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Terminal Phosphido Complexes of Ruthenium(II) and Osmium(II): Synthesis, Reactivity, and Crystal Structures of $Os(PHPh)Cl(CO)_2(PPh_3)_2$ and $Os\{PH(OMe)Ph\}(CO)_2(PPh_3)_2$

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Terminal phosphido complexes $M(PRPh)Cl(CO)_2(PPh_3)_2$ (M = Os, R = H, Ph, I, OMe; M = Ru, R = H) (**2a–e**) were prepared by deprotonation of cationic phosphine complexes containing PHRPh ligands. The nucleophilic character of the phosphorus center in **2a–e** is demonstrated by its reaction with Me^+, H^+, and I_2. However methoxide also adds to the phosphorus center in **2a,b,d,e** to give the reduced species $M\{PR(OMe)Ph\}(CO)_2(PPh_3)_2$ (M = Os, R = H, Ph, OMe; M = Ru, R = H) (**5a,b,d,e**). The iodide in $Os(PIPh)Cl(CO)_2(PPh_3)_2$ (**2c**) can be abstracted with methanolic solutions of silver(I) salts to give $[OsCl\{PH(OMe)Ph\}(CO)_2(PPh_3)_2]^+$ (**12**). Compound **2a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.369$ (1) Å, $b = 17.823$ (1) Å, $c = 22.599$ (3) Å, $\beta = 97.31$ (2)°, $V = 4142.4$ Å^3, and ρ(calcd) = 1.54 g cm^{-3}. The geometry at the phosphido phosphorus is pyramidal with a long Os–P bond to this ligand of 2.523 (7) Å. Compound **5a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.774$ (2) Å, $b = 13.292$ (4) Å, $c = 12.171$ (2) Å, $\alpha = 105.15$ (2)°, $\beta = 95.42$ (2)°, $\gamma = 85.28$ (2)° $V = 1982.1$ Å^3, and ρ(calcd) = 1.52 g cm^{-3}. There is a slightly distorted trigonal-bipyramidal geometry at the osmium with trans triphenylphosphine ligands.

Introduction

The structural evidence available for complexes of the terminal phosphido ligand ($L_nM–PR_2$) suggests that two distinct binding modes predominate with either a pyramidal[1–5] or a planar[6–14] geometry found at the phosphorus atom. While a wide range of metals is known to bind to the terminal phosphido ligand, iridium[5,15] and rhodium[16] are the only platinum group metals which have so far provided examples. Amido complexes show a similar trend in the frequency of their occurrence across the d block.[17] Typical methods for the synthesis of metal complexes of PR_2 ligands include (A) metal carbonylate anion nucleophilic attack on halophosphines,[6,18] (B) transmetalation of metal halides with metalated phosphines,[9] (C) biphosphine cleavage with metal–metal bonded dinuclear species,[19] and (D) oxidative addition of PX_3 species (X = halogen or hydrogen)[15] to low-valent metal substrates. Only method D has been used previously in the synthesis of terminal phosphido complexes of group VIII (8^{40}) metals.

The nucleophilic character of the pyramidal phosphido ligand is well-documented.[20] However, characterization of planar phosphido ligand reactivity lags well behind,[12,21] with only a single study,[14,22] of the planar $\overline{POC(CH_3)_2C(CH_3)_2O}$ ligand in $W(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POC(CH_3)_2C(CH_3)_2O}]$, suggesting that the phosphorus center has electrophilic character. If HX abstraction from a suitable terminal phosphido complex, $L_nXM—PHR$, is to lead to the synthesis of a terminal phosphinidene complex, $L_nM{=}PR$, then the geometry of the phosphido ligand will be an important factor in the success of this strategy. We report here (1) instances where methoxide adds to the phosphido ligand rather than eliminating HCl from the complex and (2) a case where iodide abstraction from the –PIPh ligand leads to products which suggest the intermediacy of a terminal phosphinidene complex. Preliminary accounts of aspects of this work have appeared.[1,23]

Results and Discussion

There is a relationship between the synthesis of alkylidene complexes by α-hydrogen abstraction[24] from coor-

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(1) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 865.

(2) Barrow, M. J.; Sim, G. A.; Dobbie, R. C.; Mason, P. R. *J. Organomet. Chem.* **1974**, *69*, C4. Barrow, M. J., Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 291.

(3) Peters, K.; Weber, D. *Cryst. Struct. Commun.* **1981**, *10*, 1259. Weber, D.; Fluck, E.; Schnering, H. G.; Peters, K. *Z. Naturforsch., Anorg. Chem., Org. Chem.* **1982**, *37B*, 594.

(4) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254.

(5) Ebsworth, E. A. V.; Gould, R. O.; McManus, N. T.; Pilkington, N. J.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2561.

(6) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 4521.

(7) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L. Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

(8) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(9) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763.

(10) Domaille, P. J.; Foxman, B. M.; McNeese, T. J.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4114.

(11) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.

(12) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.

(13) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1984**, *3*, 399.

(14) Gross, E.; Jörg, K.; Fiederling, K.; Göttlein, A.; Malisch, W.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 738.

(15) Ebsworth, E. A. V.; McManus, N. T.; Pilkington, N. J.; Rankin, D. W. H. *J. Chem. Soc., Chem. Commun.* **1983**, 484. Ebsworth, E. A. V.; Gould, R. O.; McManus, N. T.; Rankin, D. W. H.; Walkingshaw, M. D.; Whitelock, J. D. *J. Organomet. Chem.* **1983**, *249*, 227. Schunn, R. A. *Inorg. Chem.* **1973**, *12*, 1573.

(16) Ebsworth, E. A. V.; McManus, N. T.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2573.

(17) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Ltd.: Chichester, 1980.

(18) For example, see: Malisch, W.; Kuhn, M. *J. Organomet. Chem.* **1974**, *73*, C1. Malisch, W.; Alsmann, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 769.

(19) For example, see: Dobbie, R. C.; Mason, P. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1124. Grobe, J.; Rau, R. *Z. Anorg. Allg. Chem.* **1975**, *414*, 19.

(20) For example, see: Dobbie, R. C.; Mason, P. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2439. Dobbie, R. C.; Mason, P. R. *J. Chem. Soc., Dalton Trans.* **1976**, 189.

(21) Wade, S. R.; Malcom, G. H.; Wallbridge, M. G.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2555.

(22) Luksza, M.; Himmel, S.; Malisch, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 416.

(23) Bohle, D. S.; Roper, W. R. *J. Organomet. Chem.* **1984**, *273*, C4.

(24) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

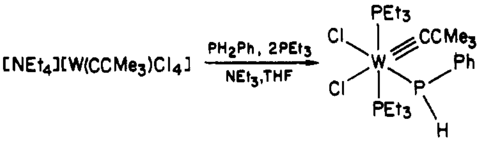
0276-7333/86/2305-1612$01.50/0

Table I. Experimental Data for the X-ray Diffraction Studies

	{Os(PHPh)Cl(CO)$_2$(PPh$_3$)$_2$}EtOH	{Os[PH(OMe)Ph](CO)$_2$(PPh$_3$)$_2$}
	(a) Crystal Data at 25 °C[a]	
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.369 (1)	12.774 (2)
b, Å	17.823 (1)	13.292 (4)
c, Å	22.599 (3)	12.171 (2)
α, deg		105.15 (2)
β, deg	97.31 (2)	95.42 (2)
γ, deg		85.28 (2)
V, Å^3	4142.4	1982.1
Z	4	2
mol wt	961.3	911.0
ρ(calcd), g cm^{-3}	1.54	1.52
	(b) Measurement of Intensity Data	
radiatn	monochromated Mo Kα ($\bar{\lambda}$ = 0.71069 Å)	
scan type	θ(crystal)–2θ(counter)	
2θ range, deg	4.0–50.0	
reflectns collected	4193 [2646 > 3$\sigma(F_o)$][b]	4732 [3858 > 3$\sigma(F_o)$]
	(data > 3$\sigma(F_o)$ used in refinement)	
absorptn coeff, cm^{-1}	31.4	32.2

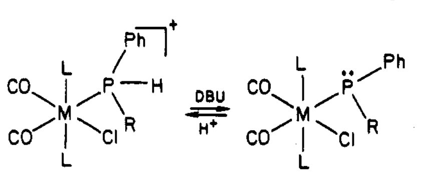
[a] Unit-cell parameters were obtained from a least squares fit to the setting angles of 25 reflections. [b] Due to crystal decomposition it was necessary to use four separate crystals for the data collection. Corrections were made for crystal decomposition and separate scale factors refined for the data from each crystal.

