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Synthetic Routes to Terminal Phosphido Complexes of Group VIII ($8^{\dagger}$) Metals: Neutral and Cationic Complexes of Phenyl- and Diphenylphosphine

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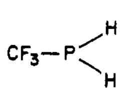
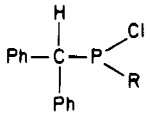
The phosphines PHRPh (R = H, Ph) have been introduced into $MHCl(CO)(PPh_3)_3$ to give $MHCl(PHRPh)(CO)(PPh_3)_2$ (M = Ru, Os). Hydride cleavage with $HClO_4$ in MeCN gives $[MCl(PHRPh)(CO)(MeCN)(PPh_3)_2]ClO_4$ and carbonylation of these salts produces $[MCl(PHRPh)(CO)_2(PPh_3)_2]ClO_4$. The reactions of $M(CO)_2(PPh_3)_3$ with PHRPh indicate that a simple substitution of PPh_3 is the predominant reaction and not oxidative addition of the P–H bond. In most cationic complexes of PHRPh rapid H/D exchange of the phosphorus-bound proton occurs in the presence of D_2O.

Introduction

Transition-metal–phosphorus multiple bonding has been the subject of sustained interest from the early hypothesis[1] of π-back-bonding to phosphine ligands in $L_nM—PR_3$ to the recent attempts[2-6] to synthesize a stable terminal phosphinidene complex, $L_nM═PR$. The least contentious examples of M–P multiple bonding are found in planar terminal phosphido ligands, L_nMPR_2, which have significantly shortened M–P bond lengths.[7-14] By analogy with the synthesis of phosphaalkenes,[15] $RP═CR'_2$, via dehydrohalogenation of species such as A or B, a feasible, but as yet unreported, synthetic approach to a terminal phosphinidene complex is by abstraction of HCl from terminal phosphido complexes such as C or D. However, as complexes like C and D are unusual,[16] a general synthetic route to these species was first needed.



A



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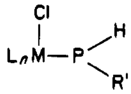
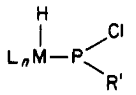


C

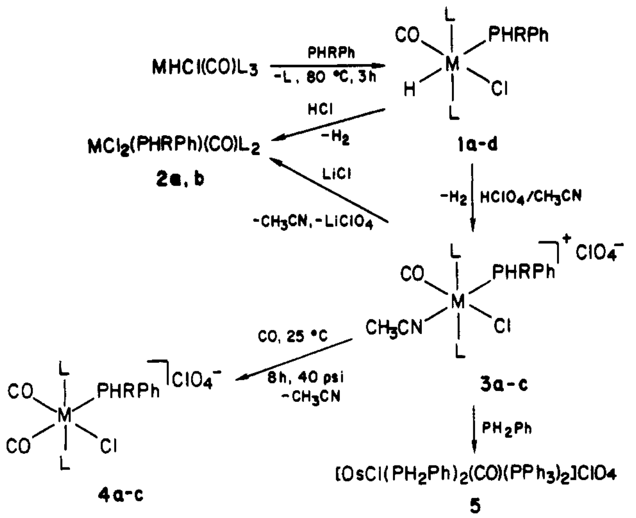


D

R = mesityl

Complexes of primary phosphines and dihalophosphines are potential precursors for C and D, respectively. But while complexes of RPH_2 and $RPCl_2$ are known for many transition metals,[17,18] there is only a single example of the synthesis of a planar phenylphosphido complex like C from a phenylphosphine complex.[10] In this paper a general three-step synthesis of cationic phosphine complexes of Ru(II) and Os(II) is described as are attempts to prepare compounds analogous to D by oxidative addition of P–H bonds to coordinatively unsaturated d^8 species. As detailed in the following paper these cationic phosphine complexes are precursors for species such as C. A preliminary report of some of these results has appeared.[14]

Scheme I



a, M = Os, R = H; b, M = Os, R = Ph; c, M = Ru, R = H; d, M = Ru, R = Ph; L = PPh_3

Results and Discussion

The synthesis of $[MCl(PHRPh)(CO)_2(PPh_3)_2]ClO_4$ (M = Os, R = H, Ph; M = Ru, R = H) (**4a–c**) is outlined in Scheme I. A labile triphenylphosphine ligand in

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[†] 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.)

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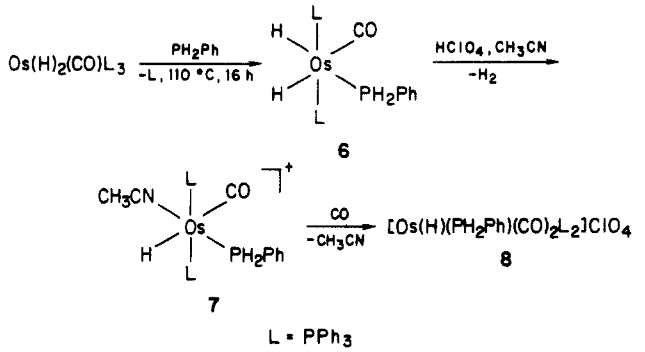
Scheme II



