Doubly and Triply Bridged Dihapto Phenylethynyl Triosmium Clusters by Oxidative Addition of Phenylethynyl Gold Compounds. *X*-Ray Crystal Structure of $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$†

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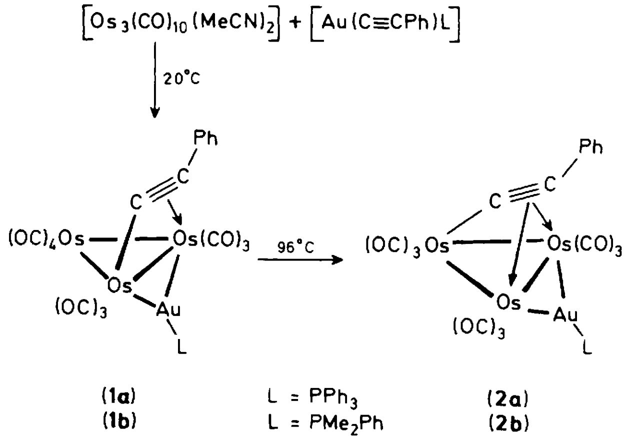
Oxidative addition of $[Au(C{\equiv}CPh)L]$ (L = PPh_3 or PMe_2Ph) to $[Os_3(CO)_{10}(MeCN)_2]$ gives $[Os_3(C{\equiv}CPh)(AuL)(CO)_{10}]$. The single-crystal *X*-ray structure for the compound with L = PMe_2Ph shows that the AuL group and the μ,η^2-phenylethynyl ligand bridge the same pair of osmium atoms. The Os–Os bond lengths are consistent with AuL being a one-electron donor. Ready decarbonylation occurs in refluxing heptane to give single products formulated as $[Os_3(\mu_3,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}AuL)(CO)_9]$.

There are many examples of the use of the group $Au(PR_3)$ as a pseudo-hydrogen atom; the two are isolobal.[1] For example, the series of compounds $[Os_3H_{2-x}(AuL)_x(CO)_{10}]$ (x = 0, 1, or 2; L = PPh_3 or PEt_3) are structurally very similar and show little variation of Os–Os lengths.[2–4] Thermal reactions of [AuX(L)] (X = Cl, Br, I, or SCN; L = tertiary phosphine) with $[Os_3(CO)_{12}]$ give the clusters $[Os_3(\mu\text{-}X)(\mu\text{-}AuL)(CO)_{10}]$; the *X*-ray structures where L = PPh_3 and X = Cl,[5] Br,[5] or SCN[6] are known. Under milder conditions $[Au(NCO)(PEt_3)]$ adds to $[Os_3(CO)_{11}(MeCN)]$ to produce a mixture of $[Os_3(NCO)\{\mu\text{-}Au(PEt_3)\}(CO)_{10}]$ and $[Os_3(NCO)\{\mu\text{-}Au(PEt_3)\}(CO)_{11}]$ while addition to $[Os_3(CO)_{10}(MeCN)_2]$ gives only the decacarbonyl compound.[7] A compound formulated as $[Os_3(C{\equiv}CPh)\{Au(PPh_3)\}(CO)_9]$ (based on mass spectroscopic data) was reported as the product of the reaction of $[Os_3(CO)_{12}]$ with LiC≡CPh and $[AuCl(PPh_3)]$ in the presence of $TlPF_6$ and also from the room-temperature reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[Au(C{\equiv}CPh)(PPh_3)]$.[8] We were interested in synthesising μ-cyanide compounds and decided to apply the same approach by using $[Au(CN)(PPh_3)]$ but the results seemed to indicate a deca- rather than a nona-carbonyl product. This led us to re-examine the reported reaction of $[Au(C{\equiv}CPh)(PPh_3)]$ with $[Os_3(CO)_{10}(MeCN)_2]$ (Scheme) and we have found, contrary to the original report,[8] that the initial product is $[Os_3(C{\equiv}CPh)\{Au(PPh_3)\}(CO)_{10}]$ (**1a**) which only decarbonylates to $[Os_3(C{\equiv}CPh)\{Au(PPh_3)\}(CO)_9]$ (**2a**) at much higher temperatures (96 °C, 1 h). This compound (**2a**) is not the same as the reported compound with the same formulation.[8] The reported i.r. spectrum around 2 000 cm^{-1} is fairly close to but not quite identical with that we observed for the decacarbonyl compound described here. Most likely the reported nonacarbonyl is the same as the compound we now unambiguously formulate as the decacarbonyl. The incorrect formulation[8] was probably made because thermal decarbonylation occurred in obtaining the mass spectrum. Corresponding compounds (**1b**) and (**2b**) with PMe_2Ph instead of PPh_3 are also reported together with the *X*-ray structure of $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$, (**1b**).



