1,1,2,2,2,2,3,3,3,3-Decacarbonyl-1-(η-cyclohexa-1,3-diene)-*triangulo*-triosmium: A Novel Intermediate in Synthetic Osmium Cluster Chemistry

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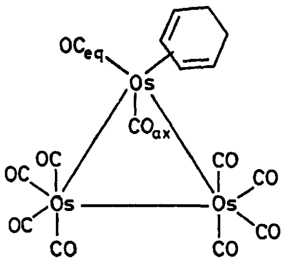
Cyclohexadiene reacts with $[Os_3(CO)_{10}H_2]$ under moderate conditions to give $[Os(CO)_{10}(C_6H_8)]$. Some reactions of this compound with alcohols, thiols, amines, halogen and organic acids, ethylenes, and acetylenes have been examined, and it is shown that cyclohexa-1,3-diene is a very good ' leaving group ' and provides a convenient route to a number of *triangulo*-Os_3 cluster compounds.

CURRENT interest in the synthesis of trinuclear osmium carbonyl clusters of the type $[Os_3(CO)_{10}HY]$ (Y = a three-electron donor) has revealed a number of limitations in the use of the common reagents for the synthesis of clusters of this type, *viz.* $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{10}H_2]$. Thus $[Os_3(CO)_{12}]$ tends only to react with four-electron donors at elevated temperatures [1,2] to give poor yields of derivatives, which reflects the strength of the metal–carbonyl bond, whereas $[Os_3(CO)_{10}H_2]$ reacts readily with accompanying hydrogenation [3,4] but only under forcing conditions if such a reduction is difficult.[5] The general synthetic utility of compounds in which good ' leaving groups ' are present has been previously observed in other aspects of organometallic chemistry.[6] We therefore report here the synthesis and reactivity of $[Os_3(CO)_{10}(C_6H_8)]$,[7] a compound which has provided a simple and effective intermediate for the preparation of a wide range of derivatives in high yields. Variable-temperature ^{13}C n.m.r. spectroscopy [8] has shown the compound to have a static structure corresponding to (1). Recent evidence in support of this structure comes from the single-crystal *X*-ray analysis of the butadiene analogue of (1) [9] showing clearly the axial–equatorial orientation of the butadiene ligand on one osmium atom. We have been able to show that the η-cyclohexa-1,3-diene ligand in (1) is a very good ' leaving group ' and that (1) provides a convenient route to the synthesis of a number of trinuclear osmium cluster compounds.

EXPERIMENTAL

1,1,2,2,2,2,3,3,3,3-*Decacarbonyl*-1-(η-*cyclohexa*-1,3-*diene*)-triangulo-*triosmium*, $[Os_3(CO)_{10}(C_6H_8)]$ (1).—The compound $[Os_3(CO)_{10}H_2]$ (500 mg) was added to distilled refluxing n-hexane containing an excess of cyclohexa-1,3-diene or -1,4-diene under nitrogen. After 4 h, the solvent and excess diene were removed *in vacuo* and the residue was chromatographed on silica plates using hexane–diethyl ether (19 : 1) as eluant. The required compound was removed from the plates as an intense orange band and was recrystallized from hexane at −25 °C, yield 60% (Found: C, 20.7; H, 0.9. $C_{16}H_8O_{10}Os_3$ requires C, 20.5; H, 0.85%).



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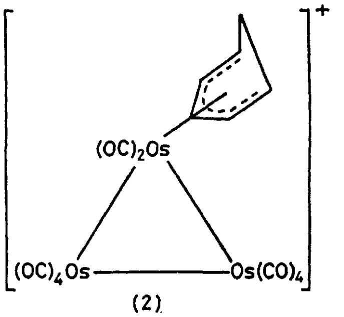

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1,1,2,2,2,2,3,3,3,3-*Decacarbonyl*-1-(1—5-η-*cyclohexadienyl*)-triangulo-*triosmium Tetrafluoroborate*, $[Os_3(CO)_{10}(C_6H_7)][BF_4]$, (2).—Compound (1) (30 mg) dissolved in dry dichloromethane (5 cm^3) was added to $[CPh_3][BF_4]$ (100 mg)

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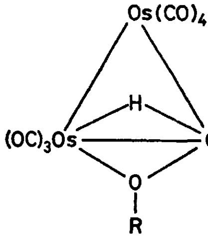
dissolved in dry dichloromethane (10 cm^3). After stirring for 1 h at room temperature under nitrogen, aqueous diethyl ether (100 cm^3) was added to give (2) as a yellow solid (80%) (Found: C, 20.0; H, 0.9. $C_{16}H_7BF_4O_{10}Os_3$ requires C, 19.8; H, 0.88%).



