# Triosmium Cluster Derivatives of [60]Fullerene

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Triosmium carbonyl cluster derivatives of [60]fullerene, $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$, $Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})$, $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ and $Os_3(CO)_9(PPh_3)_2(\eta^2\text{-}C_{60})$ are described.

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In recent years the organometallic chemistry of [60]fullerene has attracted much attention concerning the effect of metal coordination on the properties of $C_{60}$.[1] The first such complex $(C_{60})(OsO_4)(4\text{-}Bu^tC_5H_4N)_2$, an osmate ester with C–O–Os bonds was reported by Hawkins and coworkers.[2] However, the first example with a direct metal–$C_{60}$ bond, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, was reported by Fagan *et al.*[3] Recent reports of other metal coordinated [60]fullerene complexes have included those of Ta,[4] Mo,[4] Fe,[4] Rh,[4,5] Ir,[6,7] Ni[8] and Pd,[8] in which all the mononuclear metals are bound in an $\eta^2$-fashion at the 6–6 ring fusion. Herein, we report the preparation, isolation and characterization of triosmium cluster derivatives of $\eta^2\text{-}C_{60}$ as is shown in Scheme 1.

A toluene solution of $Os_3(CO)_{11}(NCMe)$ and $C_{60}$ (1 equiv.) was heated at 80 °C for 5 min. The solvent was evaporated and the residue purified by preparative TLC (silica gel, hexane : toluene, 2 : 1) at low temperature (*ca.* −15 °C) to afford a black, microcrystalline solid, $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$ **1**, (dark brown band, $R_f$ = 0.7, 44%). The MeCN derivative $Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})$ **2**, ($R_f$ = 0.5, 52%), and the phosphine-substituted complexes, $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ **3**, ($R_f$ = 0.8, 60%) and $Os_3(CO)_9(PPh_3)_2(\eta^2\text{-}C_{60})$ **4**, ($R_f$ = 0.5, 36%) were purified in the same way (green bands, hexane : toluene, 1 : 1) and isolated as black solids (Scheme 1). The double addition ($C_{60}$–$2Os_3$) products of **1**–**4** were also formed as minor products (*ca.* 10%) in these reactions; however, they were major products when 0.5 equiv. of $C_{60}$ was used. The double addition complexes are thermally much more unstable than the single addition complexes and are converted to the latter in solution at room temperature over periods up to 10 h. Complexes **1** and **2** are interconvertable either by decarbonylation of **1** with $Me_3NO$–MeCN reagent at −50 °C or by exposure of **2** to CO gas (1 atm). Complex **2** reacts with $PPh_3$ to afford **3**, which undergoes further reaction with $PPh_3$ to give **4** upon decarbonylation with $Me_3NO$. All these transformations proceed in quantitative yields.

Complexes **2**–**4** are soluble in dichloromethane and **1**–**4** in aromatic solvents to form either brown (**1**) or green (**2**–**4**) solutions, but they are insoluble in pentane and hexane. Formulation of the $C_{60}$ derivatives **1**–**4** is supported by elemental analysis and by the molecular ion ($M^+$) multiplet in the FAB positive ion MS of each compound.† The $M^+$ multiplet in the MS of **1**–**4** matches perfectly the calculated pattern [the highest peak in the $M^+$ multiplet (*m*/*z*, found, calcd): **1** (1600, 1600), **2** (1613, 1613), **3** (1834, 1834) and **4** (2068, 2068)]. The presence of MeCN ligand in **2** was confirmed by observation of the highest peak at 1616 (**2** + 3 mass unit) in the MS of the deuteriated derivative of **2**, $Os_3(CO)_{10}(CD_3CN)(\eta^2\text{-}C_{60})$. We have not yet been able to obtain crystals of **1**–**4** suitable for X-ray crystallographic analysis.

The definitive structural assignment of **1**–**4** (Fig. 1) is made on the basis of spectroscopic data ($^1H$ and $^{13}C$ NMR, and IR). The IR spectrum of **1** is identical to that of $Os_3(CO)_{11}(PPh_3)$, and the IR spectra of **3** and **4** are similar to those of $Os_3(CO)_{10}(PPh_3)_2$ and $Os_3(CO)_9(PPh_3)_3$, respectively. These results indicate that compounds **1**, **3**, and **4** are isostructural with the corresponding phosphine-substituted complex, $Os_3(CO)_{12-n}(PPh_3)_n$ ($n$ = 1–3),[9] and thus the $C_{60}$ moiety occupies an equatorial site. The IR spectra (KBr pellet) of **1**–**4** show that the band characteristic for $C_{60}$ at 576 cm$^{-1}$ becomes a doublet at 582 and 596 cm$^{-1}$ in addition to the band at 527 cm$^{-1}$ as expected for a lower symmetry $C_{60}$ moiety. The $^{13}C$ NMR spectrum of **1** (*ca.* 50% $^{13}CO$-enriched) is given in Fig. 2 and reveals eight resonances at δ 183.3, 182.9, 181.7, 172.0, 171.9, 170.3, 168.8 and 168.5 with an intensity ratio of

