Substitution Reactions of the Osmium(I) Dinuclear Compound $[Os_2(MeCO_2)_2(CO)_6]$. *X*-Ray Crystal Structure of $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$†

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The dinuclear osmium(I) compound $[Os_2(MeCO_2)_2(CO)_6]$ has labile axial CO ligands and there is no evidence for equatorial substitution in its reactions. Refluxing tetrahydrofuran (thf) gives $[Os_2(MeCO_2)_2(CO)_5(thf)]$ which reacts with tertiary phosphines to give $[Os_2(MeCO_2)_2(CO)_5L]$ (L = PPh_3 or PMe_2Ph) and with $[N(PPh_3)_2]Cl$ to give $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$, the *X*-ray crystal structure of which confirms axial substitution. Direct reaction of $[Os_2(MeCO_2)_2(CO)_6]$ with tertiary phosphines, pyridine, or acetonitrile ligands, L, gives the di-axially substituted compounds $[Os_2(MeCO_2)_2(CO)_4L_2]$ and no mono-substituted compounds were observed in most cases. Treatment of the ^{13}CO-enriched compound $[Os_2(MeCO_2)_2(CO)_6]$ with acetonitrile gives enriched $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$. This reacted with natural abundance CO to reform $[Os_2(MeCO_2)_2(CO)_6]$ which contains ^{13}CO only in sites *cis* to the Os–Os bond. Equilibration between these sites and those *trans* to the Os–Os bond is slow with $t_{\frac{1}{2}}$ = *ca.* 6 d at room temperature.

Dodecacarbonyltriosmium, $[Os_3(CO)_{12}]$, reacts with neat acetic acid at 185 °C to give good yields of the dinuclear osmium(I) compound $[Os_2(MeCO_2)_2(CO)_6]$,[1] the *X*-ray structure of which gave an Os–Os bond length of 2.731(2) Å.[2] We have been exploring the use of this dimer to prepare new osmium(I) compounds, or compounds in reduced or oxidised forms. The only reported reactions of this compound are substitutions to give $[Os_2(MeCO_2)_2(CO)_4L_2]$ [L = PPh_3 or pyridine (py)][1] and although axial substitution (*i.e.*, *trans* to the Os–Os bond) seemed likely the apparent formation of isomers when L = py created some doubt about this. We have now re-examined the substitution reactions of $[Os_2(MeCO_2)_2(CO)_6]$ to give mono- and di-substituted species, including products with halide, MeCN, and tetrahydrofuran (thf), as well as tertiary phosphines as ligands and only find evidence for axial substitution (see Scheme).

Results and Discussion

Attempting to reduce the Os^I dimer, we treated a dry thf solution of $[Os_2(MeCO_2)_2(CO)_6]$ with an excess of 1% sodium amalgam for 48 h and observed the slow conversion to a single product [ν(CO) 2 083s, 1 995vs, and 1 910m cm^{-1}]. These fairly low frequencies indicated the formation of an anionic, possibly reduced, species and this seemed to be substantiated by isolation of a $[N(PPh_3)_2]^+$ salt on addition of $[N(PPh_3)_2]Cl$ [ν(CO) ($CHCl_3$): 2 070vs, 1 981vs, and 1 898m cm^{-1}]. However, these differences in frequency are real and the above spectra turned out to be for different species. The species first formed in thf in the presence of Na-amalgam is also formed in the absence of any reducing agent and is totally formed after 3 h in refluxing thf. The crystalline $[N(PPh_3)_2]^+$ salt has been fully characterised by elemental analysis, infrared and n.m.r. spectroscopy, and by a single-crystal *X*-ray analysis of $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$. The close similarity of the infrared spectra enabled us to identify the initially formed species as $[Os_2(MeCO_2)_2(CO)_5(thf)]$, although we have not crystallised this compound. A facile substitution of this kind was also found when $[Ru_3(CO)_{12}]$ was reacted with 4-fluorobenzoic acid. The initial solution after reaction indicated that $[Ru_2(FC_6H_4CO_2)_2(CO)_6]$ had been formed but the isolated compound (*X*-ray structure) was shown to be $[Ru_2(FC_6H_4CO_2)_2(CO)_5(H_2O)]$.[3]

