Facile Carbon–Carbon Bond Formation on a Triosmium Cluster: Crystal Structures of $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(Ph)C(Ph)\}]$ and $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ †

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The organometallic cluster $[Os_3(CO)_8(NCMe)\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ reacts with a range of alkynes to produce $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(R)C(R')\}]$ ($R = R' =$ H, Me, or Ph; $R =$ Me, $R' =$ Ph) in which the incoming alkyne molecule and the previously co-ordinated pentadienone ligand have combined to produce a C_7Os_3 unit; the molecular structures of $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(Ph)C(Ph)\}]$ and $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)-C(Me)C(O)C(Me)C(Me)\}]$ have been ascertained by *X*-ray analyses.

Reactions of transition-metal clusters with excess alkyne frequently afford products where C–C bond formation has occurred to give larger, co-ordinated organic groups.[1,2] In these reactions, the clusters promote alkyne oligomerization and exert a template effect on the resulting organic moiety. Indeed, it has been tentatively proposed that the cluster employed in this work, $[Os_3(CO)_9\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**1**), contains an organic fragment derived from two alkyne molecules and a carbonyl group.[3] Our current investigation shows that the addition of an alkyne molecule to the MeCN derivative of (**1**), $[Os_3(CO)_8(NCMe)\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**2**), results in the formation of an additional C–C link to afford a novel C_7Os_3 cluster unit. Evidence for the presence of a pentadienone ligand in (**1**) and (**2**) and the probable position of the labile MeCN ligand in (**2**) has been obtained from an *X*-ray structure analysis of the phosphite derivative, $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**7**).

Results and Discussion

There are several examples where the displacement of weakly co-ordinated MeCN ligands provides an efficient means of achieving substitution under mild conditions.[2,4] The acetonitrile complex (**2**) reacts readily with RC_2R' to produce an orange product which, on the basis of analytical and spectroscopic evidence, was formulated as $[Os_3(CO)_8(RC_2R')\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ [$R = R' =$ H (**3**), Me (**4**), or Ph (**5**); $R =$ Me, $R' =$ Ph (**6**)]. An *X*-ray structure analysis of (**5**) was undertaken in order to establish its molecular geometry and in particular to elucidate the mode of co-ordination of the organic ligand(s).

The molecular structure of (**5**) (Figure 1) reveals that C–C bond formation has occurred, linking the alkyne and the pentadienone groups together. The resulting organic fragment is co-ordinated in a μ_3–η^2,η^4 fashion to a triangular array of osmium atoms, formally *via* three σ, a π, and a π-allyl bond. In this configuration the organic ligand acts as an eight-electron donor and each osmium atom obeys the 18-electron rule. Within the triangular osmium framework, the two edges bridged by the organic group are significantly shorter than the average osmium–osmium distance of 2.877(3) Å in $[Os_3(CO)_{12}]$.[5] A similar trend had been observed in other alkyne-substituted triosmium clusters.[2,6] A more detailed assessment of the Os–C and C–C interactions is not plausible because the estimated standard deviations on the associated parameters are relatively large.

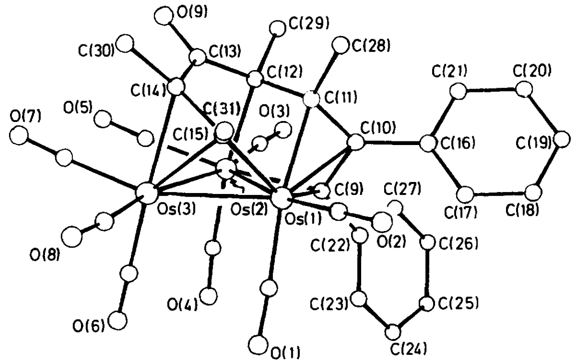

Figure 1. The molecular structure of $[Os_3(CO)_8\{C(Me)C(Me)C(O)-C(Me)C(Me)C(Ph)C(Ph)\}]$ (**5**)

In order to establish the probable position of the MeCN ligand in (**2**) and hence the most likely site for initial co-ordination of the incoming alkyne molecule, the phosphite derivative of (**2**), $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)C(Me)C(O)-C(Me)C(Me)\}]$ (**7**), was synthesised and characterised *X*-ray crystallographically.