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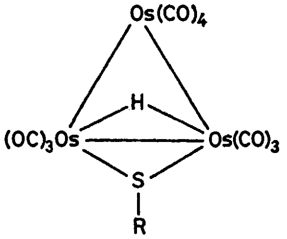

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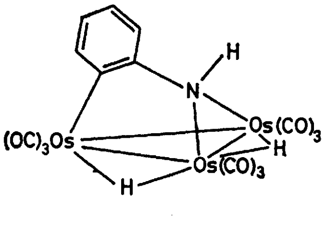

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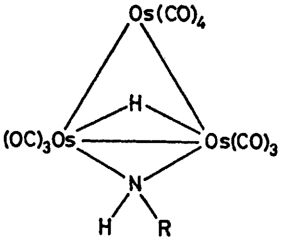

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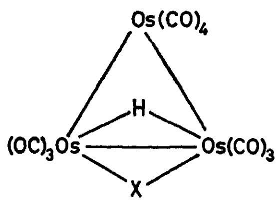

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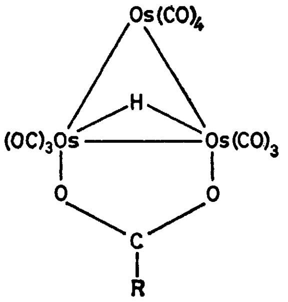

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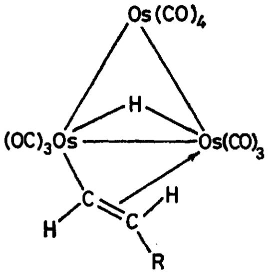

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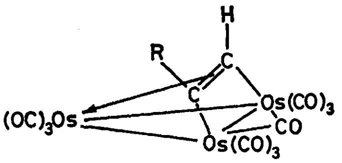

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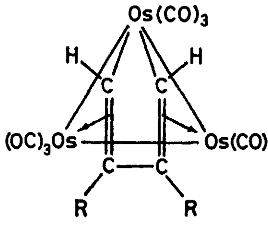

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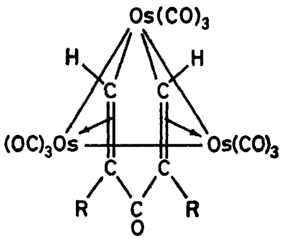

(12)

[$Os_3(CO)_{10}H(OR)$] (3; R = H, Et, C_6H_{11}, *or* Ph).—Compound (1) (30 mg) was added to refluxing cyclohexane (25 cm^3) containing an excess of the appropriate alcohol under nitrogen. The reaction was monitored by i.r. spectroscopy and, after it had gone to completion (*ca.* 3 h), the solvent and excess of alcohol were removed *in vacuo*. The residue was chromatographed on thin silica plates using hexane (R = Et, C_6H_{11}, or Ph) or chloroform (R = *H*) as eluant to give (3) as yellow crystals, yield 80 (R = Et, C_6H_{11}, or Ph) or 20% (R = H).

[$Os_3(CO)_{10}H(SR)$] (4; R = H, Et, *or* Pr^i).—Compound (1) (30 mg) was dissolved in refluxing cyclohexane (25 cm^3) containing an excess of thiol. After less than 5 min (R = H or Et) or 15 min (R = Pr^i) the solvent and excess of thiol were removed and the residue was chromatographed on thin silica plates using either hexane (R = Et or Pr^i) or chloroform (R = H) as eluant to give (4), yield = 90 (R = Et or Pr^i) or 10% (R = H).

[$Os_3(CO)_{10}H(NHR)$] (6; R = H, Ph, *or* Bu^n).—Compound (1) (30 mg) was dissolved in refluxing cyclohexane (25 cm^3) containing an excess of primary amine. After 2—3 h (depending on R) the solvent and excess of amine were removed *in vacuo*. The residue was chromatographed on thin silica plates using hexane–diethyl ether (9 : 1) as eluant. With aniline the orthometallated derivative [$Os(CO)_9H_2(NHC_6H_4)$] (5) (40%) was produced together with the expected (6; R = Ph) (50%). When R = H or Bu^n the expected derivatives (6) were produced, yield = 40 (R = Bu^n) or 20% (R = H).