The *X*-ray structure of $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$ confirms that the molecule is derived from $[Os_2(MeCO_2)_2(CO)_6]$ by substituting an axial CO by chloride (Figure 1). Bond lengths and angles for the anion $[Os_2(MeCO_2)_2Cl(CO)_5]^-$ are given in Table 1 and fractional atomic co-ordinates in Table 2. The molecular structure shows many of the main features found in the parent $[Os_2(MeCO_2)_2(CO)_6]$, for example, the acetato ligands occupy *cis* sites and three terminal ligands are facially arranged at each octahedral osmium atom. The Os–Os distance of 2.714(4) Å in the anion compares with 2.731(2) Å in the hexacarbonyl compound. The Os(2)–C(3) bond length [1.939(27) Å], *trans* to the Os–Os bond, is the longest in the molecule. The Os–C(axial) bond distances in $[Os_2(MeCO_2)_2(CO)_6]$ (average 1.96 Å) are likewise longer than those *trans* to acetate; the average Os–C(equatorial) distance is 1.79 Å.[2] Differences between the geometries at atoms Os(1) and Os(2) resulting from their different substitution are quite small. Although the acetate bridges are approximately symmetrical, Os(2) is associated with longer Os–CO bonds and slightly shorter Os–O bonds than Os(1). This is consistent with a build up of electron density at Os(1) compared with Os(2). The axial ligands are not collinear with the Os–Os bond. The O · · · O distance in each acetate ligand is less than the Os–Os distance and so the acetate bridges pinch in the molecule on one side of the Os–Os bond and lead to the observed distortions from octahedral geometry, *e.g.* Os(1)–Os(2)–C(3) is 169.0(6) and Os(2)–Os(1)–Cl(1) is 162.5(1)°. Since the position of maximum electron density in the metal–metal bond is expected to coincide with the intersection of the Os(1)–Cl(1) and the Os(2)–C(3) directions, the Os–Os bond might be considered to be bent by 28.5°.

The lengths of the axial Os–CO bonds in $[Os_2(MeCO_2)_2$-

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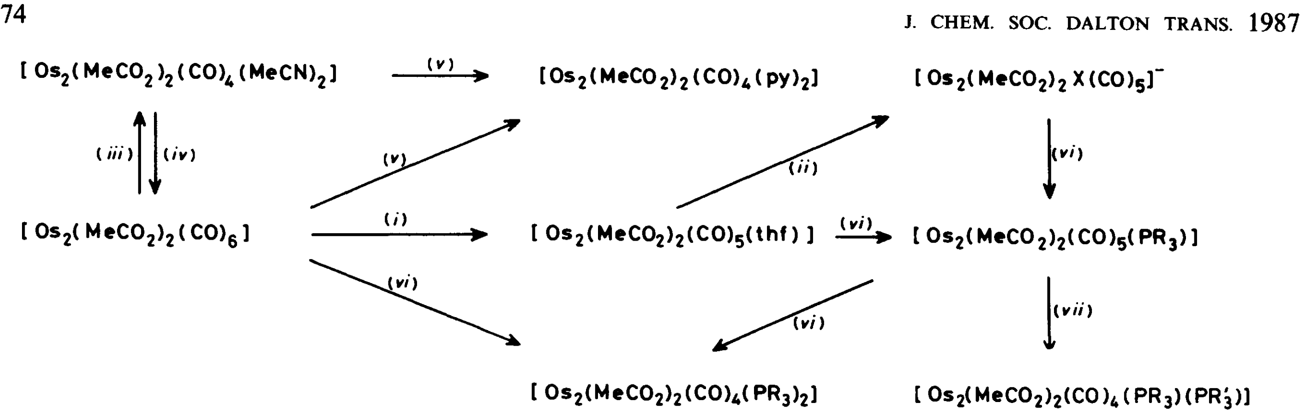
† Bis(triphenylphosphine)iminium di-μ-(acetato-*O,O'*)-1,1,1,2,2-pentacarbonyl-2-chlorodiosmate(I)(*Os–Os*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme. (*i*) Refluxing thf; (*ii*) X$^-$ (X = Cl or I); (*iii*) MeCN; (*iv*) CO; (*v*) py; (*vi*) PR$_3$ (PMe$_2$Ph or PPh$_3$); (*vii*) PR'$_3$ (PPh$_3$), where PR$_3$ = PMe$_2$Ph

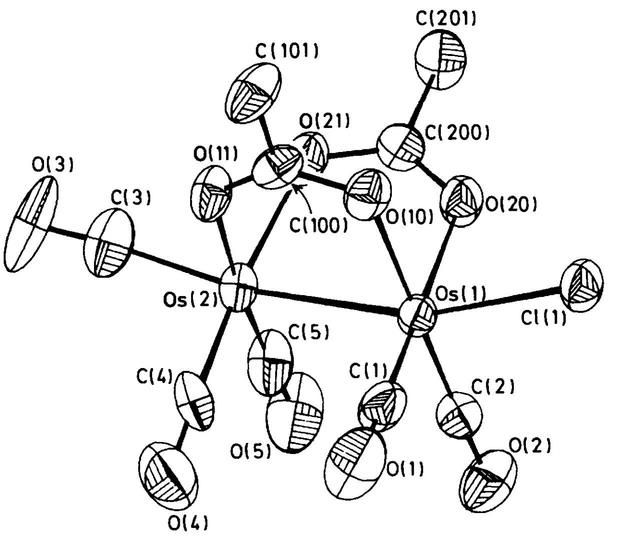


Figure 1. Molecular structure of the anion of [N(PPh$_3$)$_2$][Os$_2$(MeCO$_2$)$_2$Cl(CO)$_5$]

