Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U^a
Ru(1)	2253.2 (2)	5685.8 (2)	5537.4 (2)	20.6 (1)
Ru(2)	2252.3 (2)	6598.5 (3)	7030.4 (2)	21.9 (1)
Cl	4867 (1)	7159 (2)	5860 (1)	54.0 (6)
Cl′	4696 (13)	4993 (18)	6658 (11)	112 (8)
O(1)	2716 (2)	7120 (2)	6029 (2)	28 (1)
O(2)	1220 (2)	6139 (3)	6281 (1)	30 (1)
O(3)	2706 (2)	5156 (3)	6542 (1)	27 (1)
O(4)	4881 (4)	4937 (4)	6679 (3)	25 (1)
O(5)	148 (3)	7874 (3)	5726 (3)	71 (2)
O(6)	157 (3)	4361 (3)	6767 (2)	60 (2)
C(1)	2649 (4)	4185 (4)	4995 (3)	41 (2)
C(2)	1668 (4)	4319 (4)	4930 (2)	40 (2)
C(3)	1318 (4)	5305 (4)	4660 (2)	41 (2)
C(4)	1913 (4)	6180 (4)	4443 (2)	35 (1)
C(5)	2896 (4)	6034 (4)	4510 (2)	34 (1)
C(6)	3267 (4)	5038 (4)	4776 (2)	38 (2)
C(7)	1333 (4)	6991 (6)	7909 (6)	54 (2)
C(8)	1906 (5)	6116 (5)	8121 (2)	49 (2)
C(9)	2882 (4)	6244 (5)	8056 (2)	45 (2)
C(10)	3268 (4)	7205 (5)	7792 (2)	47 (2)
C(11)	2685 (5)	8062 (5)	7579 (3)	55 (2)
C(12)	1703 (5)	7963 (5)	7649 (3)	58 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

probable that formation of **4** and **6** involves facile exchange of bridging phenoxo groups with hydroxo ligands caused by protonation of the former by water, with subsequent release of phenol and entry of hydroxide ion into the bridging positions between the ruthenium atoms.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert-atmosphere chamber under prepurified argon. All solvents were distilled under prepurified nitrogen prior to use; acetonitrile was distilled from calcium hydride. ^{1}H NMR spectra were recorded on a Varian XL-400 spectrometer, and NMR data are listed in ppm relative to internal Me_4Si. Thallium phenoxide and ruthenium trichloride trihydrate were purchased from Aldrich Chemical Co. Neutral alumina, Brockman activity I, 80–200 mesh was purchased from Fischer Scientific. $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ was synthesized by a published method.[5] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (7). To $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ (1.50 g, 3.00 mmol) in a 250-mL Schlenk tube with stirbar was added $TlOC_6H_5$ (2.67 g, 9.00 mmol). Approximately 150 mL of CH_3CN was then added to the reaction flask, and the reaction mixture was stirred at room temperature for an 18-h period. During this time an orange solution developed, with formation of solid TlCl. Following filtration of the solution through a medium-porosity frit, the solvent was removed under vacuum affording 1.74 g (86%) of an orange solid, $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]Cl$; the ^{1}H NMR spectrum of the cation was idential with that of an authentic sample.[3b] This solid was added to 20 mL of water; the solution so formed was stirred for 10 min at room temperature and chromatographed (alumina, water eluent) by using a 1-cm-diameter column with a height of 15 cm. The eluate was collected in a 100-mL round-bottom flask equipped with a stirbar, and an orange crystalline solid, **7**, was obtained by removal of the solvent in vacuo. Yield: 1.26 g (98%). An analytical sample of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ was prepared by double recrystallization from 50/50 CH_3CN/THF: ^{1}H NMR (D_2O): δ 5.42 (C_6H_6, s).

Anal. Calcd for $C_{12}H_{21}ClO_6Ru_2$: C, 28.89; H, 4.25; Cl, 7.11. Found: C, 29.05, H, 4.16; Cl, 7.25.