The reaction of (**2**) with $P(OMe)_3$ proceeds smoothly at room temperature to afford (**7**). Consistent with the proposed structure for (**1**),[2] the molecular structure of (**7**) (Figure 2) contains a triangular array of osmium atoms and a pentadienone group with two σ bonds to one osmium atom to give an osmacyclohexadienone ring. This metallacyclic ring is π-bonded to Os(3) through C(12) and C(13) and to Os(1) through C(15) and C(16). Within the osmium triangle the two edges bridged by the organic group are significantly shorter consistent with the trend noted above. The phosphite ligand is bonded in a pseudo-equatorial position to Os(2), the osmium atom included in the metallacycle.

On the basis of the structures of (**5**) and (**7**), we propose a mechanism for the reaction of (**2**) with RCCR in which the

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† 1,1,1,2,2,2,3,3-Octacarbonyl-μ_3-[3,5,6-trimethyl-4-oxo-7,8-diphenylocta-2,6-dien-2,5-diyl-8-ylidene-$C^{2,3}(Os^1)$,$C^{5,8}(Os^2)$,$C^{2,6-8}(Os^3)$]-*triangulo*-triosmium and 1,1,1,2,2,2,3,3-octacarbonyl-μ_3-[3,5-dimethyl-4-oxohepta-2,5-dien-2,6-diyl-$C^{2,3}(Os^1)$, $C^{5,6}(Os^2)$, $C^{2,6}(Os^3)$]-3-(trimethyl phosphite)-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

initial replacement of the labile MeCN ligand with a π-bonded alkyne molecule is followed by carbon–carbon bond formation and the rearrangement of the bonding between the Os_3 unit and organic group to give the observed Os_3C_7 arrangement.

Table 1. I.r. (cm^{-1})[a] and ^1H n.m.r. data[b]

Complex	ν(CO)
(2)	2 076s, 2 036s, 2 011vs, 1 965m br, 1 606s
(3)	2 090s, 2 056vs, 2 009m, 1 990m, 1 978w sh, 1 951m, 1 622w br
(4)	2 088s, 2 053vs, 2 027vs, 2 007m, 1 987m, 1 974w sh, 1 948m, 1 607m
(5)	2 092s, 2 058vs, 2 028vs, 2 013m, 1 993m, 1 980w sh, 1 948w, 1 606s
(6)	2 090s, 2 050s, 2 028vs, 2 010m, 1 990m, 1 978w sh, 1 950m, 1 610w br
(7)	2 077s, 2 038s, 2 016vs, 2 000m sh, 1 978m, 1 585w br
	δ/p.p.m.
(3)	8.84 (d, 1 H), 6.65 (d, 1 H), 3.30 (s, 3 H), 2.54 (s, 3 H), 1.89 (s, 3 H), 1.63 (s, 3 H) (J_{H-H} 4.0 Hz)
(4)	3.27 (s, 3 H), 3.08 (s, 3 H), 2.54 (s, 3 H), 2.28 (s, 3 H), 1.83 (s, 3 H), 1.63 (s, 3 H)
(5)	7.30 (br, m, 10 H), 3.39 (s, 3 H), 2.59 (s, 3 H), 2.02 (s, 3 H), 1.86 (s, 3 H)
(6)	7.40 (br, m, 5 H), 3.31 (s, 3 H), 2.87 (s, 3 H), 2.54 (s, 3 H), 1.87 (s, 3 H), 1.66 (s, 3 H)
(7)	3.65 (d, 9 H), 3.08 (s, 3 H), 3.07 (s, 3 H), 2.35 (s, 6 H)

[a] Spectra recorded in CH_2Cl_2; vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder. [b] Spectra recorded in CD_2Cl_2; d = doublet, s = singlet.