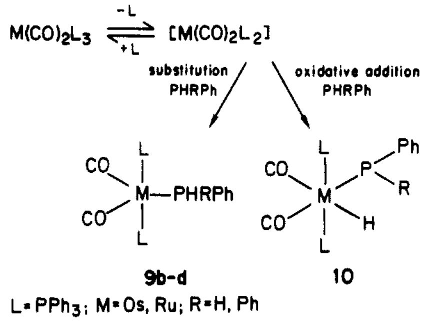
$MHCl(CO)(PPh_3)_3$ (M = Ru, Os) is completely exchanged for more compact phosphines such as phenyl- and diphenylphosphine. Steric effects dominate such exchange reactions[19,20] influencing the lability of the phosphine ligands. Isolated as white, air-stable solids, $MHCl(PHRPh)(CO)(PPh_3)_2$ (M = Os, Ru; R = H, Ph) (**1a–d**) have spectroscopic characteristics which imply the depicted geometry, which is also that found for the structurally characterized $OsHBr(CO)(PPh_3)_3$.[21] Thus these compounds have two mutually trans triphenylphosphine ligands with the third introduced phosphine trans to the hydride ligand.

Cationic complexes **3a–c** are derived from **1a–c** by cleavage of the metal–hydride bond with perchloric acid in the presence of acetonitrile. While other acids such as HBF_4 or $HSbF_6$ can be used instead of perchloric acid, the chemistry of the perchlorate salts was studied because these compounds were found to crystallize more easily than the salts of any other anion. A dihalide complex, $OsCl_2(PHRPh)(CO)(PPh_3)_2$ (R = H, Ph) (**2a–b**), is obtained when hydrochloric is used instead of perchloric acid. Alternatively, **2a,b** are also obtained by addition of lithium chloride to **3a,b**. As indicated by the $\nu(CO)$ and $\nu(OsCl)$ data in Table I, **2a,b** are prepared as a mixture of cis and trans isomers by *both* methods.

Neutral donors such as carbon monoxide and phenylphosphine can be substituted for the labile acetonitrile in **3a–c**. Prolonged carbonylation under mild conditions give $[MCl(PHRPh)(CO)_2(PPh_3)_2]ClO_4$ (M = Os, R = H, Ph; M = Ru, R = H) (**4a–c**) which is assigned a cis CO geometry on the basis of the $\nu(CO)$ data presented in Table I. Vigorous conditions (62 °C, 24 h) are required to substitute phenylphosphine for acetonitrile to give $[OsCl(PH_2Ph)_2(CO)(PPh_3)_2]ClO_4$ (**5**) which is assumed to be a single isomer (only one $\nu(CO)$ at 1978 cm^{-1}) of undetermined geometry.

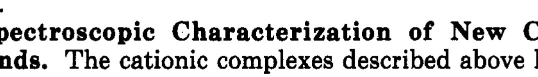
Substitution of the labile triphenylphosphine in $OsH_2(CO)(PPh_3)_3$ by phenylphosphine under forcing conditions leads to $OsH_2(PH_2Ph)(CO)(PPh_3)_2$ (**6**) (Scheme II). Cleavage of a single osmium–hydride ligand in **6** with perchloric acid in the presence of CH_3CN yields $[OsH(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**7**) which is assigned a cis arrangement of hydride and phenylphosphine ligands based on the magnitude[20,22] of the $^2J_{HP}$ data in Table I. Although excess perchloric acid is used in the preparation of **7**, cleavage of the second hydride ligands does not occur. Carbonylation of **7** requires higher temperatures than for the chloride analogue **3a** but leads to an isomeric mixture of *cis*- and *trans*-$[OsH(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**8**). Prolonged heating during carbonylation results in the formation of the cis isomer of **8**.

Scheme III



Zerovalent Complexes of Phenyl- and Diphenylphosphine. As oxidative addition of phosphine to d^8 Ir(I) species has been suggested[23] to give the terminal phosphido complex $[Ir(PH_2)(H)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$), the reactions of PHRPh (R = H, Ph) with $M(CO)_2(PPh_3)_3$ (M = Ru, Os) were investigated. Either simple subsitution of a phosphine ligand, to give the zerovalent compounds **9b–d**, or oxidative addition of the P–H bond, to give the terminal phosphido complex **10**, are possible reactions. These are depicted in Scheme III. With $Ru(CO)_2(PPh_3)_3$, phenylphosphine and diphenylphosphine substitute to give $Ru(PHRPh)(CO)_2(PPh_3)_2$ (**9c,d**). Likewise, diphenylphosphine substitutes for a triphenylphosphine ligand in $Os(CO)_2(PPh_3)_3$ to give $Os(PHPh_2)(CO)_2(PPh_3)_2$ (**9b**). But phenylphosphine reacts rapidly with $Os(CO)_2(PPh_3)_3$ to give $OsH_2(CO)_2(PPh_3)_2$ and not the expected phenylphosphido complex **10**. It is not clear what the fate of the phenylphosphinidene fragment is or what is the mechanism of this reaction. Spectral data in Table I for **9a–d** is consistent with a TBP geometry as in the structurally characterized[14] $Os\{PH(OCH_3)Ph\}(CO)_2(PPh_3)_2$.