dinated alkyl groups and terminal phosphido complexes from P–H bond cleavage in cationic primary and secondary phosphine complexes. The single previous[8] example of this principle is the synthesis of W(≡CCMe$_3$)(PHPh)Cl$_2$(PEt$_3$)$_2$ (eq 1) where the parent phenylphosphine complex was generated and deprotonated in situ. Cleavage of the P–H



(1)

bond in 1 by the nonnucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is rapid at room temperature and affords high yields of **2a–e**. (eq 2; see legend accompanying Scheme I). Synthesis of the phenyl- and di-



(2)

1a-e **2a-e**

L = PPh$_3$; M = Ru, Os

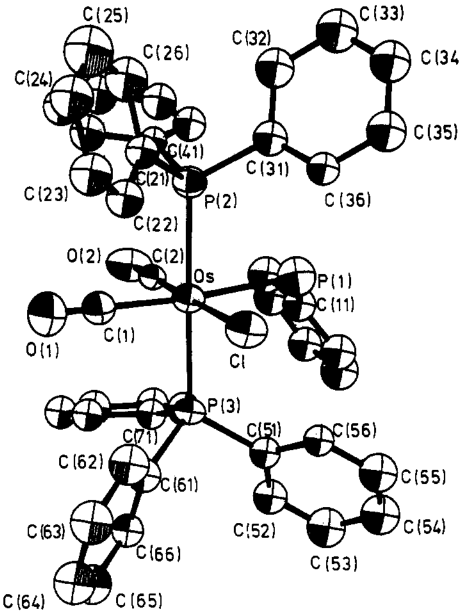


Figure 1. Structure of Os(PHPh)Cl(CO)$_2$(PPh$_3$)$_2$.

phenylphosphine complexes **1a,b,e** was described in the preceding paper, and the cationic complexes of the phenyliodophosphine **1c** and *O*-methyl phenylphosphinite **1d** are derived by modification of the phenylphosphido complex **2a**. Deprotonation of the cationic bis(phenylphosphine) complex [OsCl(PH$_2$Ph)$_2$(CO)(PPh$_3$)$_2$]ClO$_4$ (**3**) leads to a monocarbonyl terminal phosphido complex, Os(PHPh)Cl(PH$_2$Ph)(CO)(PPh$_3$)$_2$ (**4**), of unknown geometry (eq 3).

$$\underset{\mathbf{3}}{[\mathrm{OsCl(PH_2Ph)_2(CO)(PPh_3)_2]ClO_4}} \xrightarrow[\text{-DBU·HClO}_4]{\text{DBU, methanol}} \underset{\mathbf{4}}{\mathrm{Os(PHPh)Cl(PH_2Ph)(CO)(PPh_3)_2}} \quad (3)$$

X-ray Crystallographic Study of Os(PHPh)Cl(CO)$_2$(PPh$_3$)$_2$. The crystal structure of **2a** was determined by a single-crystal X-ray diffraction study. Experimental data are collected in Table I, and bond lengths and angles are tabulated in Tables II and III, respectively. Final atomic positions are contained in Table IV. As presented in Figure 1 the overall geometry is octahedral with mutually trans triphenylphosphine ligands [P(2)–Os–P(3) = 179.0 (2)°] and cis carbonyl ligands [C(1)–Os–C(2) = 88.1 (1.2)°]. A significantly longer osmium-phosphorus bond length is found for the phenylphosphido ligand [Os–P(1) = 2.523 (7) Å] than for the triphenylphosphine ligands [Os–P(2) = 2.414 (7) Å; Os–P(3) = 2.423 (6) Å]. The Os–P(1) bond length is also outside the range (2.29–2.46 Å) which is usually found for tertiary phosphine–osmium bond lengths.[25] A compact Os–P(1)–C(11) = 113.0 (1.1)°

Table II. Interatomic Distances (Å) with Esd's for [Os(PHPh)Cl(CO)$_2$PPh$_3$)$_2$]EtOH

Os–P(1)	2.523 (7)	Os–C(2)	1.871 (29)	P(2)–C(31)	1.845 (11)
Os–P(2)	2.414 (7)	C(1)–O(1)	1.082 (27)	P(2)–C(41)	1.834 (11)
Os–P(3)	2.423 (6)	C(2)–O(2)	1.160 (27)	P(3)–C(51)	1.822 (14)
Os–Cl	2.460 (5)	P(1)–C(11)	1.857 (17)	P(3)–C(61)	1.830 (15)
Os–C(1)	1.935 (29)	P(2)–C(21)	1.861 (12)	P(3)–C(71)	1.826 (13)

	i						
	1	2	3	4	5	6	7
C(*i*1)–C(*i*2)	1.39	1.39	1.41	1.39	1.39	1.40	1.40
C(*i*1)–C(*i*6)	1.43	1.39	1.39	1.40	1.40	1.39	1.39
C(*i*2)–C(*i*3)	1.42	1.38	1.39	1.40	1.39	1.40	1.40
C(*i*3)–C(*i*4)	1.36	1.39	1.41	1.39	1.40	1.40	1.39
C(*i*4)–C(*i*5)	1.41	1.40	1.39	1.40	1.40	1.40	1.40
C(*i*5)–C(*i*6)	1.37	1.40	1.38	1.39	1.38	1.40	1.40

Table III. Interatomic Angles (deg) with Esd's for $\{Os(PHPh)Cl(CO)_2(PPh_3)_2\}EtOH$

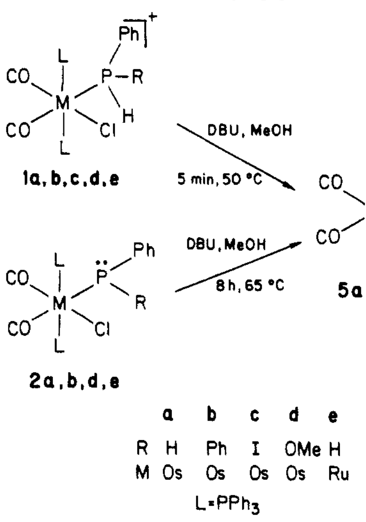
Angles and Osmium			
P(1)–Os–P(2)	85.8 (3)	P(2)–Os–C(2)	90.3 (9)
P(1)–Os–P(3)	93.4 (3)	P(3)–Os–Cl	89.5 (2)
P(1)–Os–Cl	88.2 (2)	P(3)–Os–C(1)	90.3 (9)
P(1)–Os–C(1)	175.6 (9)	P(3)–Os–C(2)	89.5 (9)
P(1)–Os–C(2)	89.5 (8)	Cl–Os–C(1)	94.2 (8)
P(2)–Os–P(3)	179.0 (2)	Cl–Os–C(2)	177.7 (8)
P(2)–Os–Cl	89.9 (2)	C(1)–Os–C(2)	88.1 (1.2)
P(2)–Os–C(1)	90.5 (9)		
Angles Involving the Phenylphosphido Ligand			
Os–P(1)–C(11)	113.0 (1.1)	C(12)–C(13)–C(14)	122.0 (3.4)
P(1)–C(11)–C(12)	119.8 (2.4)	C(13)–C(14)–C(15)	118.3 (3.7)
P(1)–C(11)–C(16)	122.6 (2.6)	C(14)–C(15)–C(16)	120.7 (3.5)
C(12)–C(11)–C(16)	117.5 (3.0)	C(15)–C(16)–C(11)	121.2 (3.2)
C(11)–C(12)–C(13)	120.0 (2.9)		
Angles Involving the Triphenylphosphine Ligands			
Os–P(2)–C(21)	117.6 (1.0)	Os–P(3)–C(51)	119.9 (1.1)
Os–P(2)–C(31)	119.8 (1.0)	Os–P(3)–C(61)	117.1 (0.9)
Os–P(2)–C(41)	107.6 (1.0)	Os–P(3)–C(71)	108.7 (1.0)

bond angle is found for the phenylphosphido ligand. Although the phosphorus-bound hydrogen was not located in Fourier difference maps, the presence of a stereochemically demanding lone pair of electrons, localized on the phosphorus in a pyramidal phosphido ligand, is implied by the magnitude of the Os–P(1)–C(11) bond angle. The chloride ligand is relatively weakly bound as is indicated by the longer than average osmium–chlorine bond length, 2.460 (5) Å, as contrasted with the usual range of these bonds, 2.35–2.51 Å, and by a low ν(OsCl) (Table VIII).