2,3-*μ-Halogeno*-2,3-*μ-hydrido*-1,1,1,1,2,2,2,3,3,3-*decacarbonyl*-triangulo-*triosmium*, [$Os_3(CO)_{10}(H)X$] (7; X = Cl *or* Br).—Compound (1) (30 mg) was dissolved in either refluxing hexane (25 cm^3; X = Br) or refluxing cyclohexane (25 cm^3; X = Cl) whilst dry halogen acid was passed through the solution. After either 3 h (X = Cl) or 10 min (X = Br) the solvent was removed and the residue was chromatographed on thin silica plates using hexane as eluant to give (7) as yellow crystals (from hexane), yield *ca.* 80%.

[$Os_3(CO)_{10}H(CO_2R)$] (8; R = H, Me, CF_3, Et, Ph, C_6H_4Cl-*p*, $C_6H_4NO_2$-*p*, *or* CO_2Et).—Compound (1) (30 mg) was dissolved in refluxing cyclohexane (25 cm^3) containing an excess of organic acid. After the reaction had gone to completion (1—2 h depending on R) the solvent was removed *in vacuo* and the residue was chromatographed on thin silica plates using hexane as eluant. Compound (8) was obtained as yellow crystals (from hexane) in a yield of 90% in all cases except R = H when the yield was 20%.

[$Os_3(CO)_{10}H(CHCHR)$] (9; R = H *or* Ph).—Compound (1) (30 mg) was dissolved in refluxing cyclohexane (25 cm^3) containing an excess of the appropriate olefin. After 3 h the solvent and excess of olefin were removed *in vacuo* and the residue was chromatographed on thin silica plates using hexane as eluant to give (9), yield 60 (R = H), or 20% (R = Ph).

[$Os_3(CO)_{10}(C_2HR)$] (10), [$Os_3(CO)_9(C_4H_2R_2)$] (11), *and* [$Os_3(CO)_9(C_4H_2R_2CO)$] (12) (R = H *or* Ph).—Compound (1) (30 mg) was dissolved in refluxing cyclohexane (25 cm^3) containing an excess of the appropriate alkyne. After 4 h the solvent and excess of alkyne were removed *in vacuo* and the residue was chromatographed on thin silica plates using hexane–diethyl ether (9 : 1) as eluant to give, in order of appearance on the plate, (10), (11) and (12). The yields depended on R. When R = H the yields were 50 (10), 20 (11), and 10% (12); when R = Ph, 0 (10), 60 (11), and 5% (12).