Cationic complexes analogous to **4** can be prepared from **9a–c** by oxidation of the metal center with suitable electrophiles. For example, perchloric acid protonates **9a** to give *trans*-$[RuH(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**11**) (eq 1).



(1)

9c 11

Reaction with the base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) removes the proton bonded to ruthenium, not phosporus, thereby regenerating **9c**. Thus **11** is not a precursor in the synthesis of a terminal phosphido complex.

Spectroscopic Characterization of New Compounds. The cationic complexes described above have labile phosphorus-bound protons which exchange readily with D^+. For example, when $[OsCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**4a**) as a solution in $CDCl_3$ is treated with D_2O, the ^1H NMR signal of the phosphine-bound protons disappears completely in 3 h. Deuterium-exchanged samples can be isolated by recrystallization with aprotic solvents, e.g., CH_2Cl_2/CCl_4, permitting observation of shifts in the phosphine deformation band, $\delta(PH)$ or $\delta(PD)$, from 906 to 643 cm^{-1} in **4a**. However, the neutral phenylphosphine complexes **1a,c**, **2a**, and **9c** do not exhibit deuterium exchange under similar conditions. That charge is not the sole criterion for the lability of phosphorus-

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Table I. Spectral Data for Ruthenium and Osmium Complexes of PHRPh (R = H, Ph)