Comparison of the crystal structure of **2a** with that[8] of $W(\equiv CCMe_3)(PHPh)Cl_2(PEt_3)_2$, which contains a planar phenylphosphido ligand (W–P–C = 140.02 (17)°) indicates that there are two distinct bonding modes for this ligand. There are also different trends in the metal–phosphorus bond lengths for the phosphido ligands and the tertiary phosphine ligands in the respective complexes. In the pyramidal phosphido complex, Os–P is ~0.1 Å *longer* for the phosphido ligand, whereas for the planar phosphido complex W–P is ~0.26 Å *shorter* for the phosphido ligand. These distinctions are also found in other structurally characterized pyramidal[2–5] and planar[6–14] phosphido ligands, where the respective ranges are 127–140° and 106–114° for the metal–phosphorus–substituent bond angles.

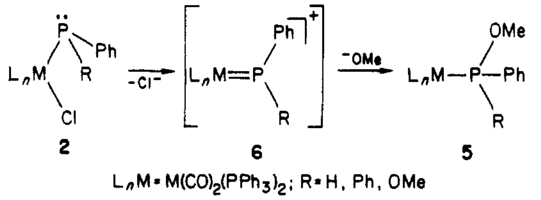
A formal description[1,39] of the bonding in terminal phosphido complexes distinguishes the two conformations by the number of electrons donated to the metal by the phosphorus. In cases of planar phosphido geometry, with a phosphorus 3p orbital available for π-bond formation, the ligand is capable of multiple-metal–phosphorus bonding. Moreover, recent dynamic ^{31}P NMR[12] and low-temperature matrix spectroscopic studies[26] suggest that there is a small (~6 kcal mol^{-1} in $Hf(\eta^5\text{-}C_5H_5)_2\{P(C_6H_{11})_2\}_2$), but significant, energy barrier which separates the planar and pyramidal geometries. Thus, like the nitrosyl ligand,[27] the terminal phosphido ligand is expected to have a non-innocent character facilitating ligand substitution reactions. Two examples which illustrate facile ligand substitution reactions are the rapid CO uptake[28] by $[Fe(CO)_4\{PN(CH_3)CH_2CH_2NCH_3\}]^+PF_6^-$, which could involve a low-energy associative substitution mechanisms via planar → pyramidal conversion, and the specific trans substitution of carbon monoxide by trimethylphosphine in $Mo(\eta^5\text{-}C_5H_5)(CO)_3(PPh_2)$,[29] where a dissociative substitution mechanism would result from pyramidal → planar conversion. However, in the first example, the strong π-acceptor character of the $^+P(NR_2)_2$ ligand has also been suggested[30] to increase the lability of the iron-bound carbonyl ligands by dissociative processes.

Scheme I



Electrophilic Character of Terminal Phosphido Complexes. Deprotonation of cationic phosphine complexes and **1a–e** in hot, basic, methanol results in the net reduction of the metal center with methoxide addition to the phosphorus to give $M\{PR(OMe)Ph\}(CO)_2(PPh_3)_2$ (M = Os, R = H, Ph, OMe; M = Ru, R = H) (**5a,b,d,e**). An alternative method for the synthesis of **5a,b,d,e** is to heat a suspension of a terminal phosphido complex, **2**, in basic methanol, as depicted in Scheme I. Differences in reaction times for these two approaches are due to the low methanol solubility of **2**. A trigonal-bipyramidal geometry with axial triphenylphosphine ligands and equatorial carbonyl and PR(OMe)Ph ligands is assigned to **5** on the basis of spectroscopic (Table VIII) and structural data.

While nucleophilic addition to a terminal planar phosphido ligand has not been reported,[41] the analogous planar $As(t\text{-}Bu)_2$ ligand in $W(\eta^5\text{-}C_5H_5)(CO)_2\{As(t\text{-}Bu)_2\}$ reacts with hydrogen chloride to give $WH(\eta^5\text{-}C_5H_5)(CO)_2\{AsCl(t\text{-}Bu)_2\}$.[22] Conversion of the pyramidal phosphido ligand in **2** to a planar phosphido ligand, which is expected to have electrophilic character, would create a cationic intermediate **6** through loss of chloride (eq 4). Intermediates such as **6** would be stabilized by polar solvents, e.g., methanol, and by the presence of π-acceptor ligands on the metal. For example, when an additional phosphine ligand is present, as in $[OsCl(PH_2Ph)_2(CO)(PPh_3)_2]^+$, a single carbonyl ligand would not stabilize **6** so effectively, and hence the failure of attempts to synthesize Os[PH(OMe)Ph]-



(4)

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(25) For the only reported Os–P bond length which is longer than that in **2a** [found in the PPh_3 bound *trans* to the hydride ligand in $OsHBr(CO)(PPh_3)_3$], see: Orioli, P. L.; Vaska, L. *Proc. Chem. Soc.* **1962**, 333.

(26) Mahmoud, K. A.; Rest, A. J.; Luksza, M.; Jörg, K.; Malisch, W. *Organometallics* **1984**, *3*, 501.

(27) Basolo, F. *Chem. Tech.* **1983**, *13*, 54.

(28) Bennett, D. W.; Parry, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 755.

(29) Malisch, W.; Maisch, R.; Colquhoun, I. J.; McFarlane, W. *J. Organomet. Chem.* **1981**, *220*, C1.

(30) Cowley, A. H.; Kemp, R. A.; Ebsworth, E. A. V.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Organomet. Chem.* **1984**, *265*, C19.

Table IV. Atomic Positions for [Os(PHPh)Cl(CO)$_2$(PPh$_3$)$_2$]EtOH

	x	*y*	*z*		*x*	*y*	*z*
Os	0.9224 (1)	0.2832 (1)	0.5092 (1)	C(1)	0.8583 (27)	0.3814 (16)	0.4834 (12)
Cl	0.7142 (5)	0.2201 (4)	0.4774 (3)	O(1)	0.8299 (22)	0.4380 (12)	0.4696 (10)
P(1)	1.0101 (7)	0.1594 (4)	0.5508 (4)	C(2)	1.0835 (27)	0.3279 (14)	0.5340 (11)
P(2)	0.8562 (6)	0.3041 (4)	0.6066 (3)	O(2)	1.1812 (17)	0.3573 (12)	0.5486 (8)
P(3)	0.9871 (6)	0.2600 (3)	0.4118 (3)				
C(11)	1.1799 (25)	0.1417 (15)	0.5360 (12)	C(44)	1.2041 (14)	0.4303 (6)	0.7090 (7)
C(12)	1.2057 (27)	0.0833 (16)	0.4983 (16)	C(45)	1.1007 (14)	0.4700 (6)	0.6782 (7)
C(13)	1.3351 (30)	0.0687 (17)	0.4882 (14)	C(46)	0.9934 (14)	0.4316 (6)	0.6495 (7)
C(14)	1.4365 (29)	0.1103 (17)	0.5135 (15)	C(51)	1.0028 (13)	0.1641 (8)	0.3854 (7)
C(15)	1.4131 (30)	0.1658 (18)	0.5552 (14)	C(52)	1.0936 (13)	0.1448 (8)	0.3474 (7)
C(16)	1.2887 (30)	0.1822 (16)	0.5654 (13)	C(53)	1.1001 (13)	0.0712 (8)	0.3270 (7)
C(21)	0.7088 (15)	0.3623 (9)	0.6107 (6)	C(54)	1.0159 (13)	0.0169 (8)	0.3446 (7)
C(22)	0.6168 (15)	0.3701 (9)	0.5604 (6)	C(55)	0.9251 (13)	0.0362 (8)	0.3825 (7)
C(23)	0.5000 (15)	0.4073 (9)	0.5647 (6)	C(56)	0.9185 (13)	0.1098 (8)	0.4029 (7)
C(24)	0.4751 (15)	0.4366 (9)	.0.6194 (6)	C(61)	0.8877 (15)	0.3018 (10)	0.3474 (6)
C(25)	0.5671 (15)	0.4288 (9)	0.6697 (6)	C(62)	0.7581 (15)	0.3216 (10)	0.3493 (6)
C(26)	0.6839 (15)	0.3917 (9)	0.6654 (6)	C(63)	0.6838 (15)	0.3501 (10)	0.2985 (6)
C(31)	0.8162 (14)	0.2241 (7)	0.6522 (7)	C(64)	0.7391 (15)	0.3590 (10)	0.2458 (6)
C(32)	0.8414 (14)	0.2286 (7)	0.7142 (7)	C(65)	0.8687 (15)	0.3393 (10)	0.2439 (6)
C(33)	0.7987 (14)	0.1718 (7)	0.7495 (7)	C(66)	0.9430 (15)	0.3107 (10)	0.2947 (6)
C(34)	0.7310 (14)	0.1105 (7)	0.7228 (7)	C(71)	1.1471 (11)	0.3027 (7)	0.4090 (7)
C(35)	0.7058 (14)	0.1060 (7)	0.6607 (7)	C(72)	1.1521 (11)	0.3795 (7)	0.3974 (7)
C(36)	0.7484 (14)	0.1628 (7)	0.6255 (7)	C(73)	1.2719 (11)	0.4156 (7)	0.3998 (7)
C(41)	0.9894 (14)	0.3534 (6)	0.6516 (7)	C(74)	1.3868 (11)	0.3751 (7)	0.4138 (7)
C(42)	1.0928 (14)	0.3137 (6)	0.6824 (7)	C(75)	1.3818 (11)	0.2983 (7)	0.4254 (7)
C(43)	1.2002 (14)	0.3521 (6)	0.7111 (7)	C(76)	1.2619 (11)	0.2621 (7)	0.4230 (7)
O(81)	0.5870 (32)	0.0081 (19)	0.3580 (16)	C(83)	0.4298 (32)	0.1309 (20)	0.3289 (16)
C(82)	0.5517 (31)	0.1057 (20)	0.3549 (18)				

