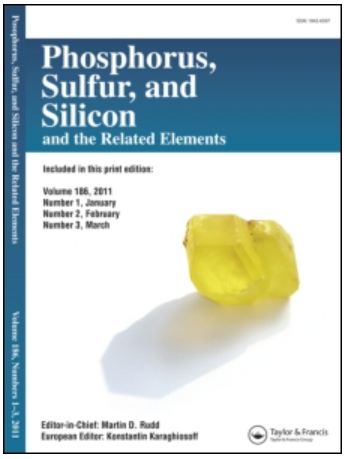

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Bartsch, Rainer , Blake, Alexander J. , Johnson, Brian F. G. , Jones, Peter G. , Müller, Christian , Nixon, John F. , Nowotny, Mathias , Schmutzler, Reinhard and Shephard, Douglas S.(1996) 'REACTION OF 3,3 DIMETHYL-1-PHOSPHABUTYNE, ^{t}BuCP, WITH TRIRUTHENIUM DODECACARBONYL AND TRIOSMIUM DODECACARBONYL', Phosphorus, Sulfur, and Silicon and the Related Elements, 115: 1, 201 — 215
To link to this Article: DOI: 10.1080/10426509608037967
URL: http://dx.doi.org/10.1080/10426509608037967

Phosphorus, Sulfur, and Silicon, 1996, Vol. 115, pp. 201–215
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REACTION OF 3,3 DIMETHYL-1-PHOSPHABUTYNE, ^{t}BuCP, WITH TRIRUTHENIUM DODECACARBONYL AND TRIOSMIUM DODECACARBONYL

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Dedicated to Professor John Verkade on the occasion of his 60th birthday

(Received March 13, 1996; in final form March 14, 1996)

Reaction of ^{t}Bu—C≡P with $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ afforded the novel phosphinidene complexes $[Ru_3(CO)_9\{PC(CO)^tBu\}_2]$ **1** or $[Os_3(CO)_9\{PC(CO)^tBu\}_2]$ **2**, respectively. A crystal structure analysis revealed a *nido* structure for both complexes in agreement with a contribution of four electrons to the cluster framework by each phosphinidene ligand. A minor product of the reaction with $[Os_3(CO)_{12}]$ is the complex $[Os_3(CO)_9\{P(C(CO)^tBu)C(^tBu)P(Os_3(CO)_{11})\}]$ **3**, consisting of two triosmium units linked by a P—C—P framework resulting from coupling of phosphinidene and phospha-alkyne fragments. Complex **3** was also characterized by means of a crystal structure analysis.

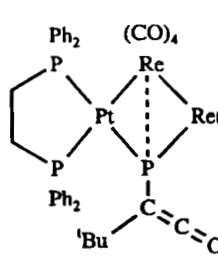
Key words: Phosphaalkyne, X-ray structure, phosphinidine, triruthenium clusters, triosmium clusters, NMR spectra.

INTRODUCTION

Phosphaalkynes show a very complex co-ordinational behaviour dominated by bonding modes involving the phosphorus carbon triple bond.[1] However, examples for the reaction of co-ordinated phosphaalkynes with carbon monoxide are rare. Some examples are shown in Scheme 1. To our knowledge complex **4** is the only reported example of an attack of carbon monoxide at the phosphaalkyne carbon atom with formation of a ketene-substituted phosphinidene ligand.[2] The R(CO)P fragment is regarded as a possible precursor in coupling reactions of phosphaalkynes resulting in the formation of the ligand PCR(CO)CRP in **5**.[3]

We wish to report the formation of a similar phosphinidene ligand in the reaction of ^{t}Bu—C≡P with either $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ at elevated temperatures, yielding the *nido*-clusters $[Ru_3(CO)_9\{PC(CO)^tBu\}_2]$ **1** and $[Os_3(CO)_9\{PC(CO)^tBu\}_2]$ **2** as the main products, respectively (Scheme 2). A competitive pathway with respect to the formation of **2** is leading to the complex **3** with a P—C—P framework linking two triosmium cluster units as a minor product.

Scheme 1. Examples of Organometallic Complexes Derived from Phospha-alkynes



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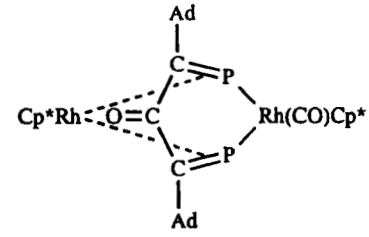

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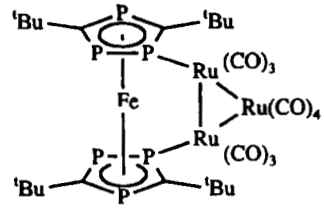

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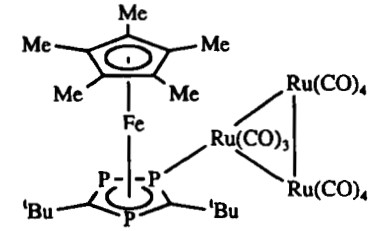

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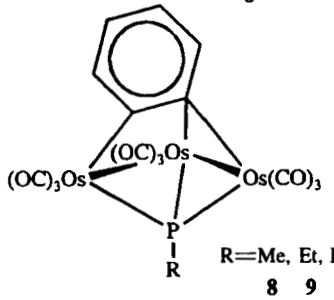
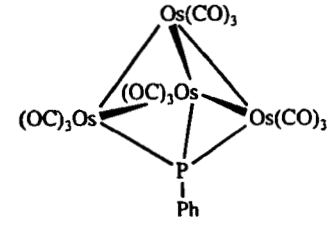


R=Me, Et, Fc

8 9 10

(Fc = Ferrocenyl)



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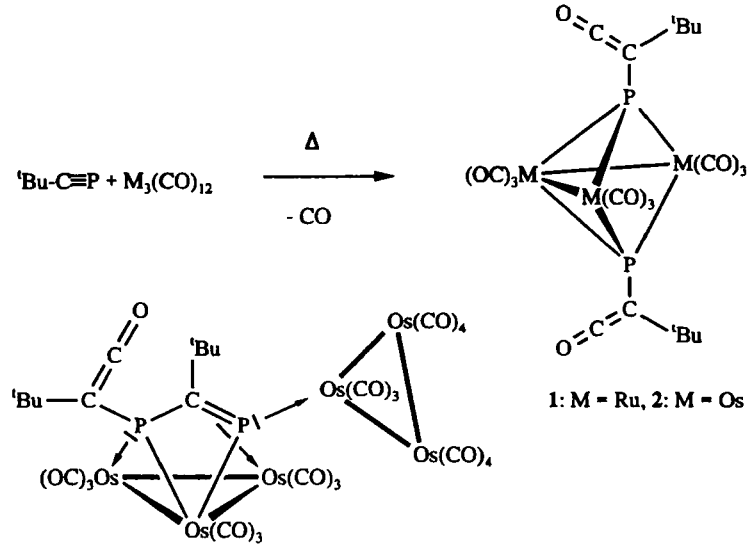
RESULTS AND DISCUSSION

Reaction of ^{t}Bu—C≡P with either $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ at elevated temperatures and subsequent separation of the reaction products either by column chromatography or thin-layer chromatography afforded the complexes $[Ru_3(CO)_9\{PC(CO)^{t}Bu\}_2]$ **1** and $[Os_3(CO)_9\{PC(CO)^{t}Bu\}_2]$ **2** in yields of 16% and 7%, respectively. In the ^{31}P NMR spectra the resonances of these complexes are spread over a wide range [**1**: 184.4, **2**: −29.9 ppm], while the only other reported example of this particular phosphinidene ligand shows an intermediate resonance at 142.0 ppm.[2] The field desorption mass spectra of both **1** and **2** exhibit the molecular ion $[M]^+$ and peaks due to successive loss either of carbonyl groups or of the phosphinidene ligand. The mechanism for the formation of the second product in the ^{t}Bu—C≡P/$[Os_3(CO)_{12}]$ system **3** is not clear; however, it is conceivable that the attack of the co-ordinated P—C—P ligand at a second triosmium carbonyl cluster prevents a subsequent attack of a further carbon monoxide at the carbon atom of the P—C—P framework, leading presumably to the formation of complex **2** via scis-

Scheme 2. The Reaction of $[M_3(CO)_{12}]$ (M = Ru or Os) with ^tBu-C≡P.



sion of the phosphaalkyne units. Therefore, complex **3** can be regarded as a side product in the reaction sequence leading to the formation of **2**, while the idea of **3** being a direct precursor of **2** can be rejected.