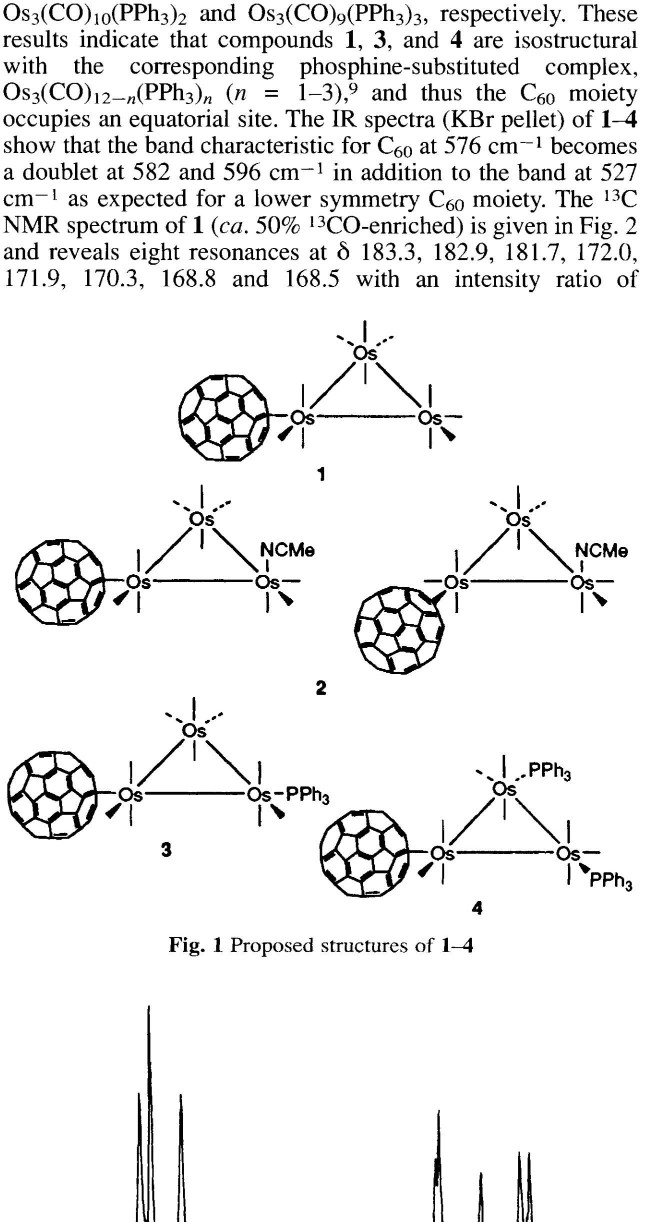

**Fig. 1** Proposed structures of **1**–**4**

$$\begin{tikzcd}
Os_3(CO)_{11}(NCMe) \arrow[r, "i"] & Os_3(CO)_{11}(\eta^2\text{-}C_{60})\ \mathbf{1} \arrow[d, shift left, "v"] \\
Os_3(CO)_{10}(NCMe)_2 \arrow[r, "ii"] & Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})\ \mathbf{2} \arrow[u, shift left, "iv"] \arrow[d, "vi"] \\
Os_3(CO)_{11}(PPh_3) \arrow[r, "iii"] & Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})\ \mathbf{3} \arrow[d, "vii"] \\
Os_3(CO)_{10}(PPh_3)_2 \arrow[r, "iii"] & Os_3(CO)_9(PPh_3)_2(\eta^2\text{-}C_{60})\ \mathbf{4}
\end{tikzcd}$$

**Scheme 1** *Reagents and conditions*: i, $C_{60}$, toluene, 80 °C, 5 min; ii, $C_{60}$, toluene, 80 °C, 15 min; iii, $Me_3NO$ (1 equiv.), MeCN, $CH_2Cl_2$, then $C_{60}$, toluene, room temp., 15 min; iv, CO (1 atm.), toluene, room temp., 2 h; v, $Me_3NO$ (1 equiv.), MeCN, toluene, −50 °C, 5 min; vi, $PPh_3$ (1 equiv.), toluene, room temp., 1 h; vii, $PPh_3$ (1 equiv.), toluene, then $Me_3NO$ (1 equiv.), $CH_2Cl_2$, −50 °C