Table V. Interatomic Distances (Å) with Esd's for [Os{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$]

Os–P(1)	2.296 (4)	C(2)–O(2)	1.149 (19)	P(2)–C(31)	1.829 (16)
Os–P(2)	2.344 (4)	P(1)–C(11)	1.810 (16)	P(2)–C(41)	1.838 (15)
Os–P(3)	2.346 (4)	P(1)–O(3)	1.517 (17)	P(3)–C(51)	1.831 (15)
Os–C(1)	1.901 (16)	O(3)–C(3)	1.486 (23)	P(3)–C(61)	1.821 (16)
Os–C(2)	1.908 (18)	P(2)–C(21)	1.813 (16)	P(3)–C(71)	1.835 (16)
C(1)–O(1)	1.156 (17)				

	i						
	1	2	3	4	5	6	7
C(*i*1)–C(*i*2)	1.36	1.41	1.38	1.38	1.38	1.39	1.39
C(*i*1)–C(*i*6)	1.41	1.38	1.37	1.38	1.40	1.38	1.37
C(*i*2)–C(*i*3)	1.37	1.39	1.44	1.42	1.38	1.38	1.37
C(*i*1)–C(*i*4)	1.35	1.37	1.34	1.30	1.35	1.33	1.35
C(*i*4)–C(*i*5)	1.32	1.37	1.41	1.38	1.41	1.36	1.32
C(*i*5)–C(*i*6)	1.39	1.40	1.40	1.41	1.38	1.43	1.47

(PH$_2$Ph)(CO)(PPh$_3$)$_2$ by using the conditions in Scheme I can be explained.

The *O*-methyl phenylphosphinite ligand in M{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$ (**5a,e**) is known to exist only in the coordination sphere of a metal.[31] As an unbound ligand it rearranges to methanol and cyclopolyphosphine (PhP)$_n$; coordination to a metal stabilizes this unusual ligand.[32] To further characterize this complex, a single-crystal X-ray diffraction study was performed.

Crystal Structure of Os{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$. As shown in Figure 2, the overall structure of Os{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$ (**5a**) is that of a distorted trigonal bipyramid. The osmium and phosphorus atoms are coplanar with the axial triphenylphosphine ligands bent away from the *O*-methyl phenylphosphinite ligand [P(2)–Os–P(3) = 170.7 (1)°]. All equatorial ligands have the metal-bound atom coplanar with the osmium. There is a large angle between the carbonyl ligands [C(1)–Os–C(2) = 133.5 (6)°]. With respect to each other the triphenylphosphine ligands are eclipsed, a feature shared with other[33] structurally characterized d^8 complexes. Experimental diffraction data is presented in Table I with final positional parameters listed in Table VII. Interatomic distances and angles appear in Tables V and VI, respectively.

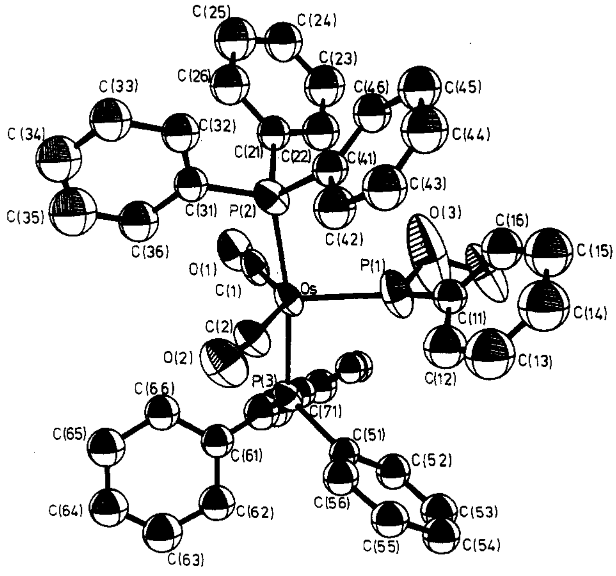

Figure 2. Structure of Os{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$.

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[31] Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1982**, *104*, 4484. Huttner, G.; Muller, H. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 571.

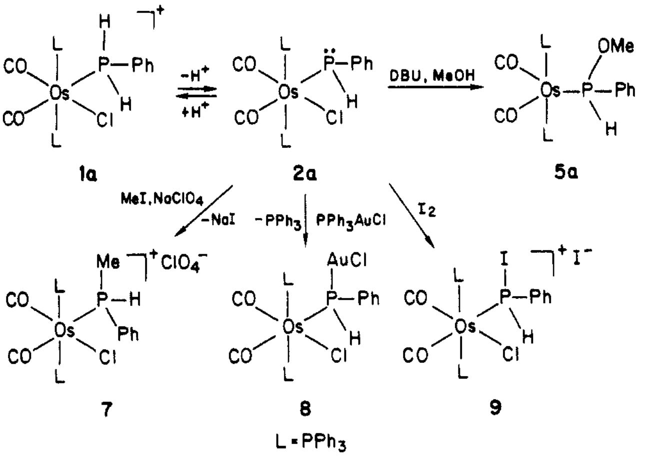
[32] Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

[33] For example, see: Field, J. S.; Wheatley, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2269. Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1771.

Table VI. Interatomic Angles (deg) with Esd's for $\{Os[PH(OMe)Ph](CO)_2(PPh_3)_2\}$

Angles around Osmium			
P(1)-Os-P(2)	95.6 (2)	P(2)-Os-C(1)	88.1 (5)
P(1)-Os-P(3)	93.7 (2)	P(2)-Os-C(2)	87.9 (6)
P(1)-Os-C(1)	114.4 (4)	P(3)-Os-C(1)	88.6 (5)
P(1)-Os-C(2)	112.2 (5)	P(3)-Os-C(2)	88.1 (6)
P(2)-Os-P(3)	170.7 (1)	C(1)-Os-C(2)	133.5 (6)
Angles Involving the Phenylmethoxyphosphine Ligand			
Os-P(1)-O(3)	120.5 (6)	C(12)-C(11)-C(16)	116.4 (1.6)
Os-P(1)-C(11)	124.1 (5)	C(11)-C(12)-C(13)	123.7 (1.8)
O(3)-P(1)-C(11)	107.7 (8)	C(12)-C(13)-C(14)	116.8 (2.0)
P(1)-O(3)-C(3)	124.1 (1.1)	C(13)-C(14)-C(15)	124.1 (2.2)
P(1)-C(11)-C(12)	121.2 (1.3)	C(14)-C(15)-C(16)	118.9 (2.0)
P(1)-C(11)-C(16)	122.4 (1.3)	C(15)-C(16)-C(11)	119.9 (1.7)
Angles Involving the Triphenylphosphine Ligands			
Os-P(2)-C(21)	116.8 (5)	Os-P(3)-C(51)	115.0 (5)
Os-P(2)-C(31)	115.2 (5)	Os-P(3)-C(61)	117.0 (5)
Os-P(2)-C(41)	115.9 (5)	Os-P(3)-C(71)	115.7 (5)

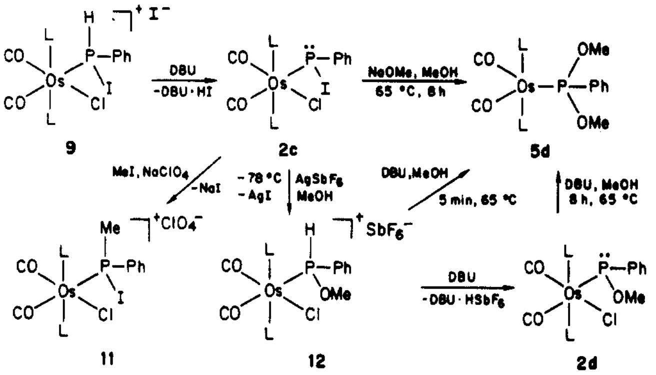
Scheme II



Bond lengths and angles for the *O*-methyl phenylphosphinite ligand are all close to the values [P–O = 1.59 ± 0.04 Å; O–C = 1.44 ± 0.04 Å; P–O–C = 120 ± 6°] found for dialkyl phenylphosphonites and alkyl diphenylphosphinites.[34] The large anisotropy associated with O(3) and C(3) in **5a** suggests that the methoxy substituent may be disordered. Thus interpretation of bond length and angles between these atoms is of limited significance. However, there is a significant reduction in the osmium–phosphorus bond length [Os–P(1) = 2.296 (4) Å] for the *O*-methyl phenylphosphinite ligand. This may result from its limited steric demands (estimated[35] cone angle, θ = 113°) and potential π-acidity.