X-Ray Studies

The molecular structures of **1** and **2** are shown in Figures 1 and 2 and the structural parameters are given in Tables I–IV. In each case the three metal atoms and the two phosphorus atoms of the cluster form a strongly distorted square based pyramid; in the case of **1** the pyramid base consists of Ru2, P1, Ru3 and P2 and the apex of Ru1, while in the case of **2** the base is formed by Os2, P1, Os3 and P1a and the apex by Os1. The mean deviation of the square base from the best plane is ±1.14 pm for **1** and ±5.3 pm for **2**. In both cases the distortion is caused by a shift of the phosphorus atoms towards the apical metal atom, resulting in a folding of the square base along the P1—P2 vector to an extent of 18.7° for **1** and along the P1—P1a vector to an extent of 9.0° for **2**. Since the phosphinidene ligands in **1** and **2** contribute four electrons to the cluster framework, according to Wade's rules[4] both complexes may be regarded as clusters with a *nido* structure comparable to B_5H_9.

The phosphorus-ruthenium bond lengths in the pyramid base of **1** lie between 233.2(9) and 234.4(8) pm and are comparable to those of the $Ru_3(CO)_{10}$-bridged hexaphosphaferrocene **6** [234.1(4) and 233.6(4) pm].[5] However, the bond lengths P1—Ru1 and P2—Ru2 are longer [237.07(8) and 238.39(8) pm, respectively], and they resemble P—Ru bond distances in η^1-bonded ruthenium cluster compounds such as **7** [P—Ru 239.1(1) pm].[6] Similarly, the phosphorus-osmium distances in the square base of **2** [P1—Os2 235.3(3), P1—Os3 237.3(3) pm] are significantly shorter than the corresponding phosphorus-apical osmium atom distance [P1—Os1 242.4(3) pm], as has been found in other complexes of phosphinidene-bridged open Os_3 tri-

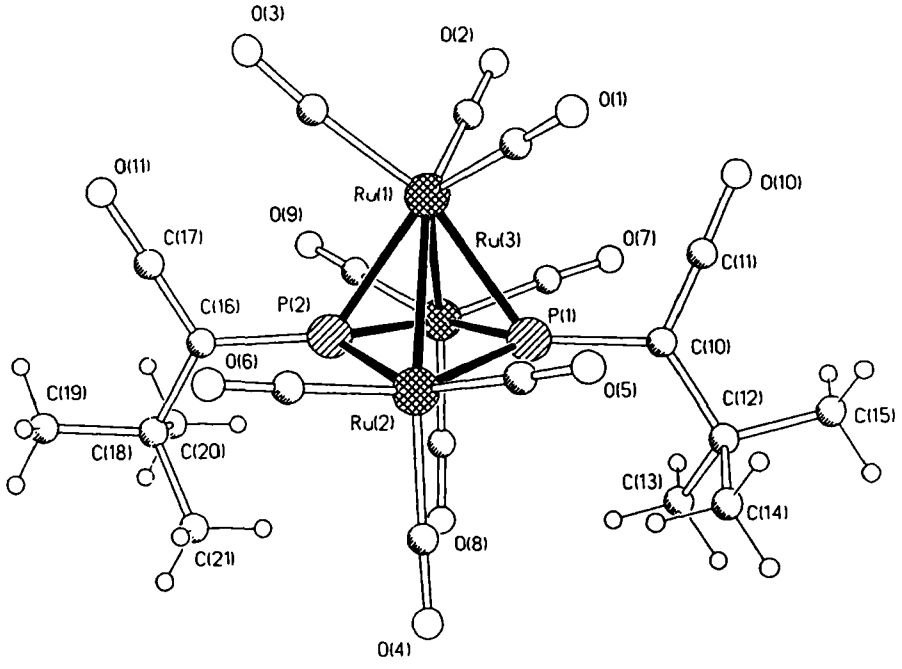


FIGURE 1 The molecular structure of $[Ru_3(CO)_9\{PC(CO)^tBu\}_2]$ **1** showing the atom numbering scheme. Selected bond lengths [pm] and angles [°] are: Ru(1)—P(1) 237.07(8), Ru(1)—P(2) 238.39(8), Ru(1)—Ru(2) 287.05(7), Ru(1)—Ru(3) 289.64(6), Ru(2)—P(2) 233.84(9), Ru(2)—P(1) 234.44(8), Ru(3)—P(1) 233.19(9), Ru(3)—P(2) 233.20(8), P(1)—C(10) 179.0(3), P(2)—C(16) 179.9(3), C(10)—C(11) 131.5(4), C(11)—O(10) 115.8(4), C(16)—C(17) 130.0(4), C(17)—O(11) 116.5(4); C(11)—C(10)—C(12) 122.7(3) C(11)—C(10)—P(1) 113.1(2), C(12)—C(10)—P(1) 124.1(2), C(17)—C(16)—C(18) 119.9(3), C(17)—C(16)—P(2) 116.5(2), C(18)—C(16)—P(2) 123.6(2).

angles, such as **8**–**11**,[7] where the bonds of the phosphorus to the terminal osmium atoms span a range from 230.0 to 233.5 pm, while the bond lengths to the central Os atoms lie between 240.0 and 242.3 pm. There is no bonding interaction between the metal atoms in the square base of **1** and **2** [Ru2, Ru3 for **1** and Os2, Os3 for **2**], which lie 378.2 and 387.0 pm apart, respectively, and no significant interaction between the phosphorus atoms.

The bond distances between ruthenium and the carbon atoms of the carbonyl groups in **1** lie between 187.6(3) and 197.3(3) pm and resemble the ruthenium carbon bond lengths in **7** between 188.6(4) and 195.8(5) pm,[6] whereas the corresponding average in $[Ru_3(CO)_{12}]$ is somewhat shorter [185 ± 0.3 pm].[8] However, there is no significant difference between the average of the osmium carbon bond lengths in **2** [191.7(17)] and the corresponding average in $[Os_3(CO)_{12}]$ [192.9(7) pm].[9]

The main difference between the structures of **1** and **2** is the presence of a mirror plane in **2** which passes through the atoms Os1, Os2, and Os3 and gives rise to an eclipsed conformation of the phosphinidene ligands in **2**. In contrast, these ligands adopt a staggered conformation in **1**, described by the angle of 19.4° between the mean planes through the atoms C10, C11, C12 and C16, C17, C18.

The P—C bond lengths of the phosphinidene groups [**1**: 179.0(3) pm for P1—C10 and 179.9(3) pm for P2—C16; **2**: 179.4(13) pm for P1—C1] are comparable

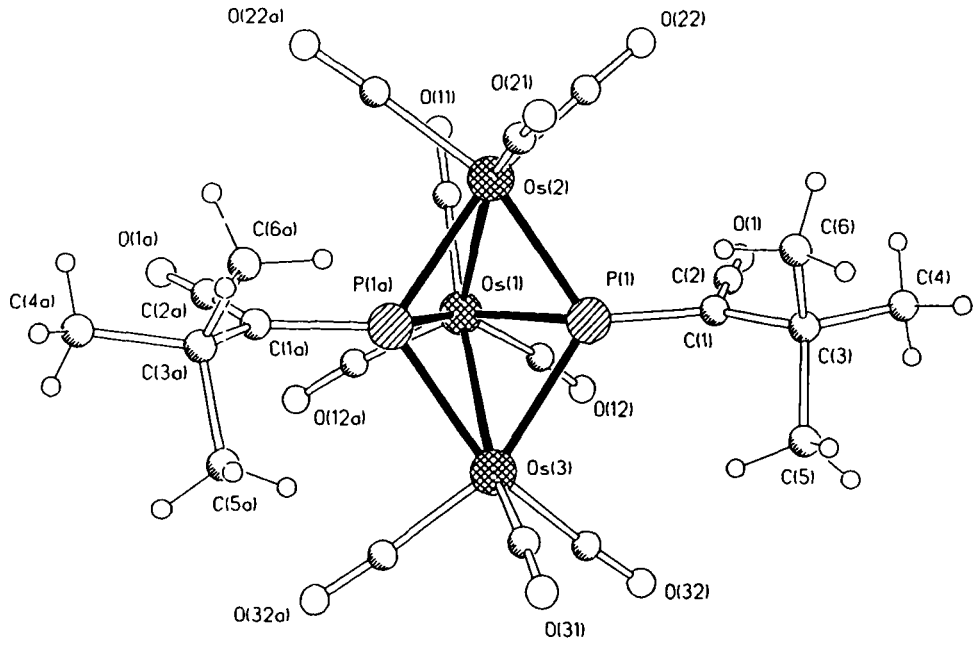


FIGURE 2 The molecular structure of $[Os_3(CO)_9\{PC(CO)^tBu\}_2]$ **2** showing the atom numbering scheme. Selected bond lengths [pm] and angles [°] are: Os(1)—P(1) 242.4(3), Os(1)—Os(3) 285.77(10), Os(1)—Os(2) 288.07(9), Os(2)—P(1) 235.3(3), Os(3)—P(1) 237.3(3), P(1)—C(1) 179.4(13), O(1)—C(2) 119(2), C(1)—C(2) 126(2), C(1)—C(3) 155(2), P(1a)—Os(1)—P(1) 67.81(14), Os(3)—Os(1)—Os(2) 84.80(3), P(1a)—Os(2)—P(1) 70.17(14), P(1a)—Os(3)—P(1) 69.48(14), Os(2)—P(1)—Os(1) 74.15(9), Os(3)—P(1)—Os(1) 73.11(8), C(2)—C(1)—C(3) 121.3(13), C(2)—C(1)—P(1) 115.9(11), C(3)—C(1)—P(1) 122.3(10), O(1)—C(2)—C(1) 177(2).