Scheme.

Results and Discussion

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[Au(C{\equiv}CPh)L]$ (L = PPh_3 or PMe_2Ph) at room temperature in dichloromethane gives the major products (**1**) as orange-red crystals with i.r. spectra resembling those of other compounds of the type $[Os_3X(AuL)(CO)_{10}]$.[5] Preparative details and spectroscopic data are given in the Experimental section. To confirm that (**1**) are decacarbonyl compounds and not nonacarbonyls as reported by Burgess *et al.*,[8] a single-crystal *X*-ray structure determination on compound (**1b**) was carried out.

The molecular structure of compound (**1b**) is shown in the Figure, atomic co-ordinates are in Table 1, and selected bond lengths and angles in Table 2. The structure is like those of other clusters of type $[Os_3(\mu\text{-}X)(AuL)(CO)_{10}]$[5] forming a butterfly Os_3Au group with a wing-tip gold atom. The idea that the $Au(PMe_2Ph)$ group is a one-electron donor is substantiated by the Os(1)–Os(2) distance of 2.912(1) Å which is only a little longer than the bridged Os–Os distances in $[Os_3H(\mu\text{-}CH{=}CHR)(CO)_{10}]$ [2.845(2) (R = H),[9] 2.834(1) (R = Et),[10] and 2.814(2) Å (R = Bu^t)[11]]. The *X*-ray structure of $[Os_3H(C{\equiv}CPh)(CO)_{10}]$[12] has not been determined. Replacement of μ-H or μ-$Au(PMe_2Ph)$ in these compounds by a three-electron donor leads to a lengthening of the Os–Os distance. For example, in $[Os_3(\mu\text{-}SPh)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ the bridged Os–Os distance is 3.328(1) Å.[13] The μ,η^2-C≡CPh ligand in compound (**1b**) [C≡C 1.173(12) Å] adopts a bent *trans*

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† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-(dimethylphenylphosphine)-aurio-1,2-μ-[phenylethynyl-$C^1(Os^1)C^{1-2}(Os^2)$]-*triangulo*-triosmium.