$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]PF_6$ (8). A solution of aqueous $AgPF_6$ (0.63 g, 2.49 mmol) was added dropwise to an aqueous solution of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (1.1 g, 2.47 mmol). The reaction mixture was stirred for 5 min at room temperature to insure complete precipitation of AgCl. Following filtration of the mixture through Celite on a medium-porosity frit, the solvent was removed from the filtrate in vacuo. The yellow solid so obtained was dissolved in water and chromatographed (water eluent) with alumina (Brockman Activity I) on a 1-cm-diameter column with a height of 10 cm. The eluate was collected and taken to dryness in vacuo, giving a yellow solid, $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]PF_6$ (yield = 1.2 g, 88%). ^{1}H NMR (D_2O): δ 5.84 (C_6H_6, s).

Table II. Selected Bond Distances and Bond Angles for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (7)[a]

(a) Bond Distances (Å)			
Ru(1)–Ru(2)	2.9812 (7)	Ru(2)–O(1)	2.070 (3)
Ru(1)–CNT(1)	1.651 (5)	Ru(2)–O(2)	2.100 (3)
Ru(2)–CNT(2)	1.638 (5)	Ru(2)–O(3)	2.073 (3)
Ru(1)–O(1)	2.071 (3)	O(1)···O(2)	2.489 (5)
Ru(1)–O(2)	2.092 (3)	O(1)···O(3)	2.563 (5)
Ru(1)–O(3)	2.073 (3)	O(2)···O(3)	2.480 (5)
(b) Bond Angles (deg)			
CNT(1)–Ru(1)–Ru(2)	174 (1)	CNT(2)–Ru(2)–O(2)	137.6 (3)
CNT(1)–Ru(1)–O(1)	137.9 (3)	CNT(2)–Ru(2)–O(3)	134.8 (3)
CNT(1)–Ru(1)–O(2)	129.3 (4)	Ru(1)–O(1)–Ru(2)	92.1 (1)
CNT(1)–Ru(1)–O(3)	139.0 (4)	Ru(1)–O(2)–Ru(2)	90.6 (1)
CNT(2)–Ru(2)–Ru(1)	177.8 (1)	Ru(1)–O(3)–Ru(2)	91.9 (1)
CNT(2)–Ru(2)–O(1)	135.1 (3)		
(c) Torsion Angle (deg)			
CNT(1)–Ru(1)–Ru(2)–CNT(2)	8.8 (4)		

[a] CNT = centroid of benzene ring.

Anal. Calcd for $C_{12}H_{15}F_6O_3PRu_2$: C, 26.00; H, 2.73; F, 20.56. Found: C, 25.76; H, 2.98; F, 20.32. Mol wt.: calcd, 554; found, 548 (H_2O).

X-ray Crystallography

Crystal data for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**7**): $C_{12}H_{21}ClO_6Ru_2$, orthorhombic, *Pbcn*, $a = 14.273$ (2) Å, $b = 12.125$ (1) Å, $c = 18.541$ (2) Å, $V = 3208.7$ (6) $Å^3$, $Z = 8$, $D(\text{calcd}) = 2.065$ g cm^{-3}, μ(Mo Kα) = 20.37 cm^{-1}, and $T(\text{max})/T(\text{min}) = 0.493/0.406$. An orange crystal (0.21 × 0.31 × 0.33 mm) was used to collect 4121 reflections (one octant, Nicolet R3m/μ diffractometer, graphite monochromator, $4° \leq 2\theta \leq 55°$, 23 °C) of which 3673 were independent and systematically present, and 2855 were considered observed ($3\sigma(F_0)$). The data were semiempirically corrected for absorption. The structure was solved by heavy-atom methods. The chloride ion is disordered over two positions with the following refined occupancies: Cl, 0.77; and Cl′, 0.23. There is likely an accompanying disorder in the water molecule occupancies, but it was unobserved. At convergence, with all non-hydrogen atoms except Cl′ anisotropic and calculated isotropic hydrogen atom contributions for the benzene rings, $R(F) = 3.38\%$, $R(wF) = 5.05\%$, GOF = 1.235, $\Delta/\sigma = 0.023$, $\Delta(\rho) = 0.71$ e Å^{-3}, and $N_0/N_v = 14.5$. All calculations used the SHELXTL program library (Nicolet Corp., Madison, WI). The atomic cooridnates and isotropical thermal parameters are collected in Table I. Selected bond distances and bond angles are listed in Table II.