to those reported for μ_3-PR ligands [180.8(13)],[10] while the C—C and C—O bond lengths of the ketene function [**1**: 131.5(4) pm for C10—C11, 130.0(4) pm for C16—C17, 115.8(4) pm for C11—O10, and 116.5(4) pm for C17—O11; **2**: 126(2) pm for C1—C2, 119(2) pm for C2—O1] possess essentially double bond character [134 pm for C=C, 120 pm for C=O].[11]

Comparable P—C, C—C, and C—O bond lengths are also observed for the ketene substituent of the ligand in **3** [P2—C6 180.9(13), C6—C100 130(2), C100—O 115(2) pm]. The molecular structure of this complex is shown in Figure 3 and the structural data are given in Tables V and VI. The bond lengths of the central unit P1—C1—P2 do not differ significantly [P1—C1 178.7(12), P2—C1 181.2(12) pm], therefore indicating mainly single bond character (*vide supra*). The binding of the atoms P1 and C1 to Os5 may be regarded as involving an η^2-co-ordination of a P=C double bond under formation of a 1-osma-2-phosphacyclopropane with a Os5—P1 distance of 243.3(4) pm and a Os5—C1 distance of 229.9(12) pm, which is significantly longer than the mean Os—C distance in η^2-alkene complexes of 216.6(55) pm.[12] In contrast, the distance of 290.9(3) pm between the atoms P2 and Os5 is too long to be regarded as a bonding interaction. The *tert*-butyl substituent of C1 is bent out of the plane P1—C1—P2 with an angle of 19.8° away from the co-ordinated atom Os5.

The phosphorus atom P2 bridges the metals Os4 and Os6 unsymmetrically with

TABLE I

Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $[Ru_3(CO)_9\{PC(CO)^tBu\}_2]$ 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Ru(1)	1422.1(2)	5266.2(2)	4110.0(1)	24.1(1)
Ru(2)	3382.7(2)	5161.2(2)	4150.0(1)	25.1(1)
Ru(3)	1543.7(2)	6162.3(2)	2464.9(1)	23.1(1)
P(1)	2422.2(5)	6659.9(6)	3712.9(4)	22.3(1)
P(2)	2283.7(5)	4588.5(6)	3059.8(4)	23.5(1)
C(1)	1601(2)	5742(3)	5252(2)	34.7(7)
C(2)	239(2)	5884(4)	3785(2)	47.4(9)
C(3)	939(3)	3826(3)	4351(2)	47.3(9)
C(4)	4378(2)	5520(3)	3557(2)	38.0(7)
C(5)	3796(2)	5804(3)	5241(2)	35.8(7)
C(6)	3722(2)	3652(3)	4468(2)	36.6(7)
C(7)	861(2)	7559(3)	2391(2)	33.2(7)
C(8)	2389(2)	6527(3)	1728(2)	31.2(6)
C(9)	629(2)	5391(3)	1667(2)	38.3(7)
C(10)	2504(2)	8048(2)	4110(2)	27.7(6)
C(11)	1833(2)	8308(3)	4543(2)	34.9(7)
C(12)	3255(3)	8875(3)	3941(2)	38.3(7)
C(13)	3381(4)	8856(4)	3020(2)	61.6(12)
C(14)	4168(3)	8555(4)	4452(3)	52.3(9)
C(15)	2989(4)	10033(3)	4203(3)	71.1(14)
C(16)	2258(2)	3235(2)	2589(2)	29.7(6)
C(17)	1743(2)	2496(3)	2889(2)	34.4(7)
C(18)	2766(3)	2943(3)	1835(2)	45.8(9)
C(19)	2827(2)	1697(3)	1749(2)	43.8(8)
C(20)	2187(4)	3382(4)	1030(3)	69.7(13)
C(21)	3688(3)	3460(4)	1929(4)	93(2)
O(1)	1718(2)	6023(2)	5925.2(14)	52.1(7)
O(2)	-473(2)	6254(4)	3650(2)	81.8(12)
O(3)	617(3)	3012(3)	4517(2)	75.2(10)
O(4)	4944(2)	5760(3)	3169(2)	60.3(8)
O(5)	4011(2)	6206(2)	5867(2)	53.2(7)
O(6)	3899(2)	2762(2)	4626(2)	57.9(7)
O(7)	512(2)	8396(2)	2384(2)	51.8(7)
O(8)	2941(2)	6718(2)	1311.3(15)	45.3(6)
O(9)	105(2)	4950(3)	1214(2)	64.0(8)
O(10)	1241(2)	8510(2)	4930(2)	51.7(7)
O(11)	1284(2)	1836(2)	3163(2)	56.1(7)

TABLE II

Bond lengths [Å] and bond angles [°] for $[Ru_3(CO)_9\{PC(CO)^tBu\}_2]$ **1**

Ru(1)-C(2)	190.1(4)	Ru(1)-C(1)	191.9(3)
Ru(1)-C(3)	193.2(4)	Ru(1)-P(1)	237.07(8)
Ru(1)-P(2)	238.39(8)	Ru(1)-Ru(2)	287.05(7)
Ru(1)-Ru(3)	289.64(6)	Ru(2)-C(4)	189.4(3)
Ru(2)-C(6)	193.8(3)	Ru(2)-C(5)	195.2(3)
Ru(2)-P(2)	233.84(9)	Ru(2)-P(1)	234.44(8)
Ru(3)-C(8)	187.6(3)	Ru(3)-C(7)	195.5(3)
Ru(3)-C(9)	197.3(3)	Ru(3)-P(1)	233.19(9)
Ru(3)-P(2)	233.20(8)	P(1)-C(10)	179.0(3)
P(2)-C(16)	179.9(3)	C(1)-O(1)	113.3(4)
C(2)-O(2)	113.1(4)	C(3)-O(3)	113.6(4)
C(4)-O(4)	113.9(4)	C(5)-O(5)	113.0(4)
C(6)-O(6)	112.6(4)	C(7)-O(7)	113.1(4)
C(8)-O(8)	114.0(4)	C(9)-O(9)	112.6(4)
C(10)-C(11)	131.5(4)	C(10)-C(12)	153.6(4)
C(11)-O(10)	115.8(4)	C(12)-C(15)	152.3(5)
C(12)-C(13)	152.4(5)	C(12)-C(14)	153.2(5)
C(16)-C(17)	130.0(4)	C(16)-C(18)	154.6(4)
C(17)-O(11)	116.5(4)	C(18)-C(21)	148.0(6)
C(18)-C(19)	151.2(5)	C(18)-C(20)	155.5(6)