Table 2. Selected interatomic distances (Å) and angles (°) for (**5**) with estimated standard deviations in parentheses

Os(1)–Os(2)	2.796(1)	C(9)–C(10)	1.44(2)
Os(1)–Os(3)	2.720(1)	C(10)–C(11)	1.40(2)
Os(2)–Os(3)	2.974(1)	C(11)–C(12)	1.53(2)
Os(1)–C(9)	2.12(2)	C(12)–C(13)	1.49(2)
Os(1)–C(10)	2.20(2)	C(13)–C(14)	1.53(2)
Os(1)–C(11)	2.25(2)	C(14)–C(15)	1.42(2)
Os(1)–C(15)	2.11(2)		
Os(2)–C(9)	2.14(2)	Os(2)–Os(1)–Os(3)	65.2(1)
Os(2)–C(12)	2.20(2)	Os(1)–Os(2)–Os(3)	56.1(1)
Os(3)–C(14)	2.30(2)	Os(1)–Os(3)–Os(2)	58.6(1)
Os(3)–C(15)	2.22(2)		

Experimental

All experiments were carried out under an atmosphere of nitrogen using Schlenk-tube techniques, unless otherwise stated. I.r. and ^1H n.m.r. data for the new compound are given in Table 1.

Synthesis of (**1**).—$[Os_3(CO)_{10}(NCMe)_2]$ (50 mg) was placed in a Carius tube and dissolved in CH_2Cl_2 (30 cm^3). An excess of Me_2C_2 (*ca.* 10 fold) was added, the Carius tube firmly closed, and the reaction mixture allowed to stir for 10 min. The resultant solution was concentrated and subject to thin-layer chromatography using hexane–CH_2Cl_2 (1 : 1) as the eluant. The first band which was yellow, gave the known cluster, $[Os_3(CO)_{10}(Me_2C_2)]$[6] (yield 42%). The second orange-red band was extracted with CH_2Cl_2 and afforded $[Os_3(CO)_9\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**1**) (yield 24%).

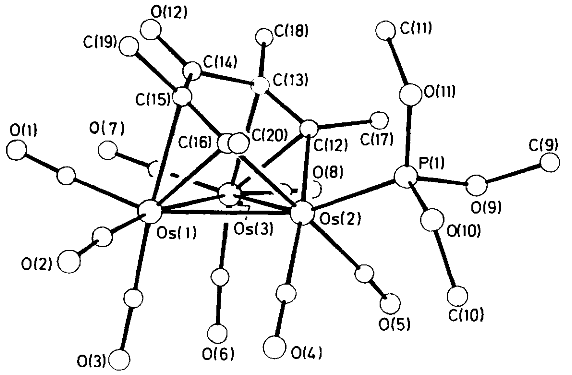

Figure 2. The molecular structure of $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**7**); molecule 1