compd	IR data,[a] cm^{-1}				^{1}H NMR data[b]
	ν(CO)	ν(PH)	δ(PH)	other bands	
$OsHCl(PH_2Ph)(CO)(PPh_3)_2$ (**1a**)	1930, [1898 (cs)], [1887 (cs)]	2340 (w), 2321 (m)	926 (s), 899 (s)	ν(OsH) 1976 (s), [1996 (cs)]; δ(OsH) 790 (m); ν(OsCl) 283 (w)	4.5–4.9 (dt, 2 H, PH_2, $^1J_{PH}$ = 301–336 Hz, $^3J_{PH}$ = 4.5 Hz), –5.07 (dt, 1 H, OsH, $^2J_{Hptrans}$ = 95.8 Hz, $^2J_{HPcis}$ = 19.5 Hz)
$OsHCl(PHPh_2)(CO)(PPh_3)_2$ (**1b**)	1933, [1897 (cs)], [1884 (cs)]	2307 (m)	939 (m), 926 (m), 913 (s)	ν(OsH) 2008; δ(OsH) 806 w; ν(OsCl) 281 (w)	6.08 (dt, 1 H, PH, $^1J_{PH}$ = 347.8 Hz, $^3J_{PH}$ = 5 Hz), –4.84 (dt, 1 H, OsH, $^2J_{HPtrans}$ = 88 Hz, $^2J_{HPcis}$ = 20.5 Hz)
$RuHCl(PH_2Ph)(CO)(PPh_3)_2$ (**1c**)	1942	2343 (w), 2321 (w)	919 (m), 886 (s)	ν(RuH) 1907 (s); δ(RuH) 786 (w); ν(RuCl) 285 (w)	4.3–4.8 (dt, 2 H, PH_2, $^1J_{PH}$ = 292–341 Hz, $^3J_{PH}$ = 5 Hz), –5.2 (dt, 1 H, RuH, $^2J_{HPtrans}$ = 119 Hz, $^2J_{HPcis}$ = 20 Hz)
$RuHCl(PHPh_2)(CO)(PPh_3)_2$ (**1d**)	1954 (br)	2311 (w)	908 (m), 896 (m)	ν(RuH) 1901 (m); δ(RuH) 793 (w); ν(RuCl) 280 (w)	6.00 (dt, 1 H, PH, $^1J_{PH}$ = 331 Hz, $^3J_{PH}$ = 5.5 Hz), –6.02 (dt, 1 H, RuH, $^2J_{HPtrans}$ = 110 Hz, $^2J_{HPcis}$ = 20.5 Hz)
cis- and *trans*-$OsCl_2(PH_2Ph)(CO)(PPh_3)_2$ (**2a**)	1970 (s), 1905 (m)	2347 (w), 2315 (m)	927 (s), 918 (s)	ν(OsCl) 351 (w), 307 (m), 268 (m)	*c*
cis- and *trans*-$OsCl_2(PHPh_2)(CO)(PPh_3)_2$ (**2b**)	1969, 1924, [1900 (cs)]	2312 (w)	956 (s), 947 (s), 917 (w), 898 (s)	ν(OsCl) 302 (m), 270 (m)	6.96 (dt, 1 H, PH, $^1J_{PH}$ = 385 Hz, $^3J_{PH}$ = 7 Hz)
$[OsCl(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3a**)	1969 (br)		943 (m), 917 (m)	ν(OsCl) 292 (w)	5.56 (dt, 2 H, PH_2, $^1J_{PH}$ = 388 Hz, $^3J_{PH}$ = 5 Hz), 1.75 (d, 3 H, CH_3, J_{PH} = 18 Hz)
$[OsCl(PHPh_2)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3b**)	1954 (br)		931 (br)	ν(OsCl) 299 (w)	6.74 (dt, 1 H, PH, $^1J_{PH}$ = 386 Hz, $^3J_{PH}$ = 7 Hz), 1.52 (s, 3 H, CH_3)
$[RuCl(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3c**)	1986 (br)		934 (s), 912 (s)	ν(RuCl) 301 (w)	5.37 (dt, 2 H, PH_2, $^1J_{PH}$ = 387 Hz, $^3J_{PH}$ = 6 Hz), 1.92 (d, 3 H, CH_3, J_{PH} = 11 Hz)
$[OsCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**4a**)	2032, 1996		934 (w), 906 (m)	ν(OsCl) 305 (m)	5.54 (dt, 2 H, PH_2, $^1J_{HP}$ = 399 Hz, $^3J_{HP}$ = 7.6 Hz)
$[OsCl(PHPh_2)(CO)_2(PPh_3)_2]ClO_4$ (**4b**)	2062 (IR, RA), 2000 (IR, RA)		934 (m), 879 (w)	ν(OsCl) 309 (m)	6.87 (dt, 1 H, PH, $^1J_{HP}$ = 392 Hz, $^3J_{HP}$ = 8.5 Hz)
$[RuCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**4c**)	2034, 2008		927 (w), 892 (m)		5.41 (dt, 2 H, PH_2, $^1J_{HP}$ = 388 Hz, $^3J_{HP}$ = 7.3 Hz)
$[OsCl(PH_2Ph)_2(CO)(PPh_3)_2]ClO_4$ (**5**)	1978	2373 (br)	931 (m), 902 (s), 844 (m)	ν(OsCl) 310 (m)	6.01 (m, 4 H, PH_2, $^1J_{HP}$ = 386 Hz, $^3J_{HP}$ = 6.4 Hz)
$Os(H)_2(PH_2Ph)(CO)(PPh_3)_2$ (**6**)	1971 (br)	2318 (m), 2310 (m)	923 (s)	ν(OsH) 1994 (m), 1873 (s); δ(OsH) 825 (m)8 786 (w)	4.4–4.8 (dtd, 2 H, PH_2, $^1J_{PH}$ = 292–342 Hz, $^3J_{PH}$ = 6.1 Hz, $^3J_{HH}$ = 3.06 Hz), –8.4 (m, 2 H, $Os(H)_2$)
$[OsH(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**7**)	1927		932 (w), 906 (m)	ν(OsH) 1954	5.13 (dt, 2 H, PH_2, $^1J_{PH}$ = 361 Hz, $^3J_{PH}$ = 7.5 Hz), –14.6 (dt, 1 H, OsH, $^2J_{H(PPhH_2)}$ = 25 Hz, $^2J_{H(PPh_3)}$ = 12 Hz, 2.01 (s, 3 H, CH_3)
$[OsH(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**8**)	2031, 2013		923 (m), 909 (s)	ν(OsH) 1977; δ(OsH) 813	5.34 (dtd, 2 H, Ph_2, $^1J_{HP}$ = 395 Hz, $^3J_{HP}$ = 9.1 Hz, $^3J_{HH}$ = 3 Hz), –7.0 (dtd, 1 H, OsH, $^2J_{HP(PhPH_2)}$ = 28 Hz, $^2J_{HP(Ph_3P)}$ = 15 Hz, $^3J_{HH}$ = 3 Hz)
$Os(PHPh_2)(CO)_2(PPh_3)_2$ (**9b**)	1903, 1848	2299w	932 (m), 911 (m)		7.3[d] (dt, 1 H, PH, $^1J_{PH}$ = 336 Hz, $^3J_{PH}$ = 12.7 Hz)
$Ru(PH_2Ph)(CO)_2(PPh_3)_2$ (**9c**)	1942 (m), 1914, 1854	2283 (w) (IR, RA)	875 (s) (IR, RA)		3.6–4.4[d] (dt, 2 H, PH_2, $^1J_{PH}$ = 232–325 Hz, $^3J_{PH}$ = 7 Hz)
$Ru(PHPh_2)(CO)_2(PPh_3)_2$ (**9d**)	1952 (m), 1908, 1857	2294 (w)	933 (w), 922 (w), 900 (w)		6.0[d] (dt, 1 H, PH, $^1J_{PH}$ = 315 Hz, $^3J_{PH}$ = 9 Hz)
trans-$[RuH(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**11**)	2005		924 (w), 891 (s)	ν(RuH) 2044	5.27 (dt, 2 H, PH_2, $^1J_{HP}$ = 354 Hz, $^3J_{HP}$ = 5 Hz), –6.88 (dt, 1 H, RuH, $^2J_{HPtrans}$ = 62 Hz, $^2J_{HPcis}$ = 15.4 Hz)

[a] All spectra recorded as Nujol mulls. Carbonyl (ν(CO)) bands are all strong and sharp unless otherwise noted; bracketed absorptions with (cs) denotes solid-state splitting as determined by comparison with CH_2Cl_2 solution spectra. Other notations include the following: s, strong; m, medium; w, weak; br, broad; IR, infrared absorption; RA, Raman scattering peak. [b] All chemical shifts report as δ relative to internal tetramethylsilane (δ 0.0). $CDCl_3$ used as solvent unless otherwise noted. Chemical shifts that are bracketed represent range of possible values. These cases correspond to samples where aromatic protons obscure sections of the phosphine resonance. [c] Too insoluble for ^{1}H NMR spectrum to be measured. [d] Freeze-degassed C_6D_6 used as solvent.

bound protons is demonstrated by *trans*-[RuH(PH_2Ph)$(CO)_2$$(PPh_3)_2$]$ClO_4$ (**11**) which does not exchange D^+ under similar conditions.