C(2)-Ru(1)-C(1)	99.1(2)	C(2)-Ru(1)-C(3)	93.6(2)
C(1)-Ru(1)-C(3)	94.82(14)	C(2)-Ru(1)-P(1)	102.82(12)
C(1)-Ru(1)-P(1)	91.94(10)	C(3)-Ru(1)-P(1)	161.03(12)
C(2)-Ru(1)-P(2)	118.98(11)	C(1)-Ru(1)-P(2)	140.03(10)
C(3)-Ru(1)-P(2)	94.37(11)	P(1)-Ru(1)-P(2)	69.45(3)
C(2)-Ru(1)-Ru(2)	154.24(12)	C(1)-Ru(1)-Ru(2)	88.59(10)
C(3)-Ru(1)-Ru(2)	110.32(13)	P(1)-Ru(1)-Ru(2)	52.08(2)
P(2)-Ru(1)-Ru(2)	51.85(2)	C(2)-Ru(1)-Ru(3)	76.08(10)
C(1)-Ru(1)-Ru(3)	139.01(10)	C(3)-Ru(1)-Ru(3)	125.88(11)
P(1)-Ru(1)-Ru(3)	51.38(2)	P(2)-Ru(1)-Ru(3)	51.30(2)
Ru(2)-Ru(1)-Ru(3)	81.97(2)	C(4)-Ru(2)-C(6)	99.24(14)
C(4)-Ru(2)-C(5)	101.2(2)	C(6)-Ru(2)-C(5)	95.28(14)
C(4)-Ru(2)-P(2)	100.85(11)	C(6)-Ru(2)-P(2)	93.02(10)
C(5)-Ru(2)-P(2)	154.81(10)	C(4)-Ru(2)-P(1)	98.26(10)
C(6)-Ru(2)-P(1)	158.05(10)	C(5)-Ru(2)-P(1)	94.22(9)
P(2)-Ru(2)-P(1)	70.67(3)	C(4)-Ru(2)-Ru(1)	144.28(10)
C(6)-Ru(2)-Ru(1)	105.67(10)	C(5)-Ru(2)-Ru(1)	101.53(10)
P(2)-Ru(2)-Ru(1)	53.29(2)	P(1)-Ru(2)-Ru(1)	52.91(2)
C(8)-Ru(3)-C(7)	97.66(13)	C(8)-Ru(3)-C(9)	98.30(13)
C(7)-Ru(3)-C(9)	93.73(14)	C(8)-Ru(3)-P(1)	98.74(10)
C(7)-Ru(3)-P(1)	93.12(9)	C(9)-Ru(3)-P(1)	160.61(10)
C(8)-Ru(3)-P(2)	98.16(10)	C(7)-Ru(3)-P(2)	159.08(9)
C(9)-Ru(3)-P(2)	97.44(11)	P(1)-Ru(3)-P(2)	71.00(3)
C(8)-Ru(3)-Ru(1)	142.38(9)	C(7)-Ru(3)-Ru(1)	106.71(9)
C(9)-Ru(3)-Ru(1)	108.03(10)	P(1)-Ru(3)-Ru(1)	52.59(2)
P(2)-Ru(3)-Ru(1)	52.92(2)	C(10)-P(1)-Ru(3)	123.75(10)
C(10)-P(1)-Ru(2)	126.94(10)	Ru(3)-P(1)-Ru(2)	107.97(3)
C(10)-P(1)-Ru(1)	125.51(10)	Ru(3)-P(1)-Ru(1)	76.03(3)
Ru(2)-P(1)-Ru(1)	75.00(3)	C(16)-P(2)-Ru(3)	125.39(11)
C(16)-P(2)-Ru(2)	124.25(11)	Ru(3)-P(2)-Ru(2)	108.17(3)
C(16)-P(2)-Ru(1)	128.83(10)	Ru(3)-P(2)-Ru(1)	75.77(2)
Ru(2)-P(2)-Ru(1)	74.86(3)	O(1)-C(1)-Ru(1)	179.2(3)
O(2)-C(2)-Ru(1)	175.2(3)	O(3)-C(3)-Ru(1)	175.9(3)
O(4)-C(4)-Ru(2)	176.4(3)	O(5)-C(5)-Ru(2)	177.4(3)
O(6)-C(6)-Ru(2)	177.3(3)	O(7)-C(7)-Ru(3)	175.5(3)
O(8)-C(8)-Ru(3)	176.0(3)	O(9)-C(9)-Ru(3)	179.7(3)
C(11)-C(10)-C(12)	122.7(3)	C(11)-C(10)-P(1)	113.1(2)
C(12)-C(10)-P(1)	124.1(2)	O(10)-C(11)-C(10)	178.3(4)
C(15)-C(12)-C(13)	110.6(3)	C(15)-C(12)-C(14)	108.6(3)
C(13)-C(12)-C(14)	108.6(3)	C(15)-C(12)-C(10)	109.3(3)
C(13)-C(12)-C(10)	110.0(3)	C(14)-C(12)-C(10)	109.7(3)
C(17)-C(16)-C(18)	119.9(3)	C(17)-C(16)-P(2)	116.5(2)
C(18)-C(16)-P(2)	123.6(2)	O(11)-C(17)-C(16)	179.5(4)
C(21)-C(18)-C(19)	111.4(4)	C(21)-C(18)-C(16)	110.4(3)
C(19)-C(18)-C(16)	109.7(3)	C(21)-C(18)-C(20)	109.8(4)
C(19)-C(18)-C(20)	107.1(3)	C(16)-C(18)-C(20)	108.4(3)

TABLE III

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[Os_3(CO)_9\{PC(CO)^tBu\}_2]$ **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	0.35583(4)	0.2500	-0.04552(7)	0.0443(3)
Os(2)	0.26707(4)	0.2500	-0.32338(7)	0.0422(3)
Os(3)	0.18431(4)	0.2500	0.07670(7)	0.0439(3)
P(1)	0.2325(2)	0.31384(13)	-0.1208(3)	0.0417(7)
O(11)	0.5064(10)	0.2500	-0.257(2)	0.132(9)
C(11)	0.4489(13)	0.2500	-0.179(2)	0.062(5)
O(12)	0.4296(9)	0.3524(7)	0.150(2)	0.133(6)
C(12)	0.4068(11)	0.3153(8)	0.073(2)	0.090(5)
O(21)	0.1076(9)	0.2500	-0.514(2)	0.073(4)
C(21)	0.1703(14)	0.2500	-0.444(2)	0.054(5)
O(22)	0.3608(7)	0.3600(5)	-0.4769(14)	0.085(3)
C(22)	0.3282(9)	0.3182(6)	-0.4233(14)	0.053(3)
O(31)	-0.0126(9)	0.2500	0.084(2)	0.082(5)
C(31)	0.060(2)	0.2500	0.077(2)	0.050(5)
O(32)	0.2020(9)	0.3590(6)	0.2932(12)	0.101(4)
C(32)	0.1957(9)	0.3170(6)	0.218(2)	0.064(4)
O(1)	0.3780(9)	0.4481(6)	-0.110(2)	0.121(5)
C(1)	0.2341(8)	0.3984(6)	-0.1294(14)	0.054(3)
C(2)	0.3086(12)	0.4239(7)	-0.123(2)	0.081(5)
C(3)	0.1511(10)	0.4378(7)	-0.162(2)	0.076(4)
C(4)	0.1737(14)	0.5072(7)	-0.174(3)	0.147(10)
C(5)	0.0861(14)	0.4284(12)	-0.039(4)	0.19(2)
C(6)	0.113(2)	0.4159(11)	-0.307(3)	0.161(12)

a significantly shorter Os6—P2 distance of 229.2(3) pm, compared to 239.2(4) pm for the distance Os4—P2, while the phosphorus atom P1 forms an almost symmetrical bridge between the atoms Os4 and Os5 with distances of 241.4(3) and 243.3(4), respectively. These osmium phosphorus distances lie within the range of 237.9(51) pm for μ_2—PR_2—Os complexes,[12] with the exception of the distance Os6—P2, which resembles the bond lengths of 228.3(2) pm found in osmium complexes with the strong σ-donor ligand $P(OMe)_3$.[12] Similarly, the Os2—P1 distance of 234.1(4) pm lies in the typical range of Os—P bond lengths in phosphine complexes (PMe_3 typically is 232.3(29) pm).[12] Therefore, the co-ordination of the phosphorus atoms can be considered to involve each P atom contributing one electron to an osmium phosphorus σ-bond towards Os4, while the remaining electron pairs upon P1 and P2 are donated in a Lewis-type interaction to the metal atoms Os2 and Os6, respectively, as indicated in Scheme 1. In this picture each metal centre gains an 18 VE configuration.