Table 3. Atomic co-ordinates (× 10^4) for (**5**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	4 758(1)	2 766(1)	2 907(1)	C(10)	5 039(14)	3 786(8)	2 371(7)
Os(2)	6 530(1)	3 522(1)	3 967(1)	C(11)	6 280(14)	3 431(8)	2 199(7)
Os(3)	6 547(1)	2 000(1)	3 871(1)	C(12)	7 572(15)	3 502(8)	2 786(8)
C(1)	3 261(18)	2 457(10)	3 612(9)	C(13)	8 562(18)	2 896(9)	2 831(9)
C(2)	3 503(19)	2 469(10)	2 079(10)	C(14)	7 908(16)	2 180(8)	2 738(8)
C(3)	6 879(17)	4 481(10)	4 078(8)	C(15)	6 400(18)	2 073(9)	2 544(9)
C(4)	5 276(17)	3 518(9)	4 903(9)	C(16)	4 050(10)	4 160(5)	1 752(5)
C(5)	8 312(15)	3 290(8)	4 540(8)	C(17)	2 551(10)	4 026(5)	1 664(5)
C(6)	5 425(21)	2 019(11)	4 863(11)	C(18)	1 696(10)	4 418(5)	1 136(5)
C(7)	8 345(17)	1 793(9)	4 409(8)	C(19)	2 340(10)	4 943(5)	696(5)
C(8)	6 228(21)	1 026(12)	3 736(10)	C(20)	3 840(10)	5 077(5)	784(5)
O(1)	2 370(14)	2 282(7)	4 068(8)	C(21)	4 695(10)	4 685(5)	1 312(5)
O(2)	2 736(15)	2 287(7)	1 567(8)	C(22)	3 517(10)	4 317(4)	3 505(5)
O(3)	7 106(16)	5 058(7)	4 084(8)	C(23)	2 286(10)	4 106(4)	3 928(5)
O(4)	4 533(15)	3 525(7)	5 434(7)	C(24)	1 252(10)	4 587(4)	4 174(5)
O(5)	9 366(13)	3 193(7)	4 877(7)	C(25)	1 448(10)	5 279(4)	3 997(5)
O(6)	4 868(17)	2 014(9)	5 436(8)	C(26)	2 679(10)	5 491(4)	3 574(5)
O(7)	9 425(13)	1 664(7)	4 692(7)	C(27)	3 714(10)	5 010(4)	3 327(5)
O(8)	6 052(19)	467(8)	3 694(11)	C(28)	6 678(19)	3 270(11)	1 327(9)
O(9)	9 895(12)	2 958(7)	2 923(7)	C(29)	8 463(17)	4 141(9)	2 556(9)
C(9)	4 714(14)	3 821(7)	3 213(7)	C(30)	9 034(18)	1 644(10)	2 553(10)
				C(31)	6 001(21)	1 502(11)	1 994(11)

Synthesis of (**2**).—A solution of dry Me_3NO (4.0 mg, 0.053 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise to a stirred suspension of (**1**) (50.0 mg, 0.052 mmol) in $MeCN-CH_2Cl_2$ (1:10, 40 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 1 h, filtered through silica, and taken to dryness. The remaining red residue afforded $[Os_3(CO)_8(NCMe)\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**2**), which was used without further purification.

Synthesis of (**3**).—C_2H_2 was bubbled through a CH_2Cl_2 (30 cm^3) solution of (**2**) (40 mg) for *ca.* 3 h. The resulting solution was concentrated and subject to thin-layer chromatography. Elution with hexane–CH_2Cl_2 (1:9) afforded an orange band which was extracted with CH_2Cl_2 and gave $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(H)C(H)\}]$ (**3**) (yield *ca.* 50%).

Table 4. Selected interatomic distances (Å) and angles (°) for (**7**) with estimated standard deviations in parentheses (averaged values of the three crystallographically independent molecules)

Os(1)–Os(2)	2.792(2)	C(12)–C(13)	1.36(5)
Os(1)–Os(3)	2.857(2)	C(13)–C(14)	1.53(6)
Os(2)–Os(3)	2.799(2)	C(14)–C(15)	1.46(5)
Os(2)–P(1)	2.29(1)	C(15)–C(16)	1.40(5)
Os(1)–C(15)	2.30(3)		
Os(1)–C(16)	2.27(4)	Os(2)–Os(1)–Os(3)	59.4(1)
Os(2)–C(12)	2.16(3)	Os(1)–Os(2)–Os(3)	61.4(1)
Os(2)–C(16)	2.19(4)	Os(1)–Os(3)–Os(2)	59.2(1)
Os(3)–C(12)	2.24(3)		
Os(3)–C(13)	2.29(4)		

Synthesis of (**4**).—An excess (*ca.* 10 fold) of Me_2C_2 was added to a CH_2Cl_2 (30 cm^3) solution of (**2**) (40 mg) in a Carius tube, the tube was firmly closed, and the reaction mixture stirred for 4 h. The resulting solution was worked-up as for (**3**) to give $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(Me)C(Me)\}]$ (**4**) (yield *ca.* 35%)..