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Registry No. 7, 114928-93-7; 8, 114928-94-8; $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl$, 60829-93-8; $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$, 37366-09-9; $TlOC_6H_5$, 25491-50-3; $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]Cl$, 114928-92-6.

Supplementary Material Available: A stereoview of the unit-cell packing for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ and tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Binuclear Reductive Elimination of Water: New Route to the (Triphenylstannyl)pentacarbonyltungsten Anion, $Ph_3SnW(CO)_5^-$

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Salts of the anions $R_3EM(CO)_5^-$ (E = Si, Ge, Sn; M = Cr, Mo, W) are quite stable and are readily prepared by one of the routes, illustrated for the title anion, shown in eq 1 and 2.[1,2]

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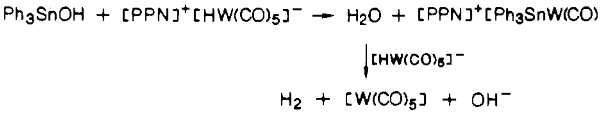
$$Na_2W(CO)_5 + Ph_3SnCl \xrightarrow{[Et_4N][Br]} [Et_4N][Ph_3SnW(CO)_5] + NaBr + NaCl \quad (1)$$

$$[Et_4N][ClW(CO)_5] + LiSnPh_3 \rightarrow [Et_4N][Ph_3SnW(CO)_5] + LiCl \quad (2)$$

While investigating the reactions of hydroxy derivatives of group 14 elements with the anionic transition-metal hydrides $[HM(CO)_5]^-$ (M = Cr, W), we uncovered an alternate and quite interesting route to $[Ph_3SnM(CO)_4L]^-$ (M = W, L = CO, $P(OMe)_3$; M = Cr, L = $P(OMe)_3$). As indicated in eq 3, water



$$\begin{array}{l} Ph_3SnOH + [PPN]^+[HW(CO)_5]^- \rightarrow H_2O + [PPN]^+[Ph_3SnW(CO)_5]^- \\ \qquad\qquad\qquad\qquad \downarrow [HW(CO)_5]^- \\ \qquad\qquad\qquad H_2 + [W(CO)_5] + OH^- \end{array} \quad (3)$$

is observed as a product and its subsequent reaction with the starting hydride accounts for the production of H_2, also observed as a reaction product. This study is reported below, along with the X-ray crystal structure determination of $[PPN]^+[Ph_3SnW(CO)_5]^-$ ($[PPN]^+$ = bis(triphenylphosphine)nitrogen(1+)).

Experimental Section

A. Methods and Materials. All reactions, sample transfers, and sample manipulations were carried out under standard Schlenk techniques (N_2 atmosphere) and/or in an argon atmosphere glovebox. All solvents were distilled under N_2 from appropriate drying agents (tetrahydrofuran from Na/benzophenone) and then stored in dried, N_2-filled flasks over activated 4-Å molecular sieves. A nitrogen purge was used on these solvents prior to use, and transfers to the reaction vessels were via stainless steel cannulas under a positive N_2 pressure. Triphenyltin hydroxide (Strem Chemicals Co.) was used as received. The anions $[HW(CO)_5]^-$ and *cis*-$[HW(CO)_4P(OCH_3)_3]^-$ were prepared as their $[PPN]^+$ salts as described elsewhere.[5,6]

B. Preparation of the $[PPN][Ph_3SnW(CO)_5]$ Complex. To a yellow solution of $[PPN][HW(CO)_5]$ (0.12 g, 0.14 mmol) in 20 mL of THF was added Ph_3SnOH (0.06 g, 0.16 mmol). The mixture was stirred for 2 days at room temperatue, with occasional IR monitoring of the still yellow solution, which was then concentrated to 10 mL and placed in a refrigerator. Light yellow, air-stable crystals were formed; yield 0.104 g (62%). IR (THF solution; ν(CO), cm^{-1}): 2034 m, 1904 vs, 1879 m. Anal. Calcd for $C_{59}H_{45}O_5NP_2SnW$: C, 58.40; H, 3.71; N, 1.15. Found: C, 57.86; H, 3.66; N, 0.95. Analysis of the gas over the reaction mixture by gas chromatography indicated the presence of H_2. Analysis of the volatiles by GC in the solution indicated the presence of water. A comparison of the IR spectra of starting materials showed no water present whereas the product mixture contained significant quantities.