The intensity of ν(PH) for the complexes in Table I also is a function of charge. In the neutral complexes **1a–d**, **2a,b**, **6**, and **9b–d** ν(PH) is a sharp absorption of medium to weak intensity. However, in cationic complexes **3a–c**, **4a–c**, **7**, **8**, and **11** the ν(PH) region of the spectrum (~2300 cm^{-1}) is featureless, but the δ(PH) band is present. Thus, the intensity of ν(PH) band is useful empirical diagnostic feature for the charge of a phosphine complex in this series of compounds.

Experimental Section

Standard Schlenk techniques were used for the manipulation of phenylphosphine, diphenylphosphine, and phosphido complexes of ruthenium and osmium. However, the derived cations from these complexes are air-stable and can be handled in the open.

Benzene, THF, hexane, and toluene were all distilled from sodium–benzophenone under an atmosphere of nitrogen prior to use. Methanol was distilled from alkaline pyrogallol under nitrogen for work with zerovalent compounds and terminal phosphido species. Dichloromethane, hexane, and cyclohexane for non air-sensitive recrystallizations were passed through a 10-cm column of activated alumina prior to use. Ethanol, methanol, and 2-propanol were filtered before use in recrystallization. For use with zerovalent complexes benzene was subjected to two freeze–thaw cycles beforehand. Diphenylphosphine[24] and phenylphosphine[25] were prepared by literature methods and used as dilute (~3 M) solutions in benzene.

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film. All spectra were recorded as Nujol mulls between KBr plates or as a dichloromethane solution in KBr solution cells. Far-infrared spectra (400–200 cm^{-1}) were recorded as concentrated Nujol mulls between CsI plates. ^1H NMR spectra were recorded on Varian Associates E.M. 360L or T-60 spectrometer or a JEOL FX-60 Fourier transform spectrometer. Air-sensitive solutions were prepared and sealed under a nitrogen atmosphere by using a cannula to transfer the solution to the microcell or NMR sample tube. Tetramethylsilane was used as an internal reference. Melting points were determined on a Reichert microscope hot stage and are uncorrected.

Elemental analyses for hydrogen, carbon, and nitrogen were performed by Professor A. D. Campbell and associates of the University of Otago and are gratefully acknowledged.

Hydridochloro(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (1a). $OsHCl(CO)(PPh_3)_3$[26] (0.5 g, 0.48 mmol) was suspended in 30 mL of deoxygenated benzene. Phenylphosphine (0.2 mL of 3 M benzene solution) was syringed in and the suspension gradually warmed to reflux. Within 30 min of heating a colorless uniform solution resulted. After an additional 2.5 h at reflux, the solution was cooled, and white crystals of product formed. All volatiles were removed in vacuo, and the white residue was taken up in dichloromethane. White crystals of the product (0.41 g, 95%) were obtained by recrystallization with ethanol; mp 181–182 °C (white rods). Anal. Calcd for $C_{43}H_{38}ClOOsP_3$: C, 58.07; H, 4.31. Found: C, 57.98; H, 4.05.

Hydridochloro(diphenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (1b). Same procedure as for **1a** was used, with diphenylphosphine (1.73 mL of 0.5 M benzene solution, 0.86 mmol) used in place of phenylphosphine. Yield from 0.75 g (0.72 mmol) of $OsHCl(CO)(PPh_3)_3$ is 0.65 g (94%). ^1H NMR indicates 1:1 dichloromethane solvate, mp 170–171 °C. Anal. Calcd for $C_{49}H_{42}ClOOsP_3{\cdot}CH_2Cl_2$: C, 57.17; H, 4.23. Found: C, 57.25; H, 4.73.

Hydridochloro(phenylphosphine)carbonylbis(triphenylphosphine)ruthenium(II) (1c). $RuHCl(CO)(PPh_3)_3$[26] (1 g, 1.05 mmol) was suspended in 40 mL of oxygen-free benzene, and to this was added phenylphosphine (0,53 mL of 3 M benzene solution, 1.6 mmol) via syringe. This solution was brought to a very gentle reflux during which time all starting material dissolved to produce a yellow solution. After being refluxed (3–4 h), the solution was cooled and all volatiles were removed in vacuo. The off-white residue was dissolved in dichloromethane and large white crystals obtained by recrystallization with ethanol (0.78 g, 93%); mp 163–165 °C (prisms). Anal. Calcd for $C_{43}H_{38}ClOP_3Ru$: C, 64.52; H, 4.80. Found: C, 64.21; H, 4.60.