Synthesis of (**5**).—An excess (*ca.* 2 fold) of Ph_2C_2 was added to a CH_2Cl_2 (30 cm^3) solution of (**2**) (40 mg) and the reaction mixture stirred for 4 h. The resulting solution was worked-up as for (**3**) to give $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(Ph)C(Ph)\}]$ (**5**) (yield *ca.* 30%).

Synthesis of (**6**) *and* (**7**).—The compounds $[Os_3(CO)_8\{C(Me)C(Me)C(O)C(Me)C(Me)C(Me)C(Ph)\}]$ (**6**) and $[Os_3(CO)_8\{P(OMe)_3\}\{C(Me)C(Me)C(O)C(Me)C(Me)\}]$ (**7**) were synthesised using the conditions described for (**5**) and the appropriate ligand [yields: *ca.* 28% for (**6**), *ca.* 22% for (**7**)].

X-*Ray Structure Determination of* (**5**).—*Crystal data.* $C_{31}H_{22}O_9Os_3$, M = 1 108.6, monoclinic, space group $P2_1/n$ (alt. setting $P2_1/c$, no. 14), a = 9.100(3), b = 19.512(6), c = 16.683(4) Å, β = 90.80(5)°, U = 2 962 Å^3 (refined from 2θ values of 36 strong reflections in the range 18—25°), D_c = 2.49 g

Table 5. Atomic co-ordinates (× 10^4) for (**7**) with estimated standard deviations in parentheses