Table 1. Bond lengths (Å) and angles (°) for the anion in [N(PPh$_3$)$_2$][Os$_2$(MeCO$_2$)$_2$Cl(CO)$_5$]

Os(2)–Os(1)	2.714(4)	C(1)–Os(1)	1.772(25)
C(2)–Os(1)	1.775(21)	O(10)–Os(1)	2.150(14)
O(20)–Os(1)	2.154(15)	Cl(1)–Os(1)	2.476(7)
C(3)–Os(2)	1.939(27)	C(4)–Os(2)	1.901(26)
C(5)–Os(2)	1.815(25)	O(11)–Os(2)	2.093(14)
O(21)–Os(2)	2.119(15)	O(1)–C(1)	1.223(30)
O(2)–C(2)	1.178(24)	O(3)–C(3)	1.134(34)
O(4)–C(4)	1.112(32)	O(5)–C(5)	1.193(30)
C(100)–O(10)	1.280(27)	C(100)–O(11)	1.242(27)
C(101)–C(100)	1.476(26)	C(200)–O(20)	1.246(28)
C(200)–O(21)	1.282(28)	C(201)–C(200)	1.483(28)
C(1)–Os(1)–Os(2)	98.6(9)	C(2)–Os(1)–Os(2)	97.1(8)
C(2)–Os(1)–C(1)	87.5(10)	O(10)–Os(1)–Os(2)	81.0(5)
O(10)–Os(1)–C(1)	94.8(8)	O(10)–Os(1)–C(2)	177.2(7)
O(20)–Os(1)–Os(2)	82.0(5)	O(20)–Os(1)–C(1)	177.1(7)
O(20)–Os(1)–C(2)	95.2(8)	O(20)–Os(1)–O(10)	82.5(6)
Cl(1)–Os(1)–Os(2)	162.5(1)	Cl(1)–Os(1)–C(1)	94.1(9)
Cl(1)–Os(1)–C(2)	95.4(8)	Cl(1)–Os(1)–O(10)	85.9(5)
Cl(1)–Os(1)–O(20)	84.7(5)	C(3)–Os(2)–Os(1)	169.0(6)
C(4)–Os(2)–Os(1)	89.2(9)	C(4)–Os(2)–C(3)	96.5(11)
C(5)–Os(2)–Os(1)	94.2(9)	C(5)–Os(2)–C(3)	95.4(11)
C(5)–Os(2)–C(4)	87.9(11)	O(11)–Os(2)–Os(1)	84.7(5)
O(11)–Os(2)–C(3)	85.5(8)	O(11)–Os(2)–C(4)	94.4(9)
O(11)–Os(2)–C(5)	177.4(8)	O(21)–Os(2)–Os(1)	83.5(5)
O(21)–Os(2)–C(3)	90.3(8)	O(21)–Os(2)–C(4)	172.2(8)
O(21)–Os(2)–C(5)	95.3(9)	O(21)–Os(2)–O(11)	82.3(6)
O(1)–C(1)–Os(1)	174.0(18)	O(2)–C(2)–Os(1)	176.1(18)
O(3)–C(3)–Os(2)	172.7(19)	O(4)–C(4)–Os(2)	174.0(23)
O(5)–C(5)–Os(2)	175.4(22)	C(100)–O(10)–Os(1)	123.7(13)
C(100)–O(11)–Os(2)	123.4(13)	O(11)–C(100)–O(10)	124.0(17)
C(101)–C(100)–O(10)	117.7(20)	C(101)–C(100)–O(11)	118.3(20)
C(200)–O(20)–Os(1)	124.5(14)	C(200)–O(21)–Os(2)	123.3(14)
O(21)–C(200)–O(20)	123.1(19)	C(201)–C(200)–O(20)	118.4(20)
C(201)–C(200)–O(21)	118.5(20)		

(CO)$_6$] relate to their high lability. Direct reaction with various neutral ligands at 70 °C leads to [Os$_2$(MeCO$_2$)$_2$(CO)$_4$L$_2$] (L = PPh$_3$, AsPh$_3$, or py);[1] no intermediate mono-substituted compounds are obtained. Two ^{1}H n.m.r. Me signals were reported for the compound with L = py but we only observe one. This, together with i.r. evidence, indicates that the di-axial isomer is the only one formed. Slow reaction of [Os$_2$(MeCO$_2$)$_2$(CO)$_6$] with PMe$_2$Ph (1:1 molar ratio) at room temperature gave [Os$_2$(MeCO$_2$)$_2$(CO)$_4$(PMe$_2$Ph)$_2$], starting material, and only small amounts of [Os$_2$(MeCO$_2$)$_2$(CO)$_5$(PMe$_2$Ph)]. The mono-substituted compound may be prepared in reasonable yields, however, by treating [Os$_2$(MeCO$_2$)$_2$(CO)$_5$(thf)] or [Os$_2$(MeCO$_2$)$_2$(CO)$_5$Cl]$^-$ with the phosphine, and several other examples are given in Table 3 and the Experimental section. The bis(acetonitrile) compound, readily prepared by treating [Os$_2$(MeCO$_2$)$_2$(CO)$_6$] in refluxing acetontrile, is the best precursor to di-substituted compounds.