EXPERIMENTAL

All experiments were performed in an atmosphere of deoxygenated dinitrogen using conventional Schlenk techniques. All solvents were dry and saturated with dinitrogen. IR spectra were obtained using a Perkin Elmer 1600 series FT-IR spectrometer. NMR spectra were recorded on a Bruker AC 200

TABLE IV

Bond lengths [Å] and bond angles [°] for $[Os_3(CO)_9\{PC(CO)^tBu\}_2]$ **2**

Os(1)-C(11) 1.88(2)	Os(3)-P(1a) 2.373(3)
Os(1)-C(12a) 1.93(2)	Os(3)-P(1) 2.373(3)
Os(1)-C(12) 1.93(2)	P(1)-C(1) 1.794(13)
Os(1)-P(1a) 2.424(3)	O(11)-C(11) 1.13(2)
Os(1)-P(1) 2.424(3)	O(12)-C(12) 1.11(2)
Os(1)-Os(3) 2.8577(10)	O(21)-C(21) 1.15(2)
Os(1)-Os(2) 2.8807(9)	O(22)-C(22) 1.13(2)
Os(2)-C(21) 1.85(2)	O(31)-C(31) 1.11(2)
Os(2)-C(22a) 1.950(14)	O(32)-C(32) 1.13(2)
Os(2)-C(22) 1.950(14)	O(1)-C(2) 1.19(2)
Os(2)-P(1a) 2.353(3)	C(1)-C(2) 1.26(2)
Os(2)-P(1) 2.353(3)	C(1)-C(3) 1.55(2)
Os(3)-C(31) 1.91(2)	C(3)-C(4) 1.51(2)
Os(3)-C(32) 1.927(14)	C(3)-C(5) 1.52(3)
Os(3)-C(32a) 1.927(14)	C(3)-C(6) 1.52(3)
C(11)-Os(1)-C(12a) 93.3(7)	C(31)-Os(3)-C(32a) 95.1(5)
C(11)-Os(1)-C(12) 93.3(7)	C(32)-Os(3)-C(32a) 94.9(9)
C(12a)-Os(1)-C(12) 91.9(10)	C(31)-Os(3)-P(1a) 108.3(4)
C(11)-Os(1)-P(1a) 114.2(4)	C(32)-Os(3)-P(1a) 154.3(4)
C(12a)-Os(1)-P(1a) 94.3(5)	C(32a)-Os(3)-P(1a) 93.5(4)
C(12)-Os(1)-P(1a) 151.4(6)	C(31)-Os(3)-P(1) 108.3(4)
C(11)-Os(1)-P(1) 114.2(4)	C(32)-Os(3)-P(1) 93.5(4)
C(12a)-Os(1)-P(1) 151.4(6)	C(32a)-Os(3)-P(1) 154.3(4)
C(12)-Os(1)-P(1) 94.3(5)	P(1a)-Os(3)-P(1) 69.48(14)
P(1a)-Os(1)-P(1) 67.81(14)	C(31)-Os(3)-Os(1) 157.1(5)
C(11)-Os(1)-Os(3) 162.6(5)	C(32)-Os(3)-Os(1) 100.3(4)
C(12a)-Os(1)-Os(3) 98.8(6)	C(32a)-Os(3)-Os(1) 100.3(4)
C(12)-Os(1)-Os(3) 98.8(6)	P(1a)-Os(3)-Os(1) 54.27(7)
P(1a)-Os(1)-Os(3) 52.62(7)	P(1)-Os(3)-Os(1) 54.27(7)
P(1)-Os(1)-Os(3) 52.62(7)	C(1)-P(1)-Os(2) 122.5(4)
C(11)-Os(1)-Os(2) 77.8(5)	C(1)-P(1)-Os(3) 127.4(4)
C(12a)-Os(1)-Os(2) 133.6(5)	Os(2)-P(1)-Os(3) 109.93(11)
C(12)-Os(1)-Os(2) 133.6(5)	C(1)-P(1)-Os(1) 124.0(5)
P(1a)-Os(1)-Os(2) 51.79(7)	Os(2)-P(1)-Os(1) 74.15(9)
P(1)-Os(1)-Os(2) 51.79(7)	Os(3)-P(1)-Os(1) 73.11(8)
Os(3)-Os(1)-Os(2) 84.80(3)	O(11)-C(11)-Os(1) 179(2)
C(21)-Os(2)-C(22a) 96.1(5)	O(12)-C(12)-Os(1) 174(2)
C(21)-Os(2)-C(22) 96.1(5)	O(21)-C(21)-Os(2) 177(2)
C(22a)-Os(2)-C(22) 95.7(8)	O(22)-C(22)-Os(2) 176.2(12)
C(21)-Os(2)-P(1a) 106.8(4)	O(31)-C(31)-Os(3) 177(2)
C(22a)-Os(2)-P(1a) 92.9(4)	O(32)-C(32)-Os(3) 175.4(13)
C(22)-Os(2)-P(1a) 154.5(4)	C(2)-C(1)-C(3) 121.3(13)
C(21)-Os(2)-P(1) 106.8(4)	C(2)-C(1)-P(1) 115.9(11)
C(22a)-Os(2)-P(1) 154.5(4)	C(3)-C(1)-P(1) 122.3(10)
C(22)-Os(2)-P(1) 92.9(4)	O(1)-C(2)-C(1) 177(2)
P(1a)-Os(2)-P(1) 70.17(14)	C(4)-C(3)-C(5) 109(2)
C(21)-Os(2)-Os(1) 154.8(5)	C(4)-C(3)-C(6) 109(2)
C(22a)-Os(2)-Os(1) 100.7(4)	C(5)-C(3)-C(6) 111(2)
C(22)-Os(2)-Os(1) 100.7(4)	C(4)-C(3)-C(1) 110.4(14)
P(1a)-Os(2)-Os(1) 54.06(7)	C(5)-C(3)-C(1) 109.0(14)
P(1)-Os(2)-Os(1) 54.06(7)	C(6)-C(3)-C(1) 108.5(13)
C(31)-Os(3)-C(32) 95.1(5)	

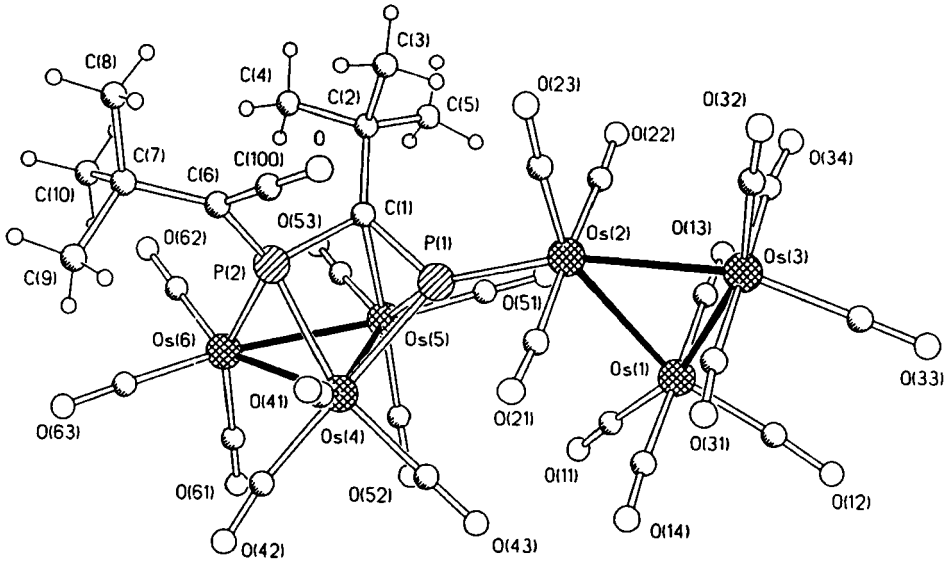


FIGURE 3 The molecular structure of $[Os_3(CO)_9\{P(C(CO)^tBu)—C(^tBu)P(Os_3(CO)_{11})\}]$ **3** showing the atom numbering scheme.

instrument (^{1}H: 200.1, ^{13}C: 50.3, ^{31}P: 81.0 MHz). Positive shifts are to lower field. Mass spectra were obtained using a Kratos MS50TC spectrometer. Reported masses are referred to the isotopes ^{102}Ru and ^{190}Os.

Preparation of $[Ru_3(CO)_9\{\mu_3—PC(CO)^tBu\}_2]$ **1**

A solution of ^{t}BuCP (0.40 g, 4.0 mmol) in 5 ml of 1,2-dimethoxyethane (DME) and $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) were placed in a Pyrex tube. The tube was sealed and the reaction mixture was heated to 60°C resulting in a colour change to dark brown after 2 h. Stirring was continued for 16 h at room temperature and the volatile material was removed *in vacuo*. The residue was extracted with *n*-hexane and fractionated over a chromatographic column (silicagel/*n*-hexane). After removal of the solvent compound **1** was obtained as a yellow solid. Recrystallization from *n*-hexane afforded single crystals, Mp: 23°C. Yield: 0.10 g (0.12 mmol, 16%).