Reactions of Terminal Phosphido Complexes. The deprotonation of cationic phosphine complexes **1a–e** is reversible as addition of perchloric acid to **2a**, for example, regenerates **1a**. Other electrophiles which react with the pyramidal PHPh ligand in **2a** are methyl iodide, (triphenylphosphine)gold(I) chloride, and iodine (Scheme II). Methylation of the phosphorus center in **2a** with methyl iodide leads to a cationic complex of the methylphenylphosphine ligand, **7**, which is isolated as the perchlorate salt.[36] A bridging phosphido complex[37] forms by displacement of the triphenylphosphorine ligand in (triphenylphosphine)gold(I) chloride by **2a** to give $Os\{PH(AuCl)Ph\}Cl(CO)_2(PPh_3)_2$ (**8**). Iodine adds to the phosphorus ligand in **2a** to give $[OsCl(PHIPh)(CO)_2(PPh_3)_2]I$ (**9**), a cationic complex of the unusual[31] phenyl phosphinous iodide ligand. An analogous reaction occurs between iodine and **4** which yields $[OsCl(PHIPh)(PH_2Ph)(CO)(PPh_3)_2]I$ (**10**) (eq 5). Slow, dropwise, addition of a

Scheme III



$$\underset{\mathbf{4}}{Os(PHPh)Cl(PH_2Ph)(CO)(PPh_3)_2} \xrightarrow[25\ ^\circ C,\ \text{benzene}]{I_2} \underset{\mathbf{10}}{[OsCl(PHIPh)(PH_2Ph)(CO)(PPh_3)_2]I} \quad (5)$$

stoichiometric amount of iodine to **2a** and **4a** prevents the formation of polyiodide anions in the products **9** and **10**, respectively. In related examples[20] treating terminal phosphido complexes with excess iodine results in the formation of polyiodide salts. Clearly, the reactions outlined in Scheme II illustrate the nucleophilic character of the pyramidal terminal phosphido ligand. Attempted dehydrochlorination of **2a** with *n*-butyllithium results in undetermined products which appear to have net alkyl substitution for the osmium-bound chloride.

In Scheme III the chemistry of the synthetically useful phenyliodophosphine complex **2c** is summarized. Deprotonation of **9** with DBU leads to $Os(PIPh)Cl(CO)_2(PPh_3)_2$ (**2c**), a reaction which is conveniently performed in situ after iodination of **2a** and without isolation of **9**. Thus this constitutes a one-pot process for the transformation of the PHPh ligand to the PIPh ligand. The nucleophilic character of the phenyliodophosphido ligand in **2c** is confirmed by its methylation with methyl iodide to give $[OsCl(PIMePh)(CO)_2(PPh_3)_2]ClO_4$ (**11**), isolated as the perchlorate salt. In keeping with the stabilization of the phosphorus iodide ligand in **9** toward rearrangement, the phosphorus iodide group is not very hydrolytically sensitive. Thus both **2c** and **11** can be recrystallized from alcohols with good return. To cleave the phosphorus–iodide bond, relative vigorous conditions are needed. For example, the substitution reaction of **2c** with methoxide is accompanied by reduction to give $Os\{P(OMe)_2Ph\}(CO)_2(PPh_3)_2$ (**5d**).

Silver(I) salts rapidly abstract iodide from **2c** at room temperature resulting in a mixture of products. At low temperatures the reaction is controlled to the extent that, at −78 °C, there is no reaction between methanol solutions of $AgSbF_6$ and THF suspensions of **2c**. When these mixtures are warmed, a successive series of distinct changes occurs. First a uniform yellow solution forms as **2c** completely dissolves in THF; then a flocculent precipitate of silver iodide from a colorless solution forms as the mixture reaches room temperature. The sole product isolated from the solution is $[OsCl\{PH(OMe)Ph\}(CO)_2(PPh_3)_2]SbF_6$ (**12**) (85% yield).

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(34) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974.

(35) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(36) For other examples of this reaction, see: Linder, E.; Starz, K. A.; Eberle, H. J.; Hiller, W. *Chem. Ber.* **1983**, *116*, 1209. Angerer, W.; Luksza, M.; Malisch, W. *J. Organomet. Chem.* **1983**, *253*, C36.

(37) For a related example, see: Schäfer, H. *Z. Anorg. Allg. Chem.* **1980**, *467*, 105.

Table VII. Atomic Positions for $[Os\{PH(OMe)Ph\}(CO)_2(PPh_3)_2]$

	x	y	z		x	y	z
Os	0.26926 (4)	0.22519 (4)	0.10412 (5)	C(1)	0.1287 (11)	0.2726 (11)	0.1387 (12)
P(1)	0.3768 (3)	0.3555 (3)	0.1045 (4)	O(1)	0.0428 (8)	0.2994 (8)	0.1591 (10)
P(2)	0.3077 (3)	0.2295 (3)	0.2975 (3)	C(2)	0.3413 (11)	0.0905 (11)	0.0679 (12)
P(3)	0.2143 (3)	0.1979 (3)	−0.0903 (3)	O(2)	0.3794 (9)	0.0070 (9)	0.0479 (11)
O(3)	0.3422 (11)	0.4692 (11)	0.1530 (20)	C(3)	0.3693 (18)	0.5567 (15)	0.1078 (21)
C(11)	0.5191 (11)	0.3436 (11)	0.1222 (12)	C(44)	0.6519 (14)	0.2776 (14)	0.4276 (15)
C(12)	0.5749 (14)	0.2621 (14)	0.0568 (14)	C(45)	0.5796 (14)	0.3509 (14)	0.4839 (15)
C(13)	0.6826 (17)	0.2498 (17)	0.0654 (17)	C(46)	0.4733 (12)	0.3387 (12)	0.4415 (13)
C(14)	0.7345 (17)	0.3264 (16)	0.1407 (17)	C(51)	0.3184 (10)	0.2010 (10)	−0.1828 (11)
C(15)	0.6881 (16)	0.4067 (16)	0.2104 (17)	C(52)	0.3243 (12)	0.2781 (12)	−0.2393 (13)
C(16)	0.5785 (14)	0.4189 (14)	0.2020 (14)	C(53)	0.4099 (13)	0.2795 (13)	−0.2995 (14)
C(21)	0.2302 (11)	0.3243 (12)	0.3983 (12)	C(54)	0.4922 (13)	0.2083 (13)	−0.3041 (14)
C(22)	0.2144 (14)	0.4279 (14)	0.3882 (15)	C(55)	0.4876 (13)	0.1288 (13)	−0.2482 (13)
C(23)	0.1587 (15)	0.5050 (15)	0.4654 (16)	C(56)	0.4020 (12)	0.1254 (12)	−0.1877 (13)
C(24)	0.1181 (15)	0.4795 (15)	0.5538 (16)	C(61)	0.1607 (11)	0.0727 (11)	−0.1619 (12)
C(25)	0.1281 (16)	0.3786 (16)	0.5648 (17)	C(62)	0.1530 (13)	0.0360 (13)	−0.2806 (14)
C(26)	0.1849 (14)	0.3020 (15)	0.4871 (15)	C(63)	0.1042 (15)	−0.0551 (15)	−0.3320 (15)
C(31)	0.2892 (11)	0.1082 (11)	0.3354 (12)	C(64)	0.0679 (14)	−0.1125 (14)	−0.2710 (15)
C(32)	0.3452 (12)	0.0858 (12)	0.4300 (13)	C(65)	0.0746 (14)	−0.0810 (14)	−0.1554 (14)
C(33)	0.3258 (13)	−0.0077 (13)	0.4621 (14)	C(66)	0.1222 (13)	0.0139 (13)	−0.0983 (13)
C(34)	0.2542 (15)	−0.0719 (15)	0.4011 (16)	C(71)	0.1113 (11)	0.2913 (11)	−0.1259 (12)
C(35)	0.1990 (16)	−0.0514 (16)	0.3028 (17)	C(72)	0.1273 (12)	0.3970 (12)	−0.0955 (12)
C(36)	0.2170 (14)	0.0401 (14)	0.2736 (14)	C(73)	0.0501 (12)	0.4661 (12)	−0.1223 (13)
C(41)	0.4443 (11)	0.2541 (11)	0.3538 (12)	C(74)	−0.0430 (14)	0.4354 (14)	−0.1770 (15)
C(42)	0.5227 (13)	0.1837 (13)	0.3034 (14)	C(75)	−0.0629 (17)	0.3359 (16)	−0.2074 (17)
C(43)	0.6299 (14)	0.1979 (14)	0.3435 (14)	C(76)	0.0168 (15)	0.2579 (14)	−0.1802 (15)