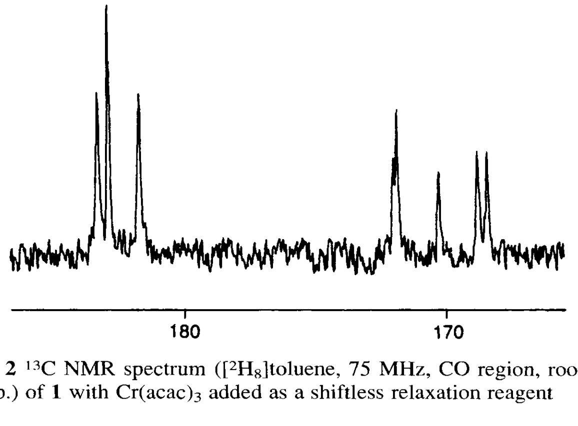

**Fig. 2** $^{13}C$ NMR spectrum ([$^2H_8$]toluene, 75 MHz, CO region, room temp.) of **1** with $Cr(acac)_3$ added as a shiftless relaxation reagent

2 : 2 : 2 : 1 : 1 : 1 : 1 : 1. The three lower-field (higher-intensities) resonances are considered to be due to three sets of the six axial carbonyl ligands and the rest are attributed to the five inequivalent equatorial carbonyl ligands.[10] These data are entirely consistent with the low-temperature limit structure of **1**, with $\eta^2$-$C_{60}$ occupying an equatorial position at an osmium centre. The $^{13}C$ signals for the $C_{60}$ moiety are too weak to be detected. The $^1H$ NMR spectrum of **2** reveals two singlets due to MeCN at $\delta$ 3.02 and 2.85 in a ratio of 2 : 1 indicating that **2** exists as two isomers. Upon addition of $CD_3CN$ the two resonances for the major and minor isomers slowly (2 h) lose intensity at room temperature and are replaced by a sharp singlet at $\delta$ 1.98 due to free MeCN, which is consistent with facile displacement of coordinated MeCN by the deuterated solvent. In compound **2**, the MeCN ligand may be coordinated at an axial site of an osmium atom as shown in $Os_3(CO)_{12-n}(NCMe)_n$ ($n$ = 1, 2)[11] and the bulky $\eta^2$-$C_{60}$ ligand bonded to either one of the two inequivalent equatorial sites of an adjacent osmium atom producing two isomers. The double addition complexes are supposed to be *para* complexes, in which the $Os_3$ triangle is bonded to opposite portions of $C_{60}$, as previously shown in both $(C_{60})[Ir_2Cl_2(1,5\text{-}COD)_2]_2$[7] and $(C_{60})[Ir(CO)Cl(PMe_2Ph)_2]_2$.[12] Only the double addition products have been observed in these bulky triosmium carbonyl clusters, although hexa-substituted mononuclear complexes have been reported in $(C_{60})[M(PEt_3)_2]_6$ (M = Pt, Pd).[13]

The reactivities, fluxional processes and electrochemical properties of **1–4** are being investigated.

*Received, 20th September 1994; Com. 4/05726K*

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## Footnote

† *Selected data* for **1**: $^{13}C$ NMR ($[^2H_8]$toluene, 25 °C) $\delta_{CO}$ 183.3, 182.9, 181.7, 172.0, 171.9, 170.3, 168.8, 168.5; IR ($CH_2Cl_2$) $\nu_{CO}$/cm$^{-1}$ 2122(m), 2074(s), 2059(m), 2038(vs), 2016(m), 2006(m), 1990(w); MS *m/z*, $^{192}Os$, FAB$^+$ 1604(M$^+$). For **2**: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 3.02 (s, 3H, major isomer), 2.85 (s, 3H, minor isomer); isomer ratio ~2 : 1; IR ($CH_2Cl_2$) $\nu_{CO}$/cm$^{-1}$ 2110(m), 2101(w), 2064(s), 2055(m), 2032(s), 2018(vs), 1988(m), 1958(w); MS *m/z*, $^{192}Os$, FAB$^+$ 1617(M$^+$). For **3**: IR ($CH_2Cl_2$) $\nu_{CO}$/cm$^{-1}$ 2099(m), 2051(m), 2034(m), 2017(vs), 1993(m), 1975(sh); MS *m/z*, $^{192}Os$, FAB$^+$ 1838(M$^+$). For **4**: IR ($CH_2Cl_2$) $\nu_{CO}$/cm$^{-1}$ 2109(w), 2083(w), 2072(w), 2051(m), 2017(s), 1999(vs), 1964(m), 1941(sh); MS *m/z*, $^{192}Os$, FAB$^+$ 2072(M$^+$).

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