Hydridochloro(diphenylphosphine)carbonylbis(triphenylphosphine)ruthenium(II) (1d). $RuHCl(CO)(PPh_3)_3$ (0.25 g, 0.26 mmol) was suspended in 30 mL of deoxygenated benzene. Diphenylphosphine (0.8 mL of 0.5 M benzene solution, 0.39 mmol) was added via syringe and the resulting solution stirred at room temperature (4 h). Brief (15 min) gentle heat caused dissolution of remaining solid affording a uniform light yellow solution. All volatiles were removed in vacuo, and the white residue was taken up in dichloromethane and large white crystals of the product (0.2 g, 88%) were obtained by recrystallization with ethanol; mp 115–116 °C (white prisms). ^1H NMR ($CDCl_2CDCl_2$) indicated dichloromethane solvate (5.2 ppm (s, 2 H)). Anal. Calcd for $C_{49}H_{42}ClOP_3Ru{\cdot}CH_2Cl_2$: C, 62.47; H, 4.62. Found: C, 62.35; H, 5.08.

***cis*- and *trans*-Dichloro(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (2a).** $OsHCl(PH_2Ph)(CO)(PPh_3)_2$ (**1a**) (0.11 g, 0.12 mmol) was dissolved in 30 mL of benzene and 10 mL of saturated ethanolic HCl added. This mixture was heated under reflux (6 h) and the light yellow solution cooled. After all solvents were stripped off, the sample was recrystallized from dichloromethane–ethanol to yield white chunky crystals (0.93 g, 84%), mp 232–233 °C (white cubes). Anal. Calcd for $C_{43}H_{37}Cl_2OOsP_3$: C, 55.90; H, 4.05. Found: C, 55.63; H, 4.38.

***cis*- and *trans*-Dichloro(diphenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (2b).** [$OsCl(PHPh_2)(CH_3CN)(CO)(PPh_3)_2$]$ClO_4$ (**3b**) (0.25 g, 0.23 mmol) was dissolved in a minimum of dichloromethane (~5 mL). To this solution was added a solution of LiCl (0.1 g, 2.3 mmol) in 10 mL of ethanol. Immediately following addition, a white precipitate slowly formed. After 2 h at room temperature, the dichloromethane was stripped off and the white crystals were filtered. Further recrystallization from dichloromethane–ethanol gave large white crystals of product (0.212 g, 92%), mp 214–215 °C (white cubes). Anal. Calcd for $C_{49}H_{41}Cl_2OOsP_3$: C, 58.85; H, 4.14. Found: C, 59.11; H, 5.00.

Chloro(phenylphosphine)(acetonitrile)carbonylbis(triphenylphosphine)osmium(II) Perchlorate (3a). $OsHCl(PH_2Ph)(CO)(PPh_3)_2$ (**1a**) (0.37 g, 0.42 mmol) was dissolved in 25 mL of dichloromethane, and a solution of 0.25 mL of perchloric acid in 15 mL acetonitrile was added. Within 10 min hydrogen evolution had virtually ceased, and the colorless solution was stirred for an additional 2.5 h. Solvent was then completely stripped off and the oily colorless residue taken up in dichloromethane. The flocculent white product (0.39 g, 91%) was recrystallized with 2-propanol; mp 156–158 °C (white rods). Anal. Calcd for $C_{45}H_{40}Cl_2NO_5OsP_3$: C, 52.52; H, 4.13. Found: C, 52.47; H, 4.30.

Chloro(diphenylphosphine)(acetonitrile)carbonylbis(triphenylphosphine)osmium(II) Perchlorate (3b). $OsHCl(PHPh_2)(CO)(PPh_3)_2$ (**1b**) (0.5 g, 0.52 mmol) was treated with the same procedure as **3a** to give large white crystals (0.46 g, 82%) after recrystallization from dichloromethane–ethanol; mp 133–135 °C (needles). Anal. Calcd for $C_{51}H_{44}Cl_2NOOsP_3$: C, 55.43; H, 4.02; N, 1.27. Found: C, 55.97; H, 4.64; N, 1.25.

Chloro(phenylphosphine)(acetonitrile)carbonylbis(triphenylphosphine)ruthenium(II) Perchlorate (3c). $RuHCl(PH_2Ph)(CO)(PPh_3)_2$ (**1c**) (0.5 g, 0.57 mmol) was dissolved in 30 mL of dichloromethane, and to this solution was slowly added a solution of 0.25 mL of perchloric acid in 20 mL of acetonitrile. Vigorous hydrogen gas evolution ceased within 5 min of addition of the acid solution. After an additional 30 min the colorless solution was stripped of all solvents. The oily residue was taken up in dichloromethane and the flocculent white product (0.49 g, 91%) recrystallized with dichloromethane–2-propanol; mp 141 °C (white cubes). Anal. Calcd for $C_{45}H_{40}Cl_2NO_5P_3Ru$: C, 57.51; H, 4.30; N, 1.49. Found: C, 57.35; H, 4.83; N, 1.34.

Chloro(phenylphosphine)dicarbonylbis(triphenylphosphine)osmium(II) Perchlorate (4a). [$OsCl(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2$]$ClO_4$ (**3a**) (0.39 g, 0.38 mmol) was dissolved

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in 30 mL of dichloromethane and this solution carbonylated (40 psi, 8 h, 25 °C). The resulting solution was transferred to a round-botton flask, and the white flocculent product (0.36 g, 94%) was recrystallized from dichloromethane–2-propanol; mp 141–143 °C (white needles). Anal. Calcd for $C_{44}H_{37}Cl_2O_6OsP_3$: C, 52.71; H, 3.90. Found: C, 52.45; H, 4.45.