^{1}H-NMR ($CDCl_3$): δ = 1.26 [s, $C(CH_3)_3$] ppm. ^{13}C-NMR ($CDCl_3$, for the numbering of the atoms see X-ray diffraction study, Figure 1): δ = 29.3-34.4 [m, $C(CH_3)_3$], 177.8, 177.9 [2d, ^2J(PC) = 4.2 Hz, CC(:O) (C11, C17)], 192.3, 192.8 [2d, ^1J(PC) = 28.0 Hz, CC(:O) (C10, C16)], 198.5 [t, ^2J(PC) = 7.2 Hz, CO at Ru2, Ru3], 200.0 [t, ^2J(PC) = 7.3 Hz, CO at Ru1] ppm. ^{31}P-NMR ($CDCl_3$, vs. H_3PO_4): δ = 184.4 [s] ppm. FAB-MS (CH_3CN/3-NOBA): m/z (%) = 814 (26) $[M]^+$, 786 (51) $[M\text{-}CO]^+$, 730 (46) $[M\text{-}3\ CO]^+$, 702 (54) $[M\text{-}4\ CO]^+$, 674 (32) $[M\text{-}5\ CO]^+$, 646 (57) $[M\text{-}6\ CO]^+$, 618 (48) $[M\text{-}7\ CO]^+$, 590 (87) $[M\text{-}8\ CO]^+$, 562 (100) $[M\text{-}9\ CO]^+$, 534 (50) $[M\text{-}10\ CO]^+$. IR (CH_2Cl_2): ν_{CO} = 2107 (m), 2091 (s), 2074 (m), 2064 (vs), 2041 (s), 2018 (m), 1999 (m), 1976 (w, sh) cm^{-1}. $C_{21}H_{18}O_{11}P_2Ru_3$ (811.52).

Preparation of $[Os_3(CO)_9\{\mu_3—PC(CO)^tBu\}_2]$ **2** *and* $[Os_3(CO)_9\{P(C(CO)^tBu)C(^tBu)—P(Os_3(CO)_{11})\}]$ **3**

70 mg (0.7 mmol) of ^{t}BuCP were added to a suspension of 200 mg (0.18 mmol) $[Os_3(CO)_{12}]$ in 50 ml of octane. After heating the mixture to 120°C for 2 h the solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2. Filtration followed by thin-layer chromatography on plates with a 0.25 mm layer of Kieselgel 60F-254, supplied by Merck, using CH_2Cl_2/hexane (1:4 v/v) as eluent with subsequent crystallization from CH_2Cl_2/hexane resuted in the isolation of $[Os_3(CO)_9\{\mu_3\text{-}PC(CO)^tBu\}_2]$ **2** (14 mg, 7%) as yellow blocks and $[Os_3(CO)_9\{P(C(CO)^tBu)C(^tBu)P(Os_3(CO)_{11})\}]$ **3** (5 mg, 3%) as dark red tablets.

^{1}H-NMR ($CDCl_3$), δ; **2**: 1.23 [s, $C(CH_3)_3$]; **3**: 1.24 [s, $C(CO)C(CH_3)_3$], 1.32 [s, $P_2CC(CH_3)_3$] ppm. ^{31}P-NMR ($CDCl_3$, vs. H_3PO_4), δ; **2**: −29.9 [s]; **3**: 109.6 [d, ^2J(PP) = 24.6 Hz], 61.3 [d, ^2J(PP) = 24.8 Hz] ppm. FAB-MS (CH_3CN/3-NOBA), m/z (%); **2**: 1078 (15) $[M]^+$, 1050 (3) $[M\text{-}CO]^+$, 1022 (3) $[M\text{-}2\ CO]^+$, 994 (17) $[M\text{-}3\ CO]^+$, 966 (4) $[M\text{-}4\ CO]^+$, 938 (15) $[M\text{-}5\ CO]^+$, 910 (7) $[M\text{-}6\ CO]^+$, 882 (6) $[M\text{-}7\ CO]^+$, 866 (7) $[M\text{-}3\ CO\text{-}\{PC(CO)^tBu\}]^+$, 854 (9) $[M\text{-}8\ CO]^+$, 838 (19) $[M\text{-}4\ CO\text{-}\{PC(CO)^tBu\}]^+$, 826 (11) $[M\text{-}9\ CO]^+$, 810 (10) $[M\text{-}5\ CO\text{-}\{PC(CO)^tBu\}]^+$; **3**: 1928 $[M]^+$, as required. IR (CH_2Cl_2), ν_{CO}; **2**: 2110 (m), 2096 (s), 2076 (w), 2064

TABLE V

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Os_3(CO)_9\{P(C(CO)^tBu)C(^tBu)P(Os_3(CO)_{11})\}]$ **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	2175(1)	6639(1)	1638(1)	36(1)
Os(2)	3825(1)	7560(1)	547(1)	30(1)
Os(3)	1763(1)	7064(1)	-1244(1)	39(1)
Os(4)	6028(1)	6538(1)	2861(1)	27(1)
Os(5)	6030(1)	7864(1)	4915(1)	29(1)
Os(6)	7821(1)	7468(1)	5217(1)	33(1)
P(1)	5316(3)	7654(2)	2281(3)	26(1)
P(2)	7315(2)	7907(2)	3035(4)	27(1)
C(1)	6491(9)	8528(7)	3053(14)	25(3)
C(2)	6818(10)	9519(8)	3054(14)	34(3)
C(3)	6641(14)	9717(10)	1486(17)	60(5)
C(4)	7923(12)	9940(9)	3880(21)	60(5)
C(5)	6235(13)	9916(9)	3816(17)	49(4)
C(6)	7924(10)	8116(8)	1614(15)	33(3)
C(100)	7256(12)	7989(10)	359(17)	44(4)
O	6642(10)	7909(8)	-707(13)	70(3)
C(7)	9019(11)	8276(10)	1637(18)	47(4)
C(8)	9234(15)	8812(14)	486(23)	88(7)
C(9)	9172(16)	7389(12)	1333(20)	78(6)
C(10)	9748(11)	8761(11)	3142(18)	58(5)
C(11)	2837(13)	6541(10)	3581(20)	49(4)
C(12)	834(14)	6063(10)	1568(19)	55(4)
C(13)	2142(11)	7760(12)	2426(17)	48(4)
C(14)	2251(11)	5534(11)	825(17)	48(4)
C(21)	3816(10)	6452(11)	-318(16)	44(4)
C(22)	3774(11)	8663(11)	1394(17)	45(4)
C(23)	4351(10)	8086(9)	-828(17)	45(4)
C(31)	1796(11)	5952(12)	-2069(17)	48(4)
C(32)	1953(14)	7496(11)	-2970(19)	59(5)
C(33)	322(13)	6560(12)	-1703(19)	53(4)
C(34)	1761(11)	8189(13)	-464(18)	56(5)
C(41)	6017(10)	6093(8)	958(17)	35(3)
C(42)	6646(11)	5740(9)	3730(16)	40(4)
C(43)	4749(11)	5734(9)	2968(15)	35(3)
C(51)	4944(13)	8262(9)	4909(15)	46(4)
C(52)	5564(11)	7020(9)	6007(15)	37(3)
C(53)	6938(11)	8762(10)	6487(16)	40(4)
C(61)	7570(11)	6849(9)	6806(18)	40(3)
C(62)	8835(11)	8424(10)	6381(16)	41(4)
C(63)	8769(11)	6961(10)	4878(14)	40(4)
O(11)	3165(10)	6475(8)	4713(14)	68(3)
O(12)	14(11)	5677(9)	1547(18)	95(5)
O(13)	2086(9)	8377(8)	2932(13)	63(3)
O(14)	2247(9)	4884(8)	384(13)	66(3)
O(21)	3875(8)	5823(7)	-843(13)	62(3)
O(22)	3778(9)	9316(7)	1832(15)	66(3)
O(23)	4643(9)	8416(9)	-1757(14)	77(4)
O(31)	1738(9)	5299(8)	-2635(14)	71(3)
O(32)	2028(12)	7713(10)	-4016(16)	93(5)
O(33)	-501(9)	6265(9)	-1961(15)	78(4)
O(34)	1658(10)	8822(8)	-96(14)	71(4)
O(41)	6025(9)	5879(7)	-174(11)	57(3)
O(42)	6892(9)	5197(7)	4122(13)	62(3)
O(43)	4017(9)	5288(7)	3042(13)	61(3)
O(51)	4276(9)	8490(7)	4882(12)	61(3)
O(52)	5236(9)	6484(8)	6629(12)	60(3)
O(53)	7462(9)	9320(7)	7436(12)	65(3)
O(61)	7450(9)	6521(7)	7736(13)	63(3)
O(62)	9485(10)	9031(9)	7061(13)	83(4)
O(63)	9345(10)	6658(9)	4762(14)	77(4)

TABLE VI Selected bond lengths [Å] and angles [°] for $[Os_3(CO)_9\{P(C(CO)^tBu)—C(^tBu)P(Os_3(CO)_{11})\}]$ **3**