Supplementary data available (No. SUP 56394, 7 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates (× 10^4) for $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$, (**1b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	909(0.5)	1 828(0.5)	2 216(0.5)	O(7)	4 236(7)	3 436(11)	4 411(6)
Os(2)	1 189(0.5)	4 538(0.5)	3 334(0.5)	O(8)	−1 241(7)	639(10)	3 640(6)
Os(3)	1 539(0.5)	2 045(0.5)	4 207(0.5)	O(9)	2 042(10)	3 310(11)	6 335(5)
Au	−876(0.5)	2 968(0.5)	1 604(0.5)	O(10)	1 638(10)	−1 075(9)	4 383(6)
P	−2 620(2)	2 882(3)	390(2)	C(11)	2 319(8)	4 008(9)	2 545(5)
C(1)	1 930(9)	764(10)	2 234(6)	C(12)	2 981(8)	5 303(10)	2 871(6)
C(2)	−541(9)	−43(11)	1 888(7)	C(13)	3 981(8)	6 804(9)	3 086(6)
C(3)	495(9)	1 864(10)	746(6)	C(14)	4 950(9)	6 900(11)	2 820(7)
C(4)	2 346(8)	5 769(9)	4 579(6)	C(15)	5 895(9)	8 295(12)	2 956(8)
C(5)	−118(8)	4 211(10)	3 730(6)	C(16)	5 894(10)	9 636(12)	3 366(8)
C(6)	850(9)	6 035(10)	2 604(6)	C(17)	4 958(10)	9 543(12)	3 660(8)
C(7)	3 247(10)	2 961(11)	4 326(7)	C(18)	3 980(9)	8 132(10)	3 506(7)
C(8)	−215(9)	1 167(11)	3 836(6)	C(19)	−2 251(13)	4 479(17)	−233(1)
C(9)	1 881(11)	2 847(12)	5 544(7)	C(20)	−3 388(12)	1 221(15)	−605(8)
C(10)	1 625(11)	121(13)	4 342(7)	C(21)	−3 816(8)	2 962(10)	748(6)
O(1)	2 542(7)	128(9)	2 291(6)	C(22)	−4 904(9)	2 960(13)	50(8)
O(2)	−1 359(8)	−1 145(9)	1 733(6)	C(23)	−5 821(10)	2 994(14)	334(9)
O(3)	241(9)	1 804(9)	−83(5)	C(24)	−5 687(11)	3 078(12)	1 301(10)
O(4)	3 031(6)	6 545(8)	5 331(4)	C(25)	−4 674(12)	3 038(16)	1 981(9)
O(5)	−920(7)	4 031(10)	3 973(5)	C(26)	−3 715(10)	3 014(13)	1 728(7)
O(6)	644(8)	6 960(8)	2 212(6)				

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$, (**1b**)

Os(1)–Os(2)	2.912(1)	Os(1)–C(11)	2.079(10)
Os(1)–Os(3)	2.851(1)	Os(2)–C(11)	2.294(9)
Os(2)–Os(3)	2.865(1)	Os(2)–C(12)	2.457(11)
Au–Os(1)	2.770(1)	C(11)–C(12)	1.173(12)
Au–Os(2)	2.794(1)	C(12)–C(13)	1.455(13)
Au–P	2.296(4)		

Average values

Carbonyls		Phenyl rings	
Os–C	1.91_3	C–C (ring 1)	1.38_6
C–O	1.13_9	C–C (ring 2)	1.38_1

Os(2)–Os(3)–Os(1)	61.3(1)	C(11)–C(12)–C(13)	162.6(9)
Os(3)–Os(2)–Os(1)	59.1(1)	Os(2)–C(11)–Os(1)	83.4(4)
Os(3)–Os(1)–Os(2)	59.6(1)	C(12)–C(11)–Os(2)	83.6(7)
C(11)–Os(1)–Os(2)	51.5(3)	Au–Os(2)–Os(1)	58.0(1)
C(11)–Os(1)–Au	92.5(3)	Au–Os(1)–Os(3)	102.1(1)
Os(1)–C(11)–C(12)	166.9(7)	Os(2)–Au–Os(1)	63.1(1)

arrangement [Os(1)–C(11)–C(12) 166.9(7)° and C(11)–C(12)–C(13) 162.6(9)°] as in other three-electron-donor alkynyl bridges[14] and with a different geometry from one-electron donor alkynyl bridges. The compound $[Ru_3(\mu,\sigma\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)(PPh_2)_2\{(Ph_2P)C_2Bu^t\}(CO)_6]$ contains both types of alkynyl bridge.[15]

Thermal decarbonylation of compounds (**1**) in refluxing heptane occurs very cleanly within 1 h to give a yellow solution containing compounds (**2**), $[Os_3(\mu_3,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}AuL)(CO)_9]$. Compound (**2a**; L = PPh_3) was obtained as yellow crystals, but (**2b**; L = PMe_2Ph) gave an oil. We presume that these compounds contain five-electron-donating alkynyl ligands. Their i.r. spectra around 2 000 cm^{-1} are very similar and each quite different from that of the compound reported to have this formula.[8]

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[Au(CN)(PPh_3)]$ in dichloromethane at room temperature seemed to be like that with $[Au(C{\equiv}CPh)(PPh_3)]$. A red-orange solution with a similar i.r. spectrum was obtained; ν(CO) (CH_2Cl_2) 2 149w, 2 098s, 2 057vs, 2 043vs, 2 016vs, 1 987s, and 1 970s (sh) cm^{-1}. This solution was presumed to contain the compound $[Os_3(\mu,\eta^2\text{-}CN)\{Au(PPh_3)\}(CO)_{10}]$ but this could not be crystallised and t.l.c. on silica led to decomposition.

