl_2 eluent). Collection of the first yellow band gave 0.385 g (0.721 mmol, 81%) of **4a** as a yellow solid, m.p. 230 °C (dec). A more slowly moving yellow band was also collected and shown spectroscopically to be **5a** (0.035 g, 7%).

Preparation of (η-C_6Me_6)Os(CO)$(C_6H_{11})_2$ (2b) and (η-C_6Me_6)Os(CO)$(CH_2CMe_3)_2$ (4c)

Dialkyls **4b** and **4c** were both prepared from **1** and cyclohexylmagnesium chloride and neopentylmagnesium chloride in a manner similar to that described for the preparation of **4a**. **4b** was obtained as yellow needles (38% yield) from hexanes, m.p. 140 °C (dec). **4c** was obtained as yellow prisms (48% yield) from hexanes, m.p. 170 °C (dec).

Preparation of (η-C_6Me_6)Os(CO)(C_6H_5)Cl (5a)

A solution of 0.200 g (0.374 mmol) of **4a** in 75 ml of CH_2Cl_2 was cooled to −78 °C (dry-ice/acetone bath). Hydrogen chloride gas was bubbled into the solution for 10 s during which time the solution became a darker yellow. The reaction was purged with argon for 5 min and then allowed to warm to room temperature, still under an argon purge. Removal of the CH_2Cl_2 by rotary evaporation left a yellow solid which was chromatographed on a silica gel column (12 × 4.5 cm, CH_2Cl_2 eluent). Collection of the yellow fraction and removal of solvent gave 0.170 g (0.345 mmol, 92%) of **5a** as a yellow powder, m.p. 230 °C (dec).

*Preparation of (η-C_6Me_6)Os(CO)(C_6H_{11})Cl (**5b**) and (η-C_6Me_6)Os(CO)(CH_2CMe_3)Cl (**5c**)*

The preparation of **5b** and **5c** from **4b** and **4c** was analogous to that described for **5a**. However addition of hydrogen chloride gas must be carefully monitored to avoid an excess. Complex **5b** does not survive silica gel chromatography. **5b** was obtained as orange crystals (60% yield) m.p. 145 °C (dec). **5c** was obtained as yellow crystals (75% yield) m.p. 175 °C (dec).

*Preparation of (η-C_6Me_6)Os(CO)(C_6H_5)H (**6a**)*

A suspension of 0.125 g (0.254 mmol) of **5a** in 120 ml of methanol was treated with 2.0 g (30.6 mmol) of zinc dust and 0.5 ml (8.7 mmol) of glacial acetic acid. The mixture was stirred under reflux for 18 h after which the reaction was filtered to remove the excess zinc dust. Removal of the methanol by rotary evaporation left an oil which was extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with an equal volume of water, dried over anhydrous magnesium sulphate and filtered. After removal of the CH_2Cl_2 the residue was extracted with a minimum amount of hot hexanes, filtered and cooled. This gave 0.0468 g (0.102 mmol, 40%) of **6a** as off-white plates, m.p. 147 °C (dec).

*Preparation of (η-C_6Me_6)Os(CO)(C_6H_{11})H (**6b**)*

Complex **6b** was prepared from **5b** and cyclohexylmagnesium chloride in a manner similar to that described below for **6c**. **6b** was obtained as a slightly yellow powder (42% yield), m.p. 114 °C (dec).

*Preparation of (η-C_6Me_6)Os(CO)(CH_2CMe_3)H (**6c**)*

A solution of 0.100 g (0.240 mmol) of **2** in 150 ml of benzene was treated with neopentylmagnesium chloride until **2** was completely consumed (IR monitored reaction). Small amounts of **4c** and **5c** were also detected in the reaction mixture. After treating the reaction mixture with 1.0 ml of water, the benzene was dried over anhydrous magnesium sulphate, filtered and removed by rotary evaporation. The residue was extracted with hexanes and filtered through a pipet filled with neutral alumina (20% Et_2O/hexanes elutent). Removal of solvents left a powder which was recrystallized from hexanes at -78 °C to give 0.051 g (0.113 mmol, 47%) of **6c** as light yellow crystals, m.p. 80–85 °C.

General method for photolysis of 3

A solution of 10 mg **3** in 10.0 ml solvent (benzene, cyclohexane or neopentane) was freeze-thaw-degassed three times in a quartz photolysis tube (2×20 cm, equipped with Rotoflow valve). The solubility of **3** in alkanes is quite low, and probably does not exceed 2 mg/ml at room temperature. The photolysis was carried out using an Oriel (Model No. 6183) focussed beam lamp employing a 500 watt mercury arc source and irradiation times were of the order of 1–2 h. Sample cooling was important and was accomplished by passing a stream of nitrogen gas, cooled by immersion of a copper coil in an ice bath, over the sample tube; sample temperatures were not measured but are estimated to be room temperature or slightly (< 10 °C) higher. After photolysis solvent was removed under oil pump vacuum and the residue dissolved in CD_2Cl_2. The ^1H NMR of the samples showed the presence of **3**, **6a**–**6c**, and free hexamethylbenzene. The identity of **6a**–**6c** was confirmed by comparison of the ^1H NMR spectra to those of authentic samples. Integration of the hexamethylbenzene resonances gave the relative amounts of products formed. No other hexamethylbenzene resonances were observed by ^1H NMR. Photolysis was also carried out in NMR tubes in benzene-d_6 and cyclohexane-d_{12}; in both cases, only the three C_6Me_6 resonances were observed.

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