A feature of the ^{1}H n.m.r. spectra of [Os$_2$(RCO$_2$)$_2$(CO)$_4$(PMe$_2$Ph)$_2$] (R = Me or Pr^i) is that the phosphine Me signals appear as a virtual triplet with the central line broader than the outer ones. This was more clearly shown when R = Pr^i than when R = Me because there was no overlap of signals. Large values of $^2J_{PP}$ (*ca.* 500 Hz) have been used to characterise *trans* arrangements of PMe$_2$Ph ligands in mononuclear compounds since these lead to virtual Me triplets; small values (*ca.* 10 Hz) are found for *cis* arrangements. In [Os$_2$(MeCO$_2$)$_2$(CO)$_4$(PMe$_2$Ph)$_2$] $^3J_{PP}$ values are large enough to give virtual coupling. The compound [Os$_2$(MeCO$_2$)$_2$(CO)$_4$(PPh$_3$)(PMe$_2$Ph)], prepared from [Os$_2$(MeCO$_2$)$_2$(CO)$_5$(PMe$_2$Ph)] and PPh$_3$, gave two ^{31}P n.m.r. doublets ($^3J_{PP}$ = 59.3 Hz). It is probable that relatively large coupling constants such as this relate to the di-axial arrangement of the phosphines. Di-axial substitution in [Ru$_2$(Pr^{n}CO$_2$)$_2$(CO)$_4$(PBu^t$_3$)$_2$] was established[4] but in this case the bulky phosphines may have imposed that geometry.

Our results indicate that incoming ligands enter only *trans* to

Table 2. Fractional atomic co-ordinates (× 10^4) for $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	3 045(1)	2 153(1)	1 000(<0.5)	C(21)	5 929(8)	1 503(10)	2 525(6)
Os(2)	4 153(1)	1 724(1)	297(<0.5)	C(22)	4 920(12)	1 149(14)	2 529(7)
C(1)	2 462(16)	3 289(18)	768(8)	C(23)	4 890(14)	239(15)	2 741(7)
O(1)	2 153(13)	4 110(13)	618(7)	C(24)	5 807(12)	−259(15)	2 938(8)
C(2)	1 827(15)	1 565(15)	734(7)	C(25)	6 875(13)	−56(9)	2 971(8)
O(2)	987(12)	1 224(11)	564(6)	C(30)	8 380(15)	1 205(12)	2 081(7)
C(3)	5 185(18)	1 480(15)	−113(8)	C(31)	9 412(14)	1 004(13)	2 024(7)
O(3)	5 741(14)	1 421(13)	−381(7)	C(32)	9 568(17)	835(18)	1 552(8)
C(4)	3 374(20)	2 733(20)	−88(8)	C(33)	8 736(17)	750(16)	1 183(8)
O(4)	2 854(17)	3 262(16)	−328(7)	C(34)	7 738(17)	994(17)	1 238(8)
C(5)	3 169(20)	839(18)	1(8)	C(35)	7 540(15)	1 185(14)	1 684(7)
O(5)	2 489(15)	259(15)	−165(6)	P(2)	9 898(4)	1 333(4)	3 516(2)
O(10)	4 561(10)	2 801(9)	1 315(5)	C(40)	9 427(13)	2 164(13)	3 919(6)
O(11)	5 300(10)	2 703(9)	666(4)	C(41)	8 518(14)	1 915(13)	4 085(7)
C(100)	5 301(14)	2 997(12)	1 080(8)	C(42)	8 112(19)	2 536(17)	4 388(8)
C(101)	6 214(15)	3 604(16)	1 320(8)	C(43)	8 624(20)	3 409(18)	4 536(9)
O(20)	3 813(11)	813(10)	1 307(4)	C(44)	9 538(20)	3 666(16)	4 375(9)
O(21)	4 962(10)	701(10)	808(5)	C(45)	9 938(16)	3 032(13)	4 075(7)
C(200)	4 593(17)	412(16)	1 175(7)	C(50)	11 115(14)	1 842(14)	3 382(6)
C(201)	5 125(16)	−433(13)	1 460(8)	C(51)	11 061(18)	2 696(15)	3 079(9)
Cl(1)	2 555(4)	2 382(4)	1 797(2)	C(52)	11 934(22)	3 104(20)	2 935(9)
N(1)	9 076(11)	1 106(11)	3 043(5)	C(53)	12 927(22)	2 667(23)	3 102(10)
P(1)	8 147(4)	1 555(4)	2 658(2)	C(54)	13 061(18)	1 816(23)	3 411(10)
C(10)	8 046(13)	2 882(13)	2 654(6)	C(55)	12 135(15)	1 432(15)	3 564(8)
C(11)	8 454(14)	3 417(13)	2 332(7)	C(60)	10 226(13)	181(13)	3 852(7)
C(12)	8 417(16)	4 491(14)	2 364(8)	C(61)	9 888(15)	−711(14)	3 622(8)
C(13)	7 974(16)	4 916(17)	2 720(9)	C(62)	10 109(17)	−1 575(16)	3 865(9)
C(14)	7 559(17)	4 398(16)	3 025(8)	C(63)	10 625(20)	−1 591(18)	4 344(11)
C(15)	7 632(14)	3 360(15)	3 017(7)	C(64)	10 918(19)	−704(20)	4 574(8)
C(20)	6 682(2)	846(6)	2 750(6)	C(65)	10 713(16)	204(16)	4 321(7)