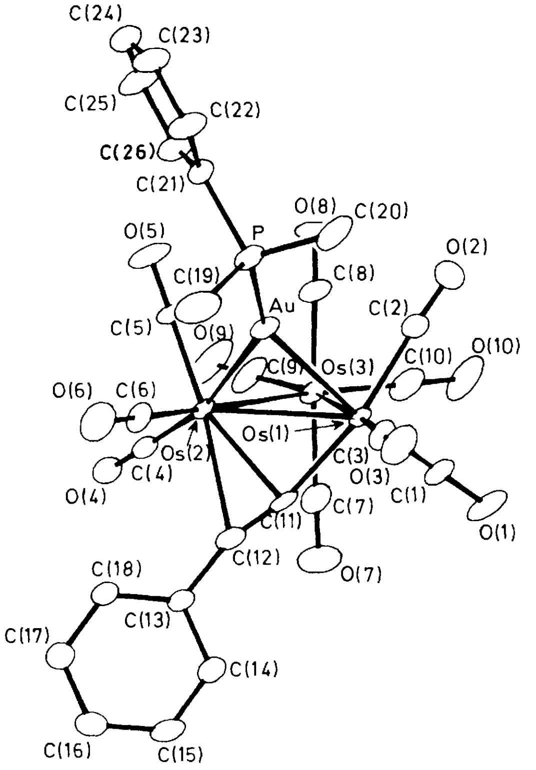

Figure. Molecular structure of $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$, (**1b**)

Experimental

The compound $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the published method,[16] $[Au(C{\equiv}CPh)(PPh_3)]$ was prepared from $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)(PMe_2Ph)]$ from $[Au(C{\equiv}CPh)]_n$.[17] Proton n.m.r. spectra were recorded on a Varian XL200 spectrometer and i.r. spectra on a Perkin-Elmer 983 spectrometer.

Preparation of $[Os_3(\mu,\eta^2\text{-}C{\equiv}CPh)\{\mu\text{-}Au(PPh_3)\}(CO)_{10}]$, (**1a**).—A yellow solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.0924 g) and $[Au(C{\equiv}CPh)(PPh_3)]$ (0.056 g, 1 mol per mol Os_3) in dichloromethane (15 cm^3) became red on standing at room temperature for 1 h. The residue after removal of solvent was separated by t.l.c. [SiO_2; eluant light petroleum (b.p. 30—40 °C)–diethyl ether (20:1 v/v)] to give as the major band compound (**1a**) (0.055 g, 39%) as orange-red crystals from light petroleum (b.p. 30—40 °C) (Found: C, 31.2; H, 1.55. $C_{36}H_{20}AuO_{10}Os_3P$ requires C, 30.65; H, 1.45%); ν(CO) (cyclo-C_6H_{12} solution) 2 090m, 2 039s, 2 033s, 2 006vs, 1 985w, 1 973m, 1 964m, and 1 955w (sh) cm^{-1}. Minor quantities of the compounds $[Os_3H(Cl)(CO)_{10}]$, $[Os_3Cl\{Au(PPh_3)\}(CO)_{10}]$ and $[Os_3(\mu\text{-}CH{=}CPh)(CO)_{10}]$ were also isolated together with some unidentified material.