Spectroscopic data for the new compounds

Compound	I.r. spectra [ν(CO)/cm^{-1}] [a]	N.m.r. spectra [b]			
		τ	Relative intensity	Assignment	J/Hz
$[Os_3(CO)_{10}H(OEt)]$	2 110m, 2 071s, 2 061s, 2 026v, 2 014v, 1 989m, 1 981m	8.52 (t)	3	CH_3	7.2
		7.34 (q)	2	CH_2	
		21.40 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(OC_6H_{11})]$	2 111m, 2 073s, 2 061s, 2 025v, 2 012v, 1 985m, 1 980m	8.75 (m)	11	CH	
		21.25 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(SH)]$	2 108m, 2 066v, 2 057s, 2 022v, 2 018m (sh), 1 998m, 1 987m, 1 976w	7.75 (b)	1	SH	
		27.52 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(SPr^i)]$	2 108m, 2 065v, 2 057s, 2 021v, 2 017m, 1 995m, 1 986m, 1 979w	8.18 (m)	1	CH	6.5
		8.63 (d)	6	CH_3	
		27.46 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(NH_2)]$	2 105w, 2 067s, 2 052m, 2 021s, 2 004s, 1 992s, 1 978w	6.25 (b)	2	NH_2	
		25.25 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(NHBu^n)]$	2 103w, 2 065s, 2 050m, 2 021s, 2 002s, 1 989m, 1 978w	6.00 (b)	2	NCH_2	
		7.25 (m)	7	CH (rest)	
		24.62 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2H)]$	2 114w, 2 076s, 2 067s, 2 025v, 2 012s, 1 989m, 1 980m	2.42 (s)	1	H	
		20.28 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2Me)]$	2 113w, 2 074s, 2 062s, 2 027s, 2 012s, 1 987m, 1 983m	8.05 (s)	3	CH_3	
		20.42 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2CF_3)]$	2 111w, 2 079s, 2 061s, 2 029s, 2 019s, 1 992m, 1 988m	20.30 (s)		OsH	
$[Os_3(CO)_{10}H(CO_2Et)]$	2 111w, 2 072s, 2 059s, 2 024s, 2 009s, 1 984m, 1 979m	7.75 (q)	2	CH_2	8.0
		9.02 (t)	3	CH_3	
		20.35 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2Ph)]$	2 111w, 2 072s, 2 061s, 2 024s, 2 013s, 2 006m, 1 983m, 1 979m	2.60 (m)	5	CH	
		20.30 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2C_6H_4Cl\text{-}p)]$	2 113w, 2 075s, 2 064s, 2 027s, 2 015s, 2 009m, 1 988m, 1 983m	2.20 (d)	2	H^2,H^6	8.2
		2.60 (d)	2	H^3,H^5	
		20.15 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2C_6H_4NO_2\text{-}p)]$	2 112w, 2 075s, 2 063s, 2 028s, 2 014s, 2 001m (sh), 1 989m, 1 984m	1.75 (d)	2	H^2,H^6	7.9
		2.05 (d)	2	H^3,H^5	
		20.10 (s)	*ca.* 1	OsH	
$[Os_3(CO)_{10}H(CO_2CO_2Et)]$	2 116w, 2 078s, 2 067s, 2 030s, 2 018s, 1 990m, 1 986m	5.88 (q)	2	CH_2	7.1
		8.80 (t)	3	CH_3	
		20.29 (s)	*ca.* 1	OsH	
$[Os_3(CO)_9(C_4H_4CO)]$	2 097m, 2 063s, 2 053s, 2 027s, 2 011m (sh), 2 005s, 1 983m, 1 637w	−0.47 (d)	2	H^1,H^4	9.5
		3.75 (d)	2	H^2,H^3	

[a] Recorded in cyclohexane solution; w = weak, m = medium, s = strong, v = very strong, sh = shoulder. [b] Recorded at 80 MHz at 35 °C using a Varian Associates CFT-20 spectrometer, solvent $CDCl_3$; s = singlet, m = multiplet, b = broad, t = triplet, q = quartet, d = doublet.

DISCUSSION

In comparison with $[Os_3(CO)_{12}]$, compound (1) reacts with thiols, alcohols, and primary amines to give improved yields of derivatives using more moderate reaction conditions.[2,10-12] Interestingly, it can be used to prepare both $[Os_3(CO)_{10}H(SH)]$ and $[Os_3(CO)_{10}H(NH_2)]$ which are unobtainable from $[Os_3(CO)_{12}]$.

It provides a direct route to the synthesis of halogen acid derivatives (7) when the only previous routes gave either very low yields from $[Os_3(CO)_{12}]$, *via* $[Os_3(CO)_{12}Cl_2]$, or were indirect from $[Os_3(CO)_{10}H_2]$ and an allyl halide.[13] It very readily forms organic acid derivatives of the type (8), previously unreported in the literature, in very high yields and purity.

With ethylene or vinylbenzene ' vinyl ' derivatives (9) are produced, previously obtained in good yields, with accompanying hydrogenation, from $[Os_3(CO)_{10}H_2]$ and a variety of acetylenes.[4,14] With acetylene or phenylacetylene (1) reacts to form three compounds (10)—(12), the relative ratio of the products depending on the substituent. The previous routes to these compounds were either from $[Os_3(CO)_{12}]$ and diphenylacetylene (11) or olefins (10) using more extreme reaction conditions [1,15] or, alternatively, from $[Os_3(CO)_{10}H_2]$ and a large excess of acetylene (12).[3]

The n.m.r., i.r., and mass spectra of these derivatives are all consistent with the proposed structures, and the data for previously unreported compounds are summarized in the Table. In conclusion, $[Os_3(CO)_{10}(C_6H_8)]$, which can be produced readily from cyclohexadiene and $[Os_3(CO)_{10}H_2]$, provides a convenient route to the synthesis of many trinuclear osmium clusters using, in most instances, more moderate reaction conditions than previously.

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