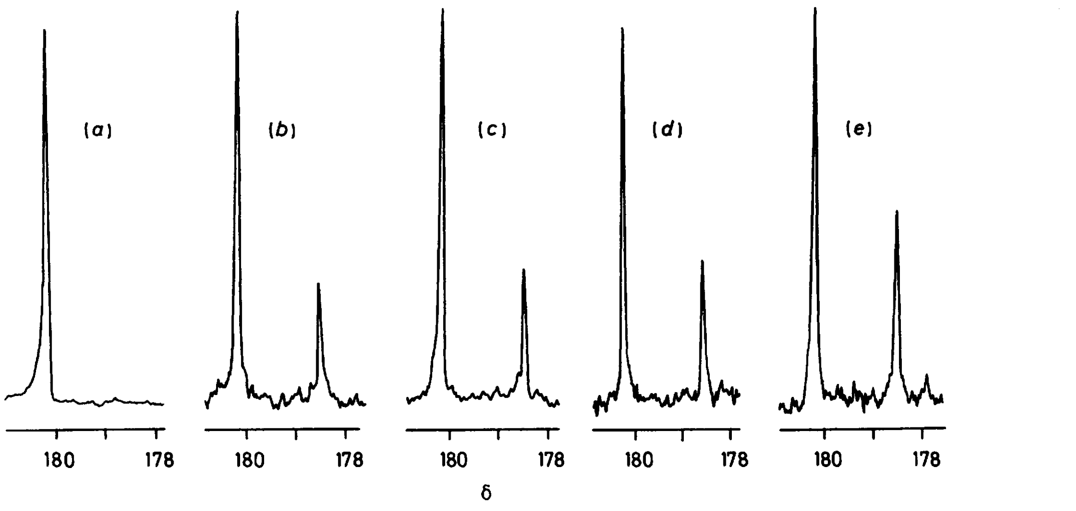


Figure 2. ^{13}C N.m.r. spectra of $CDCl_3$ solutions of $[Os_2(MeCO_2)_2(CO)_6]$, initially enriched with ^{13}C at the carbonyl sites *cis* to the Os–Os bond (*a*), and then after 9 d (*b*), 13 d (*c*), 20 d (*d*), and 24 d (*e*) at room temperature

the Os–Os bond and we have no evidence for incoming ligands occupying sites *trans* to the acetato ligands. Based on this it is possible to incorporate ^{13}CO into specific sites. The compound $[Os_2(MeCO_2)_2(CO)_6]$ was prepared from $[Os_3(CO)_{12}]$ which was enriched to 50—60% with ^{13}CO [^{13}C n.m.r. ($CDCl_3$): δ 180.3 (s) and 178.6 (s) in intensity ratio 2:1]. Displacement of the axial CO by forming $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ and subsequent replacement of the MeCN ligands by natural abundance CO gave $[Os_2(MeCO_2)_2(CO)_6]$ with ^{13}CO only *trans* to acetate (δ 180.3) and with <3% (probably only natural abundance) of ^{13}CO in the other site *trans* to the Os–Os bond. Effectively complete equilibration between the CO ligands had occurred after the solution was kept at 12 °C for 24 d ($t_{\frac{1}{2}}$ *ca.* 6 d) (Figure 2). The mechanism of CO transfer between axial and equatorial sites could either be an intramolecular twist or could involve axial CO dissociation