Preparation of Compound (**1b**).—This was prepared similarly from $[Os_3(CO)_{10}(MeCN)_2]$ (0.228 g) and $[Au(C{\equiv}CPh)(PMe_2Ph)]$ (0.107 g, 1 mol per mol Os_3) to give compound (**1b**) as orange-red crystals (0.067 g, 21%) (Found: C, 24.15; H, 1.35. $C_{26}H_{16}AuO_{10}Os_3P$ requires C, 24.25; H, 1.25%); ν(CO) (cyclo-C_6H_{12} solution) 2 090m, 2 039s, 2 032vs, 2 011 (sh), 2 007vs, 1 984w, 1 973m, 1 962m, and 1 955w cm^{-1}; ^1H n.m.r. (CD_2Cl_2, 22 °C) δ 1.84 (d) [J_{PH} 9.1 Hz (Me)] and 7.5 (m) (Ph). The sample gave single crystals suitable for *X*-ray diffraction from CH_2Cl_2–hexane mixtures.

Thermolysis of Compound (**1a**).—A red solution of $[Os_3(C{\equiv}CPh)\{Au(PPh_3)\}(CO)_{10}]$ (0.020 g) in heptane (4 cm^3) was heated under reflux for 68 min. Removal of the solvent under vacuum from the orange-yellow solution gave essentially pure $[Os_3(C{\equiv}CPh)\{Au(PPh_3)\}(CO)_9]$ (**2a**) which was recrystallised from CH_2Cl_2–hexane as yellow crystals (Found: C, 30.3; H, 1.45; O, 10.55. $C_{35}H_{20}AuO_9Os_3P$ requires C, 30.4; H, 1.45; O, 10.4%); ν(CO) (cyclo-C_6H_{12}) 2 090vw, 2 072m, 2 039vs, 1 989s, and 1 961m cm^{-1}.

Thermolysis of $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$ (**1b**).—A similar treatment of compound (**1b**) but including a chromatographic work-up [SiO_2; eluant in light petroleum (b.p. 30—40 °C)–diethyl ether (20:1 v/v)] gave $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_9]$ (**2b**) as yellow-orange oil which could not be crystallised but had a very similar i.r. spectrum to that of compound (**2a**); ν(CO) (cyclo-C_6H_{12}) 2 094vw, 2 072m, 2 051w, 2 038vs, 2 013w, 1 989vs, 1 982 (sh), and 1 961m cm^{-1}.

Crystallographic Studies.—Crystal data. $C_{26}H_{16}AuO_{10}Os_3P$, M = 1 287, triclinic, a = 12.714(3), b = 9.581(1), c = 14.627(3) Å, α = 92.52(1), β = 109.73(2), γ = 111.77(1)°, U = 1 528.1 Å^3, space group $P\bar{1}$, Z = 2, D_c = 2.80 g cm^{-3}, $F(000)$ = 1 147.8, λ = 0.710 69 Å, μ(Mo-K_α) = 166.37 cm^{-1}.

Data collection. Unit-cell parameters and intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractomer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan procedure.[18] In total, 5 348 unique reflections ($1.5 \leqslant \theta \leqslant 25°$) were measured of which 4 423 were considered observed [$I \geqslant 1.5\sigma(I)$]. A semiempirical absorption correction using normalised and averaged ψ-scan measurements[19] from three reflections was applied to the data; the maximum and minimum transmissions were 99.89 and 35.50% respectively.

Structure solution and refinement. The heavy-atom method was used to determine the positions of the gold, osmium, and phosphorus atoms and a Fourier-difference calculation revealed all other non-hydrogen atoms. Most of the hydrogen atoms were located by refinement and Fourier-difference synthesis, although the positions of some of the methyl hydrogens were calculated. All atoms were successfully refined, non-hydrogen atoms anisotropically and hydrogen atoms isotropically, using the weighting scheme $w = 1/[\sigma^2(F) + 0.000\,2F^2]$ and full-matrix least squares. The final values of R and R' were 0.028_7 and 0.027_4, respectively. All calculations were carried out using the SHELX 76[20] program on a DEC VAX-11/750 computer.

Acknowledgements

We thank the S.E.R.C. for financial support and for the use of the S.E.R.C. National *X*-Ray Crystallographic Service at Q.M.C. and Drs. M. B. Hursthouse and H. M. Dawes for their assistance. K. H. thanks the Department of Chemistry, California State University, Northridge, for leave.

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Received 28th May 1985; *Paper* 5/896