C. X-ray Structure Determination. A yellow box-shaped crystal of $[PPN][Ph_3SnW(CO)_5]$ was mounted on a glass fiber in a random orientation (see Table I for details). Preliminary examination and data collection were performed on a Nicolet R3m diffractometer.[8] Cell constants were obtained from the least-squares refinement of the setting angles of 27 reflections ($2\theta_{av}$ = 21.6°). ω scans of several intense reflections were less than 0.3° at half-height, indicating good crystal quality. Examination of the cell constants indicated a monoclinic system.

Axial photos verified the Laue group assignment of $2/m$. Systematic absences indicated that the space group was $P2_1/n$ (No. 14). The data were collected at −100 (1) °C by using θ–2θ scanning techniques with a variable scan rate. The scan range was determined as a function of $\theta_{K\alpha_1}$ and $\theta_{K\alpha_2}$. The diameter of the beam collimator was 1 mm.

Table I. Details of the Crystallographic Experiment and Computations for $[PPN][Ph_3SnW(CO)_5]$

mol formula	$C_{59}H_{45}O_5NP_2SnW$
fw	1212.5
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
lattice constants	
a, Å	10.676 (2)
b, Å	15.048 (3)
c, Å	32.423 (7)
β, deg	81.46 (2)
V, $Å^3$	5150 (1)
temp, °C	−100 (1)
Z	4
F(000)	2400
ρ(calcd), g cm^{-3}	1.56
cryst dimens, mm	0.2 × 0.4 × 0.5
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
μ, cm^{-1}	28.7
scan type	θ–2θ
geometry	bisecting
scan speed, deg min^{-1}	2.0–30.0
2θ range, deg	4.0–50.0
index restrictions	±11 (*h*), +15 (*k*), +32 (*l*)
total no. of rflns	9614
no. of unique obsd rflns	7070
obsd rfln criterion	$4\sigma(F)$
no. of least-squares params	514
data/param ratio	13.7
R^a	0.042
$R_w{}^b$	0.040
GOF^c	2.19

$^a R = (\sum|F_o - F_c|)/(\sum F_o)$. $^b R_w = (\sum w^{1/2}|F_o - F_c|)/(\sum w^{1/2}F_o)$. ^{c}GOF = error in an observation of unit weight = $[(\sum w(|F_o - F_c|)^2)/(N_{data} - N_{params})]^{1/2}$.

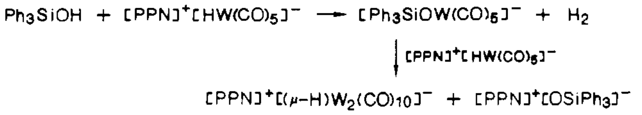
A total of 9614 reflections were collected, of which 288 reflections were standards. Lorentz and polarization corrections were applied to the data. An empirical absorption correction[9] was applied ($(\mu\tau)_{max}$ = 1.3, ψ_{start} = 0.0°, ψ_{end} = 345.0°, $\Delta\psi$ = 15.0°, T_{min} = 0.35, T_{max} = 0.43, R_{merge} before 0.06 and after 0.02).

The molecular structure was solved by direct methods (SHELXTL-PLUS by G. Sheldrick)[8] employing 9326 unique reflections, of which 7070 were flagged as observed (minimum *E* of 1.2), and 15 900 triple-phase relationships. All atoms were located in the resulting *E* map and were included for future refinement. Hydrogen atoms were placed in idealized positions, and their individual isotropic thermal motion was fixed at 0.08. The structure was refined by full-matrix least-squares methods.[8] Scattering factors were taken from ref 7. In the final cycle, phenyl groups were refined as rigid entities. All non-hydrogen atoms were refined anisotropically. The largest peak in the final Fourier map was 1.09 e $Å^{-3}$ near W, while the smallest peak was −0.76 e $Å^{-3}$.