Table 3. Infrared and n.m.r. data

Compound	ν(CO)[a]/cm^{-1}	ν(CO$_2$)[a]/cm^{-1}	^{1}H N.m.r.[b]
$[Os_2(MeCO_2)_2(CO)_6]$	2 097m, 2 063vs, 2 011vs, 1 992vs, 1 970m, 1 945w	1 569m 1 447m	2.08 (s, $MeCO_2$)
$[Os_2(Pr^iCO_2)_2(CO)_6]$	2 097vs, 2 062vs, 2 012vs, 1 995vs,	1 564m 1 430m	1.07 (d, Me) 2.58 (spt, CH)
$[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$	2 070vs, 1 981vs, 1 898s	1 573m 1 440m	2.05 (s, $MeCO_2$) 7.45 (m, Ph) 7.67 (m, Ph)
$[N(PPh_3)_2][Os_2(MeCO_2)_2I(CO)_5]$	2 068vs, 1 982vs, 1 901m	1 572m 1 440m	2.07 (s, $MeCO_2$) 7.45 (m, Ph) 7.67 (m, Ph)
$[Os_2(MeCO_2)_2(CO)_5(PPh_3)]$	2 072vs, 2 001vs, 1 978s, 1 922m	1 570m 1 446m	1.83 (s, $MeCO_2$) 7.45 (m, Ph)
$[Os_2(MeCO_2)_2(CO)_5(PMe_2Ph)]$	2 067vs, 1 999vs, 1 972s, 1 924m	1 572m 1 445m	1.97 (s, $MeCO_2$) 1.90 (d, PMe) 7.50 (m, Ph)
$[Os_2(Pr^iCO_2)_2(CO)_5(PPh_3)]$	2 071vs, 2 001vs, 1 979s, 1 922m	1 568m 1 427m	
$[Os_2(Pr^iCO_2)_2(CO)_5(PMe_2Ph)]$	2 066vs, 1 998vs, 1 970vs, 1 920m	1 565s 1 427m	0.95 (d, Me) 1.00 (d, Me) 1.92 (d, PMe) 2.44 (spt, CH) 7.50 (m, Ph)
$[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$	2 013vs, 1 961m, 1 928vs, 1 895w		2.09 (s, $MeCO_2$) 2.36 (s, MeCN)
$[Os_2(MeCO_2)_2(CO)_4(py)_2]$	2 005vs, 1 954m, 1 922vs, 1 885w	1 576s 1 482w 1 447s	2.03 (s, $MeCO_2$) 7.35—8.81 (m, py)
$[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)_2]$[c]	2 011vs, 1 969m, 1 938vs, 1 907w	1 578m 1 442m	1.83 (t, PMe + $MeCO_2$) 7.97 (m, Ph)
$[Os_2(Pr^iCO_2)_2(CO)_4(PMe_2Ph)_2]$	2 005vs, 1 961m, 1 927vs, 1 895w	1 568s 1 426m	0.90 (d, Me) 1.86 (t, PMe) 2.05 (spt, CH) 7.42 (m, Ph)
$[Os_2(MeCO_2)_2(CO)_4(PPh_3)_2]$	2 011vs, 1 968m, 1 938vs, 1 906w	1 575m 1 435m	1.83 (s, Me) 7.45 (m, Ph)
$[Os_2(MeCO_2)_2(CO)_4(PPh_3)(PMe_2Ph)]$[d]	2 009vs, 1 965m, 1 931vs, 1 898w	1 576s 1 437ms	1.71 (s, Me) 1.84 (d, PMe) 7.43 (m, Ph)

[a] In chloroform. [b] In $CDCl_3$ at 200 MHz. [c] ^{31}P N.m.r.: δ −4.2 (s) ($CHCl_3$–$CDCl_3$) relative to 85% H_3PO_4. [d] ^{31}P N.m.r.: δ 20.4 (d) and −5.9 (d), J = 59.3 Hz ($CHCl_3$–$CDCl_3$) relative to 85% H_3PO_4.

with rearrangement of the five-co-ordinate Os atom to give a much less favourable form with the vacancy *trans* to acetate rather than *trans* to osmium.

Experimental

The acetato compound $[Os_2(MeCO_2)_2(CO)_6]$ was synthesised by the reported method[1] and the isobutyrato (Pr^iCO_2) analogue was prepared similarly as given below.

Synthesis of $[Os_2(Pr^iCO_2)_2(CO)_6]$.—Isobutyric acid (2-methylpropanoic acid) (30 cm^3) and $[Os_3(CO)_{12}]$ (0.765 g) in a 100-cm^3 Carius tube were degassed and the tube sealed under vacuum. After heating at 185 ± 5 °C for 6 h, the tube was cooled, opened, and the pale yellow solution was poured into a large excess of water. The mixture was shaken for 2 h and a white crystalline solid filtered off. This was dried and recrystallised from dichloromethane–hexane mixtures by allowing the dichloromethane to evaporate slowly overnight to give the product as colourless rhombs (0.642 g, 71%) (Found: C, 23.2; H, 1.95; O, 22.2. $C_{14}H_{14}O_{10}Os_2$ requires C, 23.25; H, 1.95; O, 22.15%).