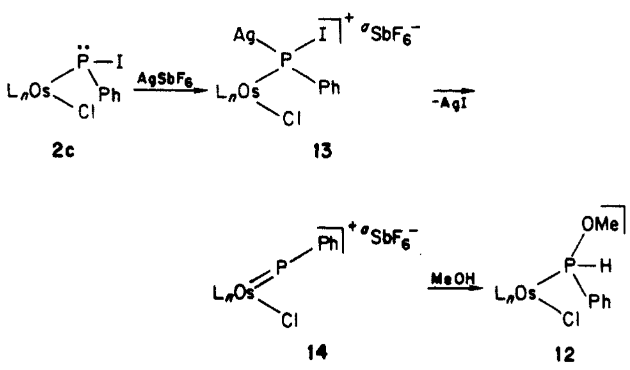
Table VIII. Spectroscopic Data for New Compounds[e]

	IR data,[a] cm^{-1}		
compd	ν(CO)	other bands	^{1}H NMR Data[b]
$Os(PHPh)Cl(CO)_2(PPh_3)_2$ (**2a**)	2018, 1953	ν(PH) 2264 (m); δ(PH) 905 (w); ν(OsCl) 283 (w)	3.70 (dt, 1 H, PH, $^1J_{PH}$ = 196 Hz, $^3J_{PH}$ = 14 Hz)
$Os(PPh_2)Cl(CO)_2(PPh_3)_2$ (**2b**)	2022, 1960	ν(OsCl) 292 (w)	
$Os(PIPh)Cl(CO)_2(PPh_3)_2$ (**2c**)	2024, 1969	ν(PI) 394 (w); ν(OsCl) 286 (w)	
$Os[P(OMe)Ph]Cl(CO)_2(PPh_3)_2$ (**2d**)	2020, 1960, [2041 (cs)]	$\nu(POCH_3)$ 1032 (s); ν(OsCl) 293 (m)	2.94 (d, 3 H, CH_3, $^3J_{PH}$ = 10.7 Hz)
$Ru(PHPh)Cl(CO)_2(PPh_3)_2$ (**2e**)	2026, 1971	ν(PH) 2270 (m); δ(PH) 903 (w); ν(RuCl) 282 (w)	2.79 (d, 1 H, PH, $^1J_{PH}$ = 116 Hz)
$Os(PHPh)Cl(PH_2Ph)(CO)(PPh_3)_2$ (**4**)	1937, [1892 (cs)]	ν(PH) 2329 (w), 2278 (w); δ(PH) 938 (m), 902 (m), 853 (w); ν(OsCl) 268 (w)	
$Os[PH(OMe)Ph](CO)_2(PPh_3)_2$ (**5a**)	1932 (w), 1904, 1847	ν(POMe) 1028 (m), 1012 (m);[c] ν(PH) 2262 (w), 2230 (w); δ(PH) 978 (m), 959 (m)[c]	7.57 (dt, 1 H, PH, $^1J_{PH}$ = 337 Hz, $^3J_{PH}$ = 8.9 Hz), 2.58 (d, CH_3, $^3J_{PH}$ = 12.2 Hz)
$Os[P(OMe)Ph_2](CO)_2(PPh_3)_2$ (**5b**)	1950 (w), 1896, 1841	ν(POMe) 1035 (s)	2.36 (d, 3 H, CH_3, $^3J_{PH}$ = 12.0 Hz)
$Os[P(OMe)_2Ph](CO)_2(PPh_3)_2$ (**5d**)	1918, 1852	ν(POMe) 1062 (m), 1011 (s)	2.34 (d, 6 H, CH_3, $^3H_{PH}$ = 12 Hz)
$Ru[PH(OMe)Ph](CO)_2(PPh_3)_2$ (**5c**)	1950 (w), 1912, 1857	ν(POMe) 1029 (m), 1013,[c] ν(PH) 2255 (w), 2223 (w); δ(PH) 975 (m), 948 (m)[c]	7.09 (dt, 1 H, PH, $^1J_{PH}$ = 339 Hz, $^3J_{PH}$ = 8 Hz), 2.1 (d, 3 H, CH_3, $^3J_{PH}$ = 12.6 Hz)
$[OsCl\{PHMePh\}(CO)_2(PPh_3)_2]ClO_4$ (**7**)	2056, 1995	δ(PH)[d] 932 (m), 913 (m); ν(OsCl) 304 (w)	6.37 (dm, 1 H, PH, $^1J_{PH}$ = 282 Hz), 1.46 (dd, 3 H, CH_3, $^2J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7 Hz)
$Os[PH(AuCl)Ph]Cl(CO)_2(PPh_3)_2$ (**8**)	2030, 1973	ν(PH) 2300 (w); δ(PH) 923 (w), 902 (m); ν(AuCl) 334 (m)	5.1–4.5 (ddd, 1 H, $^1J_{PH}$ = 300–250 Hz, $^3J_{PH}$ = 14 and 12 Hz)
$[OsCl(PHIPh)(CO)_2(PPh_3)_2]I$ (**9**)	2060, 1991	δ(PH) 921 (w), 896 (m), ν(OsCl) 307 (w)	5.81 (dt, 1 H, PH, $^1J_{PH}$ = 398 Hz, $^3J_{PH}$ = 7 Hz)
$[OsCl(PHIPh)(PH_2Ph)(CO)(PPh_3)_2]I$ (**10**)	1972	ν(PH) 2300 (br), δ(PH) 933 (m), 907 (s), 854 (w); ν(PI) 395 (m); ν(OsCl) 299 (w)	
$[OsCl(PIMePh)(CO)_2(PPh_3)_2]ClO_4$ (**11**)	2055, 1997	ρr(PMe) 894 (m); ν(PI) 378 (w); ν(OsCl) 302 (w)	2.71 (d, 3 H, CH_3, $^2J_{PH}$ = 8 Hz)
$[OsCl[PH(OMe)Ph](CO)_2(PPh_3)_2]SbF_6$ (**12**)	[2084 (cs)], 2065, [2013 (cs)], 1998	$\nu(POCH_3)$ 1020 (s); δ(PH) 903 (m); SbF_6 661 (s), 392 (s)	7.61 (dm, 1 H, PH, $^1J_{PH}$ = 402 Hz), 2.9 (d, 3 H, CH_3, $^3J_{PH}$ = 12 Hz)

[a] Carbonyl bands strong unless otherwise noted. [b] Chemical shift in ppm with respect to Me_4Si. Data in parentheses represent limiting range. Aromatic proton data not detailed. [c] Assignments tentative, possible combination of δ(PH) and $\nu(POCH_3)$ modes. [d] δ(PH) assignment tentative as combination with ρr(PCH_3) modes possible. [e] See footnotes *a* and *b* in Table I in the preceding paper.

Since the phenyliodophosphido complex **2c** is only sparingly soluble in THF at all temperatures, its dissolution in the presence of silver(I) suggests a possible association or coordination of the silver to the phosphorus lone pair to produce an intermediate **13** (Scheme IV). Intramolecular elimination of silver iodide from **13** would produce the cationic phosphinidene intermediate **14**. Insertion reactions of phosphinidene intermediates have been postulated[31] before in the synthesis of the *O*-methyl phenylphosphinite ligand. Likewise insertion of the phosphinidene **14** into the O–H bond in methanol would lead to **12**. However, attempts to trap **14** with alkynes and olefins fail to give tractable products. This might be due to the expected lability due to the large cone angle of expected

Scheme IV



ᵃnot isolated.

phosphirene[31] or phosphirane[38] ligands. Deprotonation of 12 results in Os{P(OMe)Ph}Cl(CO)$_2$(PPh$_3$)$_2$ (**2e**), which has been characterized spectroscopically (Table VIII). Reduction of **12** in basic methanol provides another method for the synthesis of **5d** with the *O,O*-dimethyl phenylphosphonite ligand.

Experimental Section

General procedures were described in the preceding paper. All of the reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques.