Results and Discussion

The anionic group 6 transition-metal hydrides behave as good hydride donors to a wide variety of substrates,[10] including the acids in eq 4 and 5. As indicated in eq 5, the $[Ph_3SiO]^-$ derivative of

$$PhOH + [PPN]^+[HW(CO)_5]^- \rightarrow [PPN]^+[PhOW(CO)_5]^- + H_2 \quad (4)$$



$$\begin{array}{l} Ph_3SiOH + [PPN]^+[HW(CO)_5]^- \rightarrow [Ph_3SiOW(CO)_5]^- + H_2 \\ \qquad\qquad\qquad\qquad \downarrow [PPN]^+[HW(CO)_5]^- \\ \quad [PPN]^+[(\mu\text{-}H)W_2(CO)_{10}]^- + [PPN]^+[OSiPh_3]^- \end{array} \quad (5)$$

$W(CO)_5$ was not isolable via this preparative route, due to its

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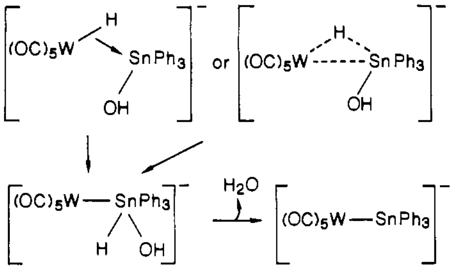
Scheme I



lability and to the great stability of the $[(\mu\text{-H})W_2(CO)_{10}]^-$ dimer.[11] Simple alkoxide and siloxide derivatives of group 6 metal carbonyls, $[ROM(CO)_5]^-$ and $[R_3SiOM(CO)_5]^-$, are also well-known for CO lability, leading in the case of R = Me to cluster formation, $[M_4(CO)_{12}(\mu_3\text{-OMe})_4]^{4-}$,[12,13] $[M_2(CO)_8(\mu\text{-OSiMe}_3)_2]^{2-}$, and $[M_4(CO)_{12}(\mu\text{-OSiMe}_3)_4]^{4-}$.[14] To our knowledge there are no examples in such metal carbonyls of R or SiR_3 migration from oxygen to the metals or of redistribution reactions leading to $[RM(CO)_5]^-$ or $[R_3SiM(CO)_5]^-$ and "[O]".

Reaction of Ph_3SnOH with $[PPN]^+[HW(CO)_5]^-$ in THF was slow; $t_{1/2}$ = 20 h. Water was detected in the solution, and H_2 was liberated, presumably due to reaction of H_2O with the starting material,[15] as indicated in eq 3. The heterobimetallic anion product $[Ph_3SnW(CO)_5]^-$ was identified by its known spectroscopic properties, elemental analysis, and X-ray crystal structure. An attempt to react $[PPN]^+[HCr(CO)_5]^-$ with Ph_3SnOH yielded no product over the course of 2 days. In marked contrast, the reaction of Ph_3SnOH with $[PPN]^+[cis\text{-HW(CO)}_4\text{P(OMe)}_3]^-$ was very rapid ($t_{1/2} \leq 4$ min), leading to a product whose ν(CO) IR spectrum was consistent with the formulation $[cis\text{-Ph}_3\text{SnW(CO)}_4\text{P(OMe)}_3]^-$ (vide infra).

Reactions with acid have shown the phosphorus-donor ligand-substituted anionic hydrides to be much better bases than the all-carbonyl $[HW(CO)_5]^-$ or $[HCr(CO)_5]^-$.[15] Hydrides of heavier metals are also better bases than those of lighter metal congeners; i.e., $[HW(CO)_5]^- > [HCr(CO)_5]^-$. Similarly, reactions with, for example, R^1Br, have demonstrated the following nucleophilicity order: $[HW(CO)_4P(OMe)_3]^- > [HW(CO)_5]^- > [HCr(CO)_5]^-$.[10] We conclude that the greater velocity observed for the reaction of Ph_3SnOH and $[cis\text{-HW(CO)}_4\text{P(OMe)}_3]^-$ is also indicative of a nucleophile/electrophile interaction along the reaction pathway. An anionic bridging hydride center involving an expansion of the coordination sphere of Sn, as shown in Scheme I, most reasonably accommodates the observed elimination of water.