Synthesis of $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$.—A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.100 g) in freshly distilled thf (25 cm^3) was refluxed under nitrogen for 3 h. The i.r. spectrum indicated the formation of $[Os_2(MeCO_2)_2(CO)_5(thf)]$. The compound $[N(PPh_3)_2]Cl$ (0.082 g) (in a 1:1 molar ratio) was added, the mixture stirred for 15 min, concentrated to 5 cm^3, and diethyl ether added to precipitate a buff solid. This was recrystallised from acetone–diethyl ether mixtures to give the product as straw coloured needles (variable yield up to 54%) (Found: C, 45.15; H, 3.2; Cl, 2.65; N, 1.15; O, 12.15; P, 5.25. $C_{45}H_{36}ClNO_9Os_2P_2$ requires C, 44.6; H, 3.0; Cl, 2.95; N, 1.15; O, 11.85; P, 5.1%).

Synthesis of $[N(PPh_3)_2][Os_2(MeCO_2)_2I(CO)_5]$.—A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.050 g) and $[N(PPh_3)_2]I$ (0.047 g) (1:1 molar ratio) in acetone (10 cm^3) was heated under reflux for 15 min to give a lemon-yellow solution. Removal of the solvent gave a yellow solid which was recrystallised from acetone to give the product as yellow needles (0.041 g, 66%) (Found: C, 40.75; H, 2.9; N, 0.9; P, 4.5. $C_{45}H_{36}INO_9Os_2P_2$ requires C, 41.45; H, 2.8; N, 1.05; P, 4.75%). The chloro species above may be prepared similarly.

Synthesis of $[Os_2(MeCO_2)_2(CO)_5(PPh_3)]$.—A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.100 g) in freshly distilled thf (30 cm^3) was heated under reflux for 2.5 h to give a lemon-yellow solution containing $[Os_2(MeCO_2)_2(CO)_5(thf)]$ which was cooled to *ca.*

0 °C and PPh_3 (0.040 g) (in a 1:1 molar ratio) added over 15 min to the stirred solution. Removal of the solvent and separation by preparative t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–CH_2Cl_2 (7:3 v/v)] gave $[Os_2(MeCO_2)_2(CO)_5(PPh_3)]$ as the major product as yellow rhombic crystals (0.065 g, 55%) (Found: C, 35.25; H, 2.35; P, 3.5. $C_{27}H_{21}O_9Os_2P$ requires C, 36.0; H, 2.35; P, 3.4%). Some starting hexacarbonyl (0.010 g) and some $[Os_2(MeCO_2)_2(CO)_4(PPh_3)_2]$ (0.015 g) were also obtained.

Synthesis of $[Os_2(MeCO_2)_2(CO)_5(PMe_2Ph)]$.—This was prepared similarly from $[Os_2(MeCO_2)_2(CO)_6]$ (0.100 g) as yellow crystals (0.060 g, 57%) (Found: C, 26.2; H, 2.25; P, 3.95. $C_{17}H_{17}O_9Os_2P$ requires C, 26.3; H, 2.2; P, 4.0%).

Synthesis of $[Os_2(Pr^iCO_2)_2(CO)_5(PMe_2Ph)]$.—This was prepared similarly from the isobutyrato compound (0.100 g) as yellow crystals (0.061 g, 51%) (Found: C, 30.35; H, 3.1; P, 3.95. $C_{21}H_{25}O_9Os_2P$ requires C, 30.3; H, 3.0; P, 3.7%).

Synthesis of $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)_2]$.—A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.150 g) and PMe_2Ph (0.065 g) in chloroform (50 cm^3) was heated under reflux for 1 h. Solvent was removed from the lemon-yellow solution and the residue separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–CH_2Cl_2 (7:3 v/v)] to give one major band which gave the product as yellow needles (0.153 g, 81%) from dichloromethane–methanol mixtures (Found: C, 33.75; H, 3.1; P, 6.95. $C_{24}H_{28}O_8Os_2P_2$ requires C, 33.65; H, 3.3; P, 7.25%). The corresponding PPh_3 complex has been reported[1] and can be prepared similarly.

Synthesis of $[Os_2(Pr^iCO_2)_2(CO)_4(PMe_2Ph)_2]$.—This was prepared similarly from the hexacarbonyl (0.095 g) and PMe_2Ph (0.040 g) to give the product as yellow crystals (0.076 g, 61%) (Found: C, 35.7; H, 3.7; P, 6.8. $C_{28}H_{36}O_8Os_2P_2$ requires C, 35.65; H, 3.85; P, 6.55%).