(Phenylphosphido)chlorodicarbonylbis(triphenylphosphine)osmium(II) (2a). [OsCl(PH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ (**1a**) (0.5 g, 0.49 mmol) was suspended in 25 mL of oxygen-free dried benzene. Addition of DBU (0.082 g, 0.081 mL, 0.54 mmol) caused complete instantaneous dissolution of the white suspension and formation of a light yellow solution. Occasionally a burgundy color momentarily appeared after addition of base but then faded within 5 min. After the solution was stirred for 45 min, light yellow crystals formed. The suspension was cooled in ice, and dry deoxygenated methanol (total ~ 70 mL) was added over the course of 15 min. Filtration followed by washes with methanol, ethanol, and hexane gave the light yellow product (0.39 g, 87%). For most uses no further purification was necessary. Analytical sample recrystallized from benzene/hexane in oxygen-free conditions; mp 156 °C (yellow cubes). Anal. Calcd for $C_{44}H_{36}ClO_2OsP_3\cdot{}^1/_4C_6H_{14}$: C, 58.32; H, 4.26. Found: C, 58.61; H, 4.00. ^{1}H NMR has multiplets at 1.02 and 0.63 ppm indicative of *n*-hexane.

(Phenyliodophosphido)chlorodicarbonylbis(triphenylphosphine)osmium(II) (2c). [OsCl(PHIPh)(CO)$_2$(PPh$_3$)$_2$]I (**10**) (0.32 g, 0.27 mmol) generated by reaction of Os(PHPh)Cl(CO)$_2$(PPh$_3$)$_2$ (**2a**) and iodine in situ as a suspension in benzene was treated with DBU (0.06 mL, 0.4 mmol). The thick, brown suspension instantly dissolved to produce an orange solution with a DBU·HI precipitate. After being stirred for 30 min, the solution was cooled in ice and dry methanol was added to effect dissolution of the DBU·HI and precipitation of the terminal phosphido complex. After addition of 90 mL of methanol, the bright orange-yellow crystals were filtered and washed with methanol, ethanol, and *n*-hexane in quick succession to give the product (0.20 g, 72%). Attempted recrystallization of this resulted in formation of an insoluble dichloromethane solvate as identified by ^{1}H NMR as a sharp singlet at 5.2 ppm (mp 132–133 °C; yellow prisms). Anal. Calcd for $C_{44}H_{35}ClIO_2OsP_3\cdot{}^1/_2CH_2Cl_2$: C, 49.32; H, 3.36. Found: C, 49.35; H, 3.89.

(*O*-Methyl phenylphosphinito)chlorodicarbonylbis(triphenylphosphine)osmium(II) (2d). [OsCl{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$]SbF$_6$ (**12**) (0.25 g, 0.21 mmol) was suspended in 10 mL of benzene, and DBU (0.05 mL) was added. Addition of the base resulted in dissolution of the white cation and concomitant production of a yellow solution with a precipitate of white oil. After 5 min of stirring, the reaction was allowed to stand and settle. A cannula was used to transfer the benzene solution to another flask under nitrogen. Care is needed not to pick up the DBU·HSbF$_6$ oil. After the benzene solution was cooled in an ice bath, addition of small portions of *n*-hexane caused crystallization of the crude yellow product which was filtered and washed in quick succession with hexane, methanol, ethanol, and then *n*-hexane. The product (0.14 g, 73%) was further recrystallized under nitrogen from benzene *n*-hexane for analytical sample, mp 135 °C.

(Phenylphosphido)chlorodicarbonylbis(triphenylphosphine)ruthenium(II) (2e). [RuCl(PH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ (**1e**) (0.51 g, 0.57 mmol) was suspended in 20 mL of dry deoxygenated benzene, and DBU (0.13 mL, 0.86 mmol) was added via syringe. A light yellow solution formed from the white suspension, and within 15 min yellow crystals of the terminal phosphido complex began to form. After 40 min the suspension was cooled and 100 mL methanol was added to crystallize the last trace of complex. Filtration followed by successive washes with methanol, ethanol, and *n*-hexane gave a faint yellow product (0.41 g, 88%), mp 120–122 °C. ^{1}H NMR: a singlet at 7.1 ppm indicative of benzene solvate. Anal. Calcd for $C_{44}H_{31}ClO_2P_3Ru\cdot C_6H_6$: C, 66.77; H, 4.16. Found: C, 66.33; H, 5.08.

(Phenylphosphido)chloro(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (4). [OsCl(PH$_2$Ph)$_2$(CO)(PPh$_3$)$_2$]ClO$_4$ (**3**) (0.34 g, 0.31 mmol) was suspended in 30 mL of benzene and DBU (0.07 g, 0.46 mmol) added via syringe. The white solid dissolved instantly, and within 5 min yellow crystals of product began to form. After 45 min of further stirring, the suspension was cooled and dried methanol (~80 mL) added. After 5 min the yellow crystals were filtered and washed successively with methanol, ethanol, and *n*-hexane. The light yellow crystals (0.39 g, 95%) can be recrystallized from CH$_2$Cl$_2$/EtOH; mp 151–152 °C (yellow cubes). ^{1}H NMR (δ 5.2 (s, 1 H)) indicates dichloromethane solvate. Anal. Calcd for $C_{49}H_{43}ClOOsP_4\cdot{}^1/_2CH_2Cl_2$: C, 57.13; H, 4.27. Found: C, 57.43; H, 4.86.

(*O*-Methyl phenylphosphinite)dicarbonylbis(triphenylphosphine)osmium(0) (5a). [OsCl(PH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ (**1a**) (0.4 g, 0.39 mmol) was suspended in 20 mL of methanol and the mixture warmed almost to reflux. DBU (0.12 g, 0.79 mmol) addition caused instant dissolution of the remaining undissolved cation producing a bright yellow solution in less than 1 min. From this solution crystals of product formed and further heating was discontinued. Gradual cooling to room temperature led to large yellow crystals which, after the Schlenk tube was cooled in an ice bath, were filtered and washed with methanol, then ethanol, and finally *n*-hexane. The analytical sample was further purified by recrystallization from benzene–methanol to give yellow crystals: mp 176 °C; 0.26 g, 73%. Anal. Calcd for $C_{45}H_{39}O_3OsP_3$: C, 59.33; H, 4.32. Found: C, 58.77; H, 4.66.

(*O*-Methyl diphenylphosphinite)dicarbonylbis(triphenylphosphine)osmium(0) (5b). [OsCl(PHPh$_2$)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ (**1b**) (0.5 g, 0.46 mmol) was dissolved in 20 mL of methanol and the mixture warmed to about 50 °C. DBU (0.174 g, 1.1 mmol, 2.5-mol excess) was added and the mixture gently heated for 30 min. Cooling the Schlenk tube in ice followed by filtration gave the product (0.32 g, 71%) after being washed with methanol, ethanol, and *n*-hexane. Attempts to recrystallize this complex from benzene-methanol resulted in contamination by oxygen adduct (Os(η^2-CO$_3$)(CO)(PPh$_3$)$_2$(Ph$_2$POMe)) as identified by band at 1680 cm^{-1} in IR; mp 179 °C (yellow rods). Anal. Calcd for $C_{51}H_{43}O_3OsP_3$: C, 62.05; H, 4.40. Found: C, 61.99; H, 4.79.

(*O,O*-Dimethyl phenylphosphonite)dicarbonylbis(triphenylphosphine)osmium(0) (5d). [OsCl{PH(OMe)Ph}(CO)$_2$(PPh$_3$)$_2$]SbF$_6$ (**12**) (0.15 g, 0.13 mmol) was suspended in methanol (10 mL), and DBU (0.05 mL, 0.32 mmol, 2.5-mol excess) was added to the warm solution. The remaining cation instantly dissolved, and a deep yellow solution produced. Once all residual solids were dissolved (~1 min), heating was discontinued and the reaction cooled in an ice bath. After 5 min bright yellow crystals of product had formed and further cooling (~30 min) led to a

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(38) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(39) Paine, R. T.; Hutchins, L. D.; Dubois, D. A.; Duesler, E. N. *Phosphorus Sulfur* **1983**, *18*, 263.

(40) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(41) Jörg, K.; Malisch, W.; Reich, W.; Meyer, U.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92.

colorless solution with copious yellow crystals. Filtration followed by consecutive washes with methanol, ethanol, and *n*-hexane to give the product (0.1 g, 94%). Analytical sample was further recrystallized from benzene–methanol; mp 168–171 °C (yellow needles). ^{1}H NMR has sharp spike at ~7.1 ppm due to benzene solvate. Anal. Calcd for $C_{46}H_{41}O_4OsP_3\cdot{}^1/_3C_6H_6$: C, 59.61; H, 4.49. Found: C, 59.35; H, 4.89.