Os(1)-C(12)	1.87(2)	Os(4)-C(43)	1.95(2)	P(2)-C(6)	1.809(13)	C(22)-O(22)	1.12(2)
Os(1)-C(11)	1.92(2)	Os(4)-P(2)	2.392(4)	P(2)-C(1)	1.812(12)	C(23)-O(23)	1.18(2)
Os(1)-C(13)	1.96(2)	Os(4)-P(1)	2.414(3)	C(1)-C(2)	1.54(2)	C(31)-O(31)	1.13(2)
Os(1)-C(14)	1.97(2)	Os(4)-Os(5)	2.824(2)	C(2)-C(4)	1.51(2)	C(32)-O(32)	1.11(2)
Os(1)-Os(3)	2.871(2)	Os(4)-Os(6)	2.877(2)	C(2)-C(5)	1.51(2)	C(33)-O(33)	1.10(2)
Os(1)-Os(2)	2.9033(13)	Os(5)-C(52)	1.86(2)	C(2)-C(3)	1.54(2)	C(34)-O(34)	1.14(2)
Os(2)-C(23)	1.830(14)	Os(5)-C(51)	1.90(2)	C(6)-C(100)	1.30(2)	C(41)-O(41)	1.12(2)
Os(2)-C(21)	1.94(2)	Os(5)-C(53)	1.90(2)	C(6)-C(7)	1.54(2)	C(42)-O(42)	1.12(2)
Os(2)-C(22)	1.96(2)	Os(5)-C(1)	2.299(12)	C(100)-O	1.15(2)	C(43)-O(43)	1.11(2)
Os(2)-P(1)	2.341(4)	Os(5)-P(1)	2.433(4)	C(7)-C(8)	1.50(2)	C(51)-O(51)	1.15(2)
Os(2)-Os(3)	2.889(2)	Os(5)-Os(6)	2.8495(11)	C(7)-C(10)	1.54(2)	C(52)-O(52)	1.15(2)
Os(3)-C(32)	1.90(2)	Os(5)-P(2)	2.909(3)	C(7)-C(9)	1.56(2)	C(53)-O(53)	1.15(2)
Os(3)-C(33)	1.92(2)	Os(6)-C(62)	1.83(2)	C(11)-O(11)	1.10(2)	C(61)-O(61)	1.10(2)
Os(3)-C(34)	1.94(2)	Os(6)-C(63)	1.91(2)	C(12)-O(12)	1.16(2)	C(62)-O(62)	1.14(2)
Os(3)-C(31)	1.96(2)	Os(6)-C(61)	1.94(2)	C(13)-O(13)	1.13(2)	C(63)-O(63)	1.13(2)
Os(4)-C(41)	1.91(2)	Os(6)-P(2)	2.292(3)	C(14)-O(14)	1.12(2)		
Os(4)-C(42)	1.94(2)	P(1)-C(1)	1.787(12)	C(21)-O(21)	1.15(2)		

C(12)-Os(1)-C(11)	99.8(7)	C(42)-Os(4)-P(2)	109.1(4)	C(63)-Os(6)-P(2)	101.9(4)
C(12)-Os(1)-C(13)	91.9(7)	C(43)-Os(4)-P(2)	157.8(4)	C(61)-Os(6)-P(2)	153.1(4)
C(11)-Os(1)-C(13)	88.7(6)	C(41)-Os(4)-P(1)	99.9(4)	C(62)-Os(6)-Os(5)	105.2(5)
C(12)-Os(1)-C(14)	90.1(7)	C(42)-Os(4)-P(1)	168.5(4)	C(63)-Os(6)-Os(5)	162.4(4)
C(11)-Os(1)-C(14)	91.6(6)	C(43)-Os(4)-P(1)	92.1(4)	C(61)-Os(6)-Os(5)	90.3(4)
C(13)-Os(1)-C(14)	177.9(6)	P(2)-Os(4)-P(1)	68.81(11)	P(2)-Os(6)-Os(5)	67.92(9)
C(12)-Os(1)-Os(3)	96.5(5)	C(41)-Os(4)-Os(5)	152.0(4)	C(62)-Os(6)-Os(4)	156.2(4)
C(11)-Os(1)-Os(3)	163.6(5)	C(42)-Os(4)-Os(5)	113.9(4)	C(63)-Os(6)-Os(4)	103.3(4)
C(13)-Os(1)-Os(3)	89.9(4)	C(43)-Os(4)-Os(5)	92.7(4)	C(61)-Os(6)-Os(4)	102.0(4)
C(14)-Os(1)-Os(3)	89.2(5)	P(2)-Os(4)-Os(5)	67.20(9)	P(2)-Os(6)-Os(4)	53.70(9)
C(12)-Os(1)-Os(2)	156.6(5)	P(1)-Os(4)-Os(5)	54.68(8)	Os(5)-Os(6)-Os(4)	59.10(3)
C(11)-Os(1)-Os(2)	103.6(5)	C(41)-Os(4)-Os(6)	124.6(4)	C(1)-P(1)-Os(2)	132.2(4)
C(13)-Os(1)-Os(2)	89.3(4)	C(42)-Os(4)-Os(6)	69.2(4)	C(1)-P(1)-Os(4)	93.8(4)
C(14)-Os(1)-Os(2)	88.6(5)	C(43)-Os(4)-Os(6)	128.2(4)	Os(2)-P(1)-Os(4)	129.9(2)
Os(3)-Os(1)-Os(2)	60.03(4)	P(2)-Os(4)-Os(6)	50.55(9)	C(1)-P(1)-Os(5)	63.9(4)
C(23)-Os(2)-C(21)	90.1(7)	P(1)-Os(4)-Os(6)	102.58(9)	Os(2)-P(1)-Os(5)	139.89(14)