Chloro(diphenylphosphine)dicarbonylbis(triphenylphosphine)osmium(II) Perchlorate (4b). $[OsCl(PHPh_2)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3b**) (0.47 g, 0.43 mmol) was carbonylated as described for **4a**. After recrystallization from cyclohexane–ethanol, the yield is 0.42 g (90%) of white prisms, mp 138–140 °C. ^{1}H NMR indicated cyclohexane solvate (δ 1.43 (s, 3 H)). Anal. Calcd for $C_{50}H_{41}Cl_2O_6OsP_3\cdot{}^1/_4C_6H_{12}$: C, 55.57; H, 3.99. Found: C, 55.56; H, 4.30.

Chloro(phenylphosphine)dicarbonylbis(triphenylphosphine)ruthenium(II) Perchlorate (4c). $[RuCl(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3c**) (2.85 g, 3.0 mmol) was dissolved in 30 mL of dichloromethane and carbonylated (40 psi, 14 h, 25 °C). The snow-white flocculent product (2.1 g, 94%) was obtained by recrystallization of the above with dichloromethane–2-propanol; mp 138 °C (white cubes). Anal. Calcd for $C_{44}H_{37}Cl_2O_6P_3Ru$: C, 57.02; H, 4.03. Found: C, 56.87; H, 4.82.

Chlorobis(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) Perchlorate (5). $[OsCl(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**3a**) (4.56 g, 4.43 mmol) was dissolved in 50 mL of degassed chloroform. To this solution was added via syringe phenylphosphine solution (2.23 mL of 3 M benzene solution, 6.7 mmol), and the solution was warmed to a gentle reflux (24 h). The colorless solution was cooled, and all volatiles were removed *in vacuo*. The residue was recrystallized from dichloromethane–ethanol to yield large snow-white crystals (4.71 g, 97%), mp 177–179 °C (white, hexagonal prisms). Anal. Calcd for $C_{49}H_{44}Cl_2O_5OsP_4$: C, 53.60; H, 4.05. Found: C, 53.30; H, 4.56.

***cis*-Dihydrido(phenylphosphine)carbonylbis(triphenylphosphine)osmium(II) (6).** $Os(H)_2(CO)(PPh_3)_3$[27] (0.5 g, 0.5 mmol) was dissolved in 40 mL of deoxygenated toluene. To this was syrined in phenylphosphine (0.2 mL of 3 M, 0.626 mmol), and the solution brought to reflux. After 16 h the light brown solution was cooled and the toluene removed in vacuo. Dichloromethane was used to redissolve the tan residue which was then recrystallized with 2-propanol to obtain fine white crystals (0.31 g, 73%), mp 194 °C dec (white needles). Anal. Calcd for $C_{43}H_{39}OOsP_3$: C, 60.41; H, 4.61. Found: C, 61.06; H, 5.43.

Hydrido(phenylphosphine)(acetonitrile)carbonylbis(triphenylphosphine)osmium(II) Perchlorate (7). $Os(H)_2(PH_2Ph)(CO)(PPh_3)_2$ (**6**) (0.1 g, 0.12 mmol) was dissolved in 20 mL of dichloromethane, and to this solution was added a second solution of 0.3 mL of perchloric acid in 15 mL of acetonitrile. Within 3 min of mixing, hydrogen evolution had ceased and a colorless solution resulted. After 45 min the solvent was stripped and the colorless gum redissolved in dichloromethane. Recrystallization with ethanol gave large white crystals (0.097 g, 81%) of product, mp 140–141 °C (white rods). Anal. Calcd for $C_{45}H_{41}ClNO_5OsP_3$: C, 54.35; H, 4.16; N, 1.41. Found: C, 54.52; H, 4.49; N, 1.61.

***cis*-Hydrido(phenylphosphine)dicarbonylbis(triphenylphosphine)osmium(II) Perchlorate (8).** $[OsH(PH_2Ph)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (**7**) (0.2 g, 0.2 mmol) was suspended in 50 mL of benzene and carbonylated (40 psi, 3 h, 80 °C). The mixture was cooled, transferred to a 100-mL flask, and completely stripped of all solvent. The white residue was recrystallized from dichloromethane–2-propanol to give white cubes (0.16 g, 79%), mp 172 °C. Carbonylation of **7** at 25 °C for shorter periods yielded mixtures with additional IR bands at 2020 and 2075 cm^{-1}. These bands disappeared on further carbonylation. Anal. Calcd for $C_{44}H_{38}ClO_6OsP_3$: C, 53.83; H, 3.91. Found: C, 53.74; H, 4.51.