	Molecule 1			Molecule 2			Molecule 3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Os(1)	670(1)	3 574(1)	9 411(1)	−355(1)	2 712(1)	5 326(1)	2 166(1)	1 010(1)	3 149(1)
Os(2)	590(1)	1 903(1)	9 326(1)	882(1)	1 872(1)	5 638(1)	2 380(1)	2 531(1)	2 733(1)
Os(3)	−499(1)	2 714(1)	9 769(1)	949(1)	3 543(1)	5 553(1)	2 904(1)	1 191(1)	2 231(1)
C(1)	206(18)	4 570(22)	9 385(13)	−921(18)	3 653(21)	5 341(13)	1 952(25)	−112(30)	3 065(18)
C(2)	1 526(20)	4 011(23)	9 230(14)	−1 151(23)	2 002(26)	5 163(16)	1 703(25)	1 030(29)	3 814(19)
C(3)	1 048(20)	3 671(23)	10 045(15)	−262(25)	2 780(29)	4 596(19)	2 927(21)	918(23)	3 539(15)
C(4)	1 505(18)	2 018(20)	9 594(13)	1 711(22)	1 967(24)	5 277(15)	3 265(21)	2 964(24)	2 597(15)
C(5)	481(20)	1 100(24)	9 908(16)	506(21)	1 178(25)	5 074(16)	2 631(21)	2 786(25)	3 474(16)
C(6)	−76(18)	2 727(21)	394(14)	1 091(21)	3 603(24)	4 827(16)	3 691(28)	1 148(30)	2 598(19)
C(7)	−1 020(19)	3 615(23)	9 850(14)	459(17)	4 513(20)	5 593(12)	2 828(23)	94(28)	2 088(17)
C(8)	−1 165(21)	2 068(24)	30(15)	1 837(18)	3 969(20)	5 682(12)	3 459(23)	1 434(26)	1 643(18)
O(1)	−54(15)	5 183(18)	9 316(11)	−1 259(17)	4 234(20)	5 306(12)	1 790(18)	−756(22)	2 979(14)
O(2)	2 096(18)	4 282(21)	9 162(13)	−1 634(18)	1 670(20)	5 029(12)	1 536(20)	983(23)	4 215(16)
O(3)	1 323(16)	3 767(19)	506(12)	4 825(17)	2 183(20)	4 155(13)	3 528(16)	891(18)	3 793(12)
O(4)	2 116(16)	2 100(17)	9 746(11)	265(15)	767(17)	4 760(11)	3 791(19)	3 261(22)	2 477(13)
O(5)	389(15)	735(17)	236(11)	2 248(17)	1 993(18)	5 133(12)	2 713(15)	2 894(18)	3 921(12)
O(6)	154(15)	2 691(18)	856(11)	1 159(15)	3 678(17)	4 391(12)	4 295(19)	1 084(21)	2 841(13)
O(7)	−1 316(16)	4 258(19)	9 850(11)	173(15)	5 146(17)	5 649(10)	2 720(18)	−568(22)	2 010(13)
O(8)	−1 623(16)	1 683(19)	199(12)	2 389(15)	4 290(16)	5 746(10)	3 749(20)	1 505(24)	1 292(16)
P(1)	847(6)	874(6)	8 774(4)	1 320(6)	809(6)	6 139(4)	1 814(6)	3 734(7)	2 607(4)
O(9)	516(14)	48(15)	8 950(10)	833(13)	44(16)	6 031(10)	2 218(16)	4 304(19)	2 254(12)
O(10)	1 629(14)	642(16)	8 742(10)	2 108(15)	505(17)	6 062(11)	1 753(16)	4 213(19)	3 164(11)
O(11)	640(14)	950(15)	8 157(10)	1 382(20)	974(23)	6 765(15)	989(16)	3 771(19)	2 393(12)
C(9)	551(22)	−682(25)	8 661(16)	978(26)	−708(31)	6 325(19)	1 897(34)	5 063(39)	1 963(24)
C(10)	2 065(20)	308(23)	9 152(15)	2 243(26)	88(30)	5 562(19)	1 234(23)	4 847(26)	3 225(16)
C(11)	−35(23)	1 243(26)	7 923(17)	1 743(60)	702(67)	7 141(43)	666(26)	3 411(31)	1 949(20)
C(12)	−529(15)	1 883(18)	9 070(11)	1 269(16)	2 725(19)	6 239(12)	2 138(19)	2 168(22)	1 908(14)
C(13)	−946(17)	2 493(19)	8 899(12)	840(19)	3 288(22)	6 424(14)	1 825(18)	1 412(20)	1 768(13)
C(14)	−558(23)	3 282(27)	8 660(16)	87(19)	3 274(23)	6 419(14)	1 373(21)	1 004(24)	2 093(15)
C(15)	161(18)	3 344(20)	8 579(13)	−376(20)	2 536(24)	6 233(14)	1 168(20)	1 285(24)	2 623(15)
C(16)	686(18)	2 800(22)	8 710(13)	−83(19)	1 839(22)	6 032(14)	1 417(15)	1 975(18)	2 896(11)
C(17)	−912(20)	1 059(23)	9 100(15)	2 057(19)	2 654(22)	6 454(14)	2 358(23)	2 720(27)	1 436(17)
C(18)	−1 692(20)	2 494(23)	8 758(14)	1 151(18)	3 898(22)	6 855(14)	1 720(22)	1 188(26)	1 179(16)
C(19)	249(20)	3 954(23)	8 152(14)	−1 109(21)	2 526(24)	6 463(15)	464(22)	910(25)	2 800(16)
C(20)	1 347(19)	2 692(22)	8 387(13)	−503(20)	1 087(23)	6 046(15)	894(21)	2 384(25)	3 274(15)
O(12)	−986(16)	3 809(19)	8 503(11)	−248(14)	3 787(16)	6 655(10)	1 053(15)	421(18)	1 922(11)

cm^{-3}, $Z = 4$, $F(000) = 2\,068$, $\lambda(\text{Mo-}K_\alpha)$ 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ 128.76 cm^{-1}. Dark red platelets; crystal dimensions, distance from face to centre: 0.086 $(0\bar{1}1, 01\bar{1})$ × 0.038 $(010, 0\bar{1}0)$ × 0.095 $(0\bar{1}\bar{1}, 011)$ × 0.257 $(10\bar{1}, \bar{1}01)$ × 0.266 $(101, \bar{1}0\bar{1})$ mm.