C(23)-Os(2)-C(22)	90.8(6)	Os(5)-Os(4)-Os(6)	59.96(4)	Os(4)-P(1)-Os(5)	71.27(10)
C(21)-Os(2)-C(22)	177.6(6)	C(52)-Os(5)-C(51)	90.2(6)	C(6)-P(2)-C(1)	111.9(6)
C(23)-Os(2)-P(1)	99.6(5)	C(52)-Os(5)-C(53)	98.2(6)	C(6)-P(2)-Os(6)	130.2(5)
C(21)-Os(2)-P(1)	86.5(4)	C(51)-Os(5)-C(53)	92.5(6)	C(1)-P(2)-Os(6)	113.2(4)
C(22)-Os(2)-P(1)	95.5(4)	C(52)-Os(5)-C(1)	162.3(5)	C(6)-P(2)-Os(4)	120.9(5)
C(23)-Os(2)-Os(3)	94.0(5)	C(51)-Os(5)-C(1)	97.5(5)	C(1)-P(2)-Os(4)	93.9(4)
C(21)-Os(2)-Os(3)	87.2(4)	C(53)-Os(5)-C(1)	97.4(5)	Os(6)-P(2)-Os(4)	75.75(11)
C(22)-Os(2)-Os(3)	90.6(4)	C(52)-Os(5)-P(1)	122.0(4)	C(6)-P(2)-Os(5)	163.9(4)
P(1)-Os(2)-Os(3)	165.00(8)	C(51)-Os(5)-P(1)	82.5(4)	C(1)-P(2)-Os(5)	52.2(4)
C(23)-Os(2)-Os(1)	153.4(5)	C(53)-Os(5)-P(1)	139.4(4)	Os(6)-P(2)-Os(5)	65.18(9)
C(21)-Os(2)-Os(1)	89.4(4)	C(1)-Os(5)-P(1)	44.3(3)	Os(4)-P(2)-Os(5)	63.51(8)
C(22)-Os(2)-Os(1)	88.8(4)	C(52)-Os(5)-Os(4)	88.9(4)	C(2)-C(1)-P(1)	132.6(9)
P(1)-Os(2)-Os(1)	106.88(9)	C(51)-Os(5)-Os(4)	126.6(4)	C(2)-C(1)-P(2)	123.6(9)
Os(3)-Os(2)-Os(1)	59.43(4)	C(53)-Os(5)-Os(4)	140.4(4)	P(1)-C(1)-P(2)	98.0(6)
C(32)-Os(3)-C(33)	103.1(7)	C(1)-Os(5)-Os(4)	73.6(3)	C(2)-C(1)-Os(5)	124.6(8)
C(32)-Os(3)-C(34)	89.3(7)	P(1)-Os(5)-Os(4)	54.05(8)	P(1)-C(1)-Os(5)	71.9(4)
C(33)-Os(3)-C(34)	91.6(7)	C(52)-Os(5)-Os(6)	91.4(4)	P(2)-C(1)-Os(5)	89.3(5)
C(32)-Os(3)-C(31)	88.9(7)	C(51)-Os(5)-Os(6)	172.3(4)	C(4)-C(2)-C(5)	107.9(12)
C(33)-Os(3)-C(31)	89.8(7)	C(53)-Os(5)-Os(6)	79.9(4)	C(4)-C(2)-C(1)	109.1(11)
C(34)-Os(3)-C(31)	177.9(7)	C(1)-Os(5)-Os(6)	83.0(3)	C(5)-C(2)-C(1)	110.5(11)
C(32)-Os(3)-Os(1)	161.4(6)	P(1)-Os(5)-Os(6)	102.88(8)	C(4)-C(2)-C(3)	109.5(13)
C(33)-Os(3)-Os(1)	95.5(5)	Os(4)-Os(5)-Os(6)	60.93(4)	C(5)-C(2)-C(3)	108.8(12)
C(34)-Os(3)-Os(1)	90.3(5)	C(52)-Os(5)-P(2)	129.4(4)	C(1)-C(2)-C(3)	111.1(10)
C(31)-Os(3)-Os(1)	91.1(4)	C(51)-Os(5)-P(2)	135.3(5)	C(100)-C(6)-C(7)	118.2(13)
C(32)-Os(3)-Os(2)	100.9(6)	C(53)-Os(5)-P(2)	99.9(4)	C(100)-C(6)-P(2)	110.2(10)
C(33)-Os(3)-Os(2)	156.1(5)	C(1)-Os(5)-P(2)	38.5(3)	C(7)-C(6)-P(2)	130.8(11)
C(34)-Os(3)-Os(2)	88.4(4)	P(1)-Os(5)-P(2)	60.33(10)	O-C(100)-C(6)	176(2)
C(31)-Os(3)-Os(2)	91.0(4)	Os(4)-Os(5)-P(2)	49.29(7)	C(8)-C(7)-C(6)	107.7(13)
Os(1)-Os(3)-Os(2)	60.54(4)	Os(6)-Os(5)-P(2)	46.90(7)	C(8)-C(7)-C(10)	110(2)
C(41)-Os(4)-C(42)	91.5(6)	C(62)-Os(6)-C(63)	91.2(6)	C(6)-C(7)-C(10)	110.7(12)
C(41)-Os(4)-C(43)	100.5(5)	C(62)-Os(6)-C(61)	95.4(6)	C(8)-C(7)-C(9)	111(2)
C(42)-Os(4)-C(43)	87.2(5)	C(63)-Os(6)-C(61)	94.7(6)	C(6)-C(7)-C(9)	110.1(13)
C(41)-Os(4)-P(2)	94.2(4)	C(62)-Os(6)-P(2)	105.2(4)	C(10)-C(7)-C(9)	107.8(13)

(vs), 2042 (s), 2010 (s), 1991 (m), 1969 (w, sh); **3**: 2115 (w), 2097 (vs), 2083 (s), 2063 (vs), 2047 (s), 2034 (m), 2026 (vs), 2008 (s), 1993 (m), 1981 (w, sh), 1959 (w, sh) cm^{-1}. **2**: $C_{21}H_{18}O_{11}Os_3P_2$ (1078.92); **3**: $C_{31}H_{18}O_{21}Os_6P_2$ (1929.59).

Single Crystal X-Ray Structure Determination of **1**

Crystal data: $C_{21}H_{18}O_{11}P_2Ru_3$, M = 811.50, monoclinic, $P2_1/c$, a = 1466.4(3), b = 1205.2(2), c = 1616.5(3) pm, β = 97.19(2)°, V = 28343 nm^3, Z = 4, D_c = 1.902 Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 1.74 mm^{-1}, F(000) = 1576, T = 143 K. *Data collection and reduction:* A yellow parallelpiped ca. 0.55 × 0.45 × 0.4 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). A total of 8853 intensities were measured to 2θ = 50°, of which 6515 were unique (R_{int} 0.021). Cell constants were refined from $\pm\omega$ angles of 64 reflections in the 2θ-range 20–22°. An absorption correction based on Ψ-scans gave transmission factors 0.71–0.85. *Structure solution and refinement:* The structure was solved by direct methods and refined on F^2 using the program SHELXL-93.[13] H atoms were included using rigid methyl groups. The final $wR(F^2)$ for all reflections was 0.066, with a conventional R(F) of 0.027, for 340 parameters and 163 restraints (to light atom temperature factors); S = 1.08, max. Δ/σ = 0.001, max $\Delta\rho$ = 0.79 e $Å^{-3}$.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD.

Single Crystal X-Ray Structure Determination of **2**

Crystal data: $C_{21}H_{18}O_{11}Os_3P_2$, M = 1078.89, orthorhombic, Pnma, a = 15.3368(14), b = 21.184(2), c = 9.1367(9) Å, V = 2968.5(5) $Å^3$ [from $\pm\omega$ angles of 64 reflections in the 2θ-range 30–36°], Z = 4, D_c = 2.414 Mg m^{-3}, μ = 12.967 mm^{-1}, F(000) = 1960, T = 293(2) K. *Data collection and reduction:* A yellow block ca. 0.53 × 0.48 × 0.48 mm was mounted on a Stoe STADI-4 diffractometer (Mo Kα, λ = 0.71073 Å, graphite monochromated). A total of 2102 reflections were collected, of which 2010 were unique (R_{int} = 0.0246, $2\theta_{max}$ = 45°, h 0 to 16, k 0 to 18, l 0 to 9). The data were corrected for absorption by means of ψ-scans (minimum and maximum transmission factors 0.005 and 0.023, respectively). 2008 reflections with $F \geq 4\sigma(F)$ were used in all calculations. *Structure solution and refinement:* The osmium atoms were located by direct methods and the remaining non-hydrogen atoms from subsequent difference Fourier synthesis and refined on F^2 using the program SHELXL-93. All non-hydrogen atoms were treated anisotropically and the hydrogen atoms were included using rigid methyl groups. At final convergence R, wR_2 = 0.0417 and 0.1080, respectively, S = 1.105 for 182 refined parameters, $(\Delta/\sigma)_{max}$ = −0.046. The final ΔF synthesis showed no $\Delta\rho$ above 1.415 and below −1.667 e $Å^{-3}$, the major features lying near the osmium atoms.

Single Crystal X-Ray Structure Determination of **3**

Crystal data: $C_{31}H_{18}O_{21}Os_6P_2$, M = 1929.59, triclinic, $P\bar{1}$, a = 14.646(7), b = 16.418(7), c = 9.614(5) Å, α = 94.35(4)°, β = 104.63(3)°, γ = 108.55(3)°, V = 2119 $Å^3$, Z = 2, D_c = 3.067 Mg m^{-3}, μ = 18.326 mm^{-1}, F(000) = 1716, T = 293(2) K. *Data collection and reduction:* A red tablet ca. 0.3 × 0.3 × 0.3 mm was mounted on a Enraf-Nonius CAD-4 diffractometer (Mo Kα, λ = 0.71073 Å, graphite monochromated). A total of 5685 reflections were collected, of which 5374 were unique (R_{int} = 0.0511, $2\theta_{max}$ = 45°, h − 15 to 14, k − 17 to 17, l 0 to 10). A ψ-scan based absorption correction gave minimum and maximum transmission factors 0.338 and 0.925, respectively). 5366 reflections with $F \geq 4\sigma(F)$ were used in all calculations. *Structure solution and refinement:* The structure was solved by a combination of direct methods and Fourier difference techniques and refined on F^2 using the program SHELXL-93. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included using rigid methyl groups, resulting in a final R, wR_2 = 0.0329 and 0.0820, respectively, S = 1.053 for 548 refined parameters, with a $(\Delta/\sigma)_{max}$ of 0.008 and a $\Delta\rho_{max}$ of 1.855 e $Å^{-3}$ in the final cycle.

Full details of the structure determinations of the complexes **2** and **3** have been deposited at ******.

ACKNOWLEDGEMENTS

R. B., P. G. J., C. M., and R. S. thank Dr. S. Hietkcamp (Council of Scientific and Industrial Research, Pretoria, South Africa) for a gift of dodecacarbonyltriruthenium and the Fonds der Chemischen Industrie for financial support. C. M. thanks the Hermann-Schlosser-Stiftung (Degussa AG) for a maintenance grant. M. N. wishes to express his gratitude towards the Deutsche Forschungsgemeinschaft (Bonn, Bad Godesberg) for a postdoctoral fellowship.

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