(Phenylphosphine)dicarbonylbis(triphenylphosphine)ruthenium(0) (9c). $Ru(CO)_2(PPh_3)_3$[28] (0.5 g, 0.53 mmol) was suspended in 30 mL of freeze-degassed benzene. Phenylphosphine (0.21 mL of 3 M solution, 0.64 mmol) was added via syringe. Within 10 min the orange solid had completely dissolved and a yellow solution formed. After 45 min at 25 °C the solution was concentrated to a volume of (~10 mL) and cooled in an ice bath. Deoxygenated hexane (10 mL) was added dropwise over the course of 15 min until large yellow crystals formed. Further additions of hexane, 50 mL total, led to a slurry of large yellow crystals. Filtration followed by washing with hexane (3 × 10 mL) yielded (0.4 g, 95%) bright yellow crystals, mp 132–133 °C (yellow prisms). Anal. Calcd for $C_{44}H_{37}O_2P_3Ru$: C, 66.75; H, 4.71. Found: C, 66.29; H, 4.50.

(Diphenylphosphine)dicarbonylbis(triphenylphosphine)ruthenium(0) (9d). $Ru(CO)_2(PPh_3)_3$ (0.68 g, 0.72 mmol) was treated as in the preparation of **9a** except that diphenylphosphine solution (1.8 mL of 0.5 M, 0.9 mmol) was used instead of phenylphosphine. Addition of hexane gave (0.49 g, 78%) of crude solid which was further recrystallized from benzene–hexane for analysis. ^{1}H NMR indicated benzene solvate (δ 7.1 (s)) with aromatic to phosphine protons integrating 50:1. Anal. Calcd for $C_{50}H_{41}O_2P_3Ru\cdot C_6H_6$: C, 71.10; H, 5.02. Found: C, 71.04; H, 5.40.

(Diphenylphosphine)dicarbonylbis(triphenylphosphine)osmium(0) (9b). $Os(CO)_2(PPh_3)_3$ (0.32 g, 0.31 mmol) was suspended in deoxygenated benzene (20 mL) and diphenylphosphine solution (0.13 mL of 3 M benzene solution, 0.39 mmol) added. This mixture was stirred for 30 min at room temperature with no apparent change in color or solubility of solids. After this period the reaction was irradiated with a quartz halogen sun lamp. Within 45 min of initial irradiation all yellow starting material had dissolved and a lemon yellow solution had formed. Concentration to ~10 mL in vacuo followed by dropwise addition of deoxygenated hexane (10 mL) to the cooled solution afforded bright yellow crystals of product; yield 0.24 g (82%). Further recrystallization from benzene–hexane gave an analytical sample. ^{1}H NMR indicated benzene solvate (δ 7.1 (s)), and integration of aromatic phosphine protons gave ratio >40:1. Anal. Calcd for $C_{50}H_{41}O_2OsP_3\cdot C_6H_6$: C, 64.97; H, 4.59. Found: C, 65.08; H, 4.87.

***trans*-Hydrido(phenylphosphine)dicarbonylbis(triphenylphosphine)ruthenium(II) Perchlorate (10).** $Ru(PH_2Ph)(CO)_2(PPh_3)_2$ (**9c**) (0.25 g, 0.32 mmol) was suspended in ethanol (20 mL). Perchloric acid (0.1 mL) followed by 30 mL of dichloromethane was added to completely dissolve all material. Upon dissolution, the bright yellow solid instantly lost all color, and within 2 min a colorless uniform solution resulted. From this solution, large white cubes of product could be isolated. Successive recrystallization from dichloromethane–ethanol gave 0.21 g (72%). Anal. Calcd for $C_{44}H_{38}ClO_6P_3Ru$: C, 59.23; H, 4.30. Found: C, 59.18; H, 4.54.

Reaction between $Os(CO)_2(PPh_3)_3$ and Phenylphosphine. $Os(CO)_2(PPh_3)_3$ (0.3 g, 0.29 mmol) was suspended in oxygen-free benzene (40 mL). Phenylphosphine (0.12 mL of 3 M solution, 0.35 mmol) was added, and the reaction was irradiated with a quartz halogen sun lamp. An orange solution formed (5 min) the color of which faded over the course of 30 min to give a colorless solution. After the reaction was cooled in an ice bath, addition of hexane caused a white solid to crystallize (0.20 g, 89%) which was identified as $Os(H)_2(CO)_2(PPh_3)_2$ by comparison with an authentic sample.[29]

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Registry No. **1a**, 102849-31-0; **1b**, 102747-34-2; **1c**, 102747-35-3; **1d**, 102747-36-4; *trans*-**2a**, 102747-25-1; *cis*-**2a**, 102849-36-5; *cis*-**2b**, 102747-37-5; *trans*-**2b**, 102849-37-6; **3a**, 102849-33-2; **3b**, 102747-39-7; **3c**, 102781-75-9; **4a**, 102849-35-4; **4b**, 102747-41-1; **4c**, 102747-43-3; **5**, 102747-27-3; **6**, 102747-28-4; **7**, 102781-73-7; **8**, 102747-30-8; **9b**, 102747-31-9; **9c**, 102747-44-4; **9d**, 102747-45-5; **10c**, 102747-33-1; $OsHCl(CO)(PPh_3)_3$, 16971-31-6; $RhHCl(CO)(PPh_3)_3$, 16971-33-8; $Os(H)_2(CO)(PPh_3)_3$, 12104-84-6; $Ru(CO)_2(PPh_3)_3$, 61647-76-5; $Os(H)_2(CO)_2(PPh_3)_2$, 18974-23-7; $Os(CO)_2(PPh_3)_3$, 64479-09-0.

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