Synthesis of $[Os_2(MeCO_2)_2(CO)_4(PPh_3)(PMe_2Ph)]$.—A solution of PPh_3 (0.018 g) and $[Os_2(MeCO_2)_2(CO)_5(PMe_2Ph)]$ (0.055 g) (1:1 molar ratio) in chloroform (15 cm^3) was heated under reflux for 40 min. Removal of the solvent gave a pale yellow solid which was purified by preparative t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (3:2 v/v)] to give pale yellow rhombic crystals (0.035 g, 60%) (Found: C, 40.45; H, 3.2; P, 5.95. $C_{34}H_{32}O_8Os_2P_2$ requires C, 40.4; H, 3.2; P, 6.1%).

Synthesis of $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$.—A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.110 g) in acetonitrile (20 cm^3) was heated under reflux for 30 min. Evaporation of the solvent gave the product as somewhat air-sensitive pale yellow plates (0.101 g, 88%) (Found: C, 21.2; H, 1.8; N, 3.9. $C_{12}H_{12}N_2O_8Os_2$ requires C, 20.8; H, 1.75; N, 4.05%). The sample was stored in the dark under nitrogen.

Synthesis of $[Os_2(MeCO_2)_2(CO)_4(py)_2]$.—A method modified from that reported by Lewis and co-workers[1] was used. A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.101 g) and pyridine (3 cm^3) in benzene (10 cm^3) was heated under reflux for 40 min to give a clear lemon-yellow solution. Removal of the solvent gave a yellow oil and white microcrystals. The oil was removed and the white crystals (0.095 g, 79%) washed with diethyl ether and dried (Found: C, 28.05; H, 2.1. N, 3.5. $C_{18}H_{16}N_2O_8Os_2$ requires C, 28.1; H, 2.1; N, 3.65%).

Synthesis of ^{13}C*-enriched* $[Os_2(MeCO_2)_2(CO)_6]$.—Enriched $[Os_3(CO)_{12}]$ was synthesised by treating $[Os_3H_2(CO)_{10}]$ (0.350 g) in hexane (58 cm^3) with ^{13}CO [1 atm (101 325 N m^{-2}), 99% ^{13}C] in a 150-cm^3 sealed glass vessel at 40 °C for 3 d and then at 60 °C for 2 d. Isolated $[Os_3(CO)_{12}]$ (0.247 g) was 50—60% enriched. This compound (0.100 g) was treated with neat acetic acid at 180 °C in a sealed glass tube for 5 h. The enriched sample of $[Os_2(MeCO_2)_2(CO)_6]$ was isolated as colourless crystals from a dichloromethane–hexane mixture (0.077 g, 70%).

Substitution Reactions of ^{13}CO*-enriched* $[Os_2(MeCO_2)_2(CO)_6]$.—Enriched $[Os_2(MeCO_2)_2(CO)_6]$ (0.030 g) was heated in refluxing acetonitrile (15 cm^3) for 2 h to give a yellow solution. Removal of the solvent under reduced pressure gave a clear oil which was dissolved in chloroform (10 cm^3). Carbon monoxide gas (natural abundance of ^{13}C) was bubbled through the solution for 5 min. Removal of solvent gave a colourless solid (0.028 g, 93%). The ^{13}C n.m.r. spectrum was recorded in $CDCl_3$ in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate) (*ca.* 0.05 mol dm^{-3}) within 5 min. The ^{13}C n.m.r. spectrum was recorded again periodically over 24 d.

Single-crystal Structure Determination for $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$.—Crystals were sealed in thin-walled glass capillaries. All crystallographic measurements were made at 293 K using a CAD4 diffractometer operating in the ω—2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[5] The data were corrected for absorption on the basis of ψ-scan measurements.[6]

The structure was solved by heavy-atom methods and refined by least squares. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions with two overall isotropic thermal parameters, one for methyl and one for phenyl. The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was applied in the final refinements with g determined so as to give acceptable agreement analysis.

Crystal data. $C_{45}H_{36}ClNO_9Os_2P_2$, M = 1 212.591, monoclinic, a = 12.703(2), b = 13.462(5), c = 28.403(3) Å, β = 100.88(9)°, U = 4 769.71 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.689 g cm^{-3}, $F(000)$ = 2 336, μ(Mo-K_α) = 52.59 cm^{-1}.

Data collection. Scan width $\omega = (0.8 + 0.35 \tan\theta)°$, scan speed 1.35—6.77° min^{-1}, $1.5 \leqslant \theta \leqslant 25°$, 8 927 data measured, 8 355 unique, 4 979 observed [$I \geqslant 1.5\sigma(I)$].

Structure refinement. Number of parameters 540, weighting scheme coefficient g = 0.000 05, R = 0.064 2, R' = 0.0530. Computer, programs, and sources of scattering factor data are given in ref. 5. Final atomic co-ordinates are in Table 2.

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