(*O*-Methyl phenylphosphinite)dicarbonylbis(triphenylphosphine)ruthenium(0) (5e). $[RuCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**1e**) (0.25 g, 0.27 mmol) was dissolved in warm deoxygenated methanol (20 mL), and DBU (0.08 mL, 0.68 mmol, 2.5-fold excess) was added. From the initial yellow solution a very light precipitate formed which on further warming (5 min) was replaced by a deep yellow solid. Cooling the Schlenk tube in ice caused further crystallization of bright yellow solid which was then filtered and washed with methanol, then ethanol, and finally *n*-hexane. This product (0.17 g, 75%) was recrystallized from benzene–methanol for analysis; mp 147–148 °C (yellow prisms). Anal. Calcd for $C_{45}H_{39}O_3P_3Ru$: C, 65.77; H, 5.03. Found: C, 65.76; H, 4.79.

Chloro(phenylmethylphosphine)dicarbonylbis(triphenylphosphine)osmium(II) Perchlorate (7). $Os(PHPh)Cl(CO)_2(PPh_3)_2$ (**2a**) (0.3 g, 0.33 mmol) was dissolved in 15 mL of degassed CH_2Cl_2 under nitrogen. To this was added iodomethane (0.07 g, 0.031 mL 0.5 mmol) via syringe after which there was an instantaneous loss of the yellow starting material color. This solution was stirred for 5 min, and then an ethanol solution of sodium perchlorate (0.2 g in 50 mL of EtOH) was added and recrystallization commenced. Within 5 min large white crystals formed, and once the dichloromethane was completely removed, the crystals were filtered and washed with ethanol and then hexane. Further recrystallization from dichloromethane–2-propanol gave (0.27 g, 80%) of large white rhombohedrons, mp 181–182 °C. Anal. Calcd for $C_{45}H_{39}Cl_2O_6OsP_3$: C, 52.48; H, 3.82. Found: C, 52.41; H, 3.99.

Chlorodicarbonylbis(triphenylphosphine)(μ-phenylphosphido)(chlorogold)osmium(II) (8). $Os(PHPh)Cl(CO)_2(PPh_3)_2$ (**2a**) (0.1 g, 0.11 mmol) and $(PPh_3)AuCl$ (0.054 g, 0.11 mmol) were warmed together in 20 mL of benzene. On dissolving the yellow color disappeared and produced a uniform colored solution from which a white flocculent solid formed within 5 min. The suspension was cooled down to room temperature over 2 h after which the Schlenk tube was cooled in ice and 60 mL of *n*-hexane added. After the white product was filtered off and washed with *n*-hexane, the crude product was recrystallized from dichloromethane–ethanol to give large white prisms (0.11 g, 86%), mp 172 °C. Anal. Calcd for $C_{44}H_{36}AuCl_2O_2OsP_3$: C, 46.04; H, 3.17. Found: C, 46.27; H, 3.86.

Chloro(phenyliodophosphine)dicarbonyl)bis(triphenylphosphine)osmium(II) Iodide (9). $Os(PHPh)Cl(CO)_2(PPh_3)_2$ (**2a**) (0.25 g, 0.273 mL) was suspended in 20 mL of benzene. A benzene solution of iodine (3 mL of 0.092 M) was added dropwise via a cannula. During addition, that is, over the course of 15 min, the original light yellow suspension became dark brown, and toward the end of addition the iodine was added very slowly as precipitation of the product made mixing very inefficient. Upon completion of addition the thick suspension was stirred for a further 10 min. At this point the next step in the preparation of the phenyliodophosphido complex was carried out, or, to isolate **9**, filtration, followed by a wash with *n*-hexane, gave (0.24 g, 82%) of brown-orange crystals. These were further purified by recrystallization from dichloromethane–hexane; mp 105–107 °C (yellow rods). Anal. Calcd for $C_{44}H_{36}ClI_2O_2OsP_3$: C, 45.20, H, 3.10. Found: C, 45.24; H, 3.80.

Chloro(phenyliodophosphine)(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) Iodide (10). $Os(PHPh)Cl(PH_2Ph)(CO)(PPh_3)_2$ (**4**) (0.2 g, 0.2 mmol) was suspended in 20 mL of benzene. A benzene solution of iodine (1.6 mL of 0.125 M) was slowly added dropwise over the course of 20 min. After a subsequent 30-min period the orange-yellow suspension was cooled in an ice bath and *n*-hexane (~50 mL) added. The filtered orange product (0.18 g, 72%) was recrystallized from CH_2Cl_2/EtOH; mp 146–147 °C (yellow microprisms). Anal. Calcd for $C_{49}H_{43}ClI_2OOsP_4$: C, 47.03; H, 3.47. Found: C, 47.21; H, 4.10.

Chloro(phenylmethyliodophosphine)dicarbonylbis(triphenylphosphine)osmium(II) Perchlorate (11). $Os(PIPh)Cl(CO)_2(PPh_3)_2$ (**2c**) (0.2 g, 0.19 mmol) was suspended in 20 mL of dry CH_2Cl_2, and iodomethane (0.054 g, 0.024 mL, 0.38 mmol) was added via syringe. Over the course of 15 min the initial orange suspension gradually dissolved to produce a deep yellow solution. Sodium perchlorate (0.2 g) in 50 mL of 2-propanol was added to the dichloromethane solution and resulting mixture recrystallized quickly by removing the CH_2Cl_2 in vacuo. Further recrystallization from CH_2Cl_2–2-propanol gave yellow crystals (0.16 g, 74%), mp 122 °C. ^{1}H NMR has doublet at 1.2 ppm from 2-propanol solvate. Anal. Calcd for $C_{45}H_{38}Cl_2IO_6OsP_3\cdot{}^1/_2C_3H_7OH$: C, 47.10; H, 3.58. Found: C, 47.11; H, 3.76.

Chloro(*O*-methyl phenylphosphinite)dicarbonylbis(triphenylphosphine)osmium(II) Hexafluoroantimate (12). $Os(PIPh)Cl(CO)_2(PPh_3)_2$ (**2c**) (0.15 g, 0.14 mmol) was suspended in 15 mL of THF and cooled to −78 °C. Dropwise addition (via a cannula) of a methanol solution of $AgSbF_6$ (0.05 g, 0.14 mmol in 10 mL of MeOH) was then carried out over the course of 10 min causing no visible change in the suspension. Once addition was complete, the reaction was allowed to gradually warm to room temperature in the dark (by surrounding the Schlenk tube with Al foil). Upon warming, a sequence of changes occurred in the following order: the initial yellow-orange suspension dissolved almost completely to give a yellow solution within 10 min of initial warming; next a general cloudiness appeared in the yellow solution; finally, copious quantities of yellow-grey flocculent solid formed and the yellow solution gradually became colorless. After 2 h at room temperature the AgI was removed by filtration through a Celite pad and the residue washed thoroughly with CH_2Cl_2. From the filtrate a white residue was recovered by completely stripping off all solvents. Large white crystals of product (0.14 g, 85%) were obtained by recrystallization from dichloromethane–ethanol; mp 218–219 °C. Anal. Calcd for $C_{45}H_{39}ClF_6O_3OsP_3Sb$: C, 45.72; H, 3.83. Found: C, 45.56; H, 3.83.

Crystal Structure Determination. Data were collected on a CAD-4 diffractometer using a crystal of dimensions 0.32 × 0.24 × 0.10 mm for $[Os\{PH(OMe)Ph\}(CO)_2(PPh_3)_2]$ (**5a**). For $[Os(PHPh)Cl(CO)_2(PPh_3)_2]$EtOH (**2a**) rapid crystal decomposition in the X-ray beam necessitated the use of four crystals for the data collection. Overlapping shells of data were collected for each crystals and common reflections used to deduce initial scale factors between data; subsequently independent scale factors were refined for each crystal. Crystallographic details are given in Table I. For **2a** systematic absences determined the space group as $P2_1/n$, and $P\bar{1}$ was assumed for **5a** and verified by subsequent structure solution. The data were corrected for Lorentz and polarization effects and decomposition of **2a**. Absorption corrections were applied by the empirical ψ scan method.

The structures were solved by conventional Patterson and difference Fourier techniques, which determined the coordinates of all non-hydrogen atoms. Full-matrix least squares refinement with hydrogen atoms in calculated positions and anisotropic thermal parameters for all atoms except phenyl carbons converged to $R = 0.069$ ($R_w = 0.072$) for **2a** and $R = 0.059$ ($R_w = 0.064$) for **5a**. Final positional parameters are listed in Table IV and VII.

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Supplementary Material Available: Listings of observed and calculated structure factors, calculated positional parameters for hydrogen atoms, and thermal parameters (31 pages). Ordering information is given on any current masthead page.