Data collection and processing. Stoe-Siemens four-circle diffractometer; 24-step ω–θ mode, scan width 0.04°, scan time per step 0.75—3.00 s; 4 309 profile fitted intensities $(5.0 \leqslant 2\theta \leqslant 45.0°)$, 3 877 unique, 3 133 with $|F| > 4\sigma(F)$; numerical absorption corrections (transmission 0.0158—0.1676); no crystal decay.

Structure solution and refinement. The structure was solved by direct methods and Fourier difference techniques, and refined by blocked full-matrix least squares (Os and O atoms anisotropic; phenyl rings refined as rigid bodies; H atoms included using a riding model and a common isotropic thermal parameter); weighting scheme, $w = 0.8179/[\sigma^2(F) + 0.002F^2]$. The final residuals were $R = 0.057$ and $R' = 0.058$. Selected bond lengths and angles are given in Table 2. Final atomic co-ordinates are given in Table 3.

X-*Ray Structure Determination of* (**7**).—*Crystal data.* $C_{20}H_{21}O_{12}Os_3P$, $M = 1\,054$, monoclinic, space group $P2_1/a$ (alt. setting $P2_1/c$, no. 14), $a = 19.032(7)$, $b = 16.669(6)$, $c = 25.409(9)$ Å, $\beta = 95.34(6)°$, $U = 8\,025$ Å^3 [refined as for (**5**)], $D_c = 2.18$ g cm^{-3}, $Z = 12$, $F(000) = 2\,068$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 143.11$ cm^{-1} Dark orange crystals; crystal dimensions, distance from face to centre: 0.038 $(001, 00\bar{1})$ × 0.038 $(0\bar{1}1, 01\bar{1})$ × 0.025 $(011, 0\bar{1}\bar{1})$ × 0.218 $(100, \bar{1}00)$ mm.

Data collection and processing. Data collected as for (**5**); 8 132 profile fitted intensities $(5.0 \leqslant 2\theta \leqslant 40.0°)$, 7 473 unique, 5 242 with $|F| > 4\sigma(F)$; absorption corrections (transmission 0.1254—0.2750); no crystal decay.

Structure solution and refinement. The structure was solved and refined as for (**5**) (Os atoms anisotropic; H atoms not included); weighting scheme, $w = 0.002/[\sigma^2(F) + 0.002F^2]$. The final residuals were $R = 0.073$ and $R' = 0.068$. In each of the three crystallographically independent molecules within the asymmetric unit, the methoxy groups around the phosphorus atom adopt a different orientation. The geometry of the remaining atoms is, however, essentially the same and the interatomic parameters given have, therefore, been averaged. Selected bond lengths and angles are given in Table 4. Final atomic co-ordinates are given in Table 5.

For both (**5**) and (**7**), additional material available from the Cambridge Crystallographic Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

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References

1 E. Sappa, A. Tiripicchio, and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
2 B. F. G. Johnson, R. Khattar, F. J. Lahoz, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1987, **319**, C51.
3 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
4 See, for example, T. Beringheli, G. Ciani, G. D'Alfronso, V. De Malde, A. Sironi, and M. Freni, *J. Chem. Soc., Dalton Trans.*, 1986, 1051; R. J. Gouldsmit, J. G. Jeffrey, B. F. G. Johnson, R. C. S. McQueen, A. J. Sanders, and J. Liu, *J. Chem. Soc., Chem. Commun.*, 1986, 25.
5 M. R. Churchill and D. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
6 C. G. Pierpont, *Inorg. Chem.*, 1977, **16**, 636.

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