The reaction is in essence a binuclear reductive elimination of water, resulting in charge redistribution according to the following arguments. Results from both theoretical[16] and spectroscopic studies[17] suggest the Ph_3Sn ligand to bind to transition metals with considerable $M_d \rightarrow Sn_d$ π-accepting character. In this connection the ν(CO) IR spectra of analogous hydride and Ph_3Sn derivatives are of interest (see Table II). The conclusion from the ν(CO) data is that the Ph_3Sn ligand holds more negative charge in the Sn–W bond, permitting less to be distributed over the CO groups, than does the hydride ligand. Hence, formally, the reducing equivalents of the hydride creates the anionic Ph_3Sn^- ligand from Ph_3SnOH.

Table II. Infrared Data

	ν(CO), cm^{-1} (THF soln)		
	A_1	E	A_1
$[PPN]^+[HW(CO)_5]^-$	2030 w	1887 vs	1857 m
$[PPN]^+[Ph_3SnW(CO)_5]^-$	2034 w	1904 vs	1875 m
	ν(CO), cm^{-1} (THF soln)		
	A′	A′ + A″	A″
$[PPN]^+[cis\text{-HW(CO)}_4\text{P(OMe)}_3]^-$	1983 w	1871 sh, 1856 vs	1822 m
$[PPN]^+[cis\text{-Ph}_3\text{SnW(CO)}_4\text{P(OMe)}_3]^-$	1991 w	1891 sh, 1873 vs	1842 m

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
W	7398 (1)	7967 (1)	1010 (1)	26 (1)
C(1)	7786 (9)	7272 (6)	463 (3)	39 (3)
O(1)	8011 (8)	6843 (5)	175 (5)	58 (3)
C(2)	6893 (8)	9044 (7)	732 (3)	41 (3)
O(2)	6578 (7)	9687 (5)	578 (3)	64 (3)
O(3)	7040 (9)	8484 (7)	1588 (3)	48 (4)
O(3)	6813 (8)	8762 (7)	1915 (3)	85 (4)
C(4)	9229 (8)	8370 (7)	972 (3)	38 (3)
O(4)	10245 (6)	8604 (5)	975 (3)	65 (3)
C(5)	5562 (8)	7562 (6)	1086 (3)	32 (3)
O(5)	4512 (6)	7379 (5)	1121 (2)	51 (3)
Sn	8172 (1)	6462 (1)	1421 (1)	26 (1)
C(11)	5585 (5)	5801 (4)	1900 (2)	36 (3)
C(12)	4745	5391	2213	44 (3)
C(13)	5174	5087	2574	44 (3)
C(14)	6443	5192	2621	40 (3)
C(15)	7283	5602	2308	36 (3)
C(16)	6853	5907	1947	35 (3)
C(17)	8377 (5)	4409 (4)	1278 (1)	36 (3)
C(18)	8776	3615	1079	43 (3)
C(19)	9524	3632	687	46 (4)
C(20)	9872	4443	495	52 (4)
C(21)	9472	5237	695	41 (3)
C(22)	8725	5220	1086	28 (3)
C(23)	11032 (5)	6267 (4)	1509 (2)	41 (3)
C(24)	12166	6433	1660	49 (4)
C(25)	12195	7035	1986	51 (4)
C(26)	11090	7472	2160	56 (4)
C(27)	9955	7306	2009	39 (3)
C(28)	9926	6704	1684	31 (3)

The reductive elimination of small molecules from reaction of a metal hydride with an active functional group on a second metal center has been observed many times before and in fact is an accepted synthetic route to heterometallic complexes.[18] Such reactions have typically involved neutral metal hydrides. Precise bond-forming paths are not delineated in all cases; however, a proton-transfer mechanism has been argued for in the case of methane elimination from the reaction of Cp_2ZrMe_2 and $CpM(CO)_3H$ (M = Cr, Mo, W)[19] and probably holds for elimination of alkylamines from the reaction of $CpMo(CO)_3H$ with $[Ti(O\text{-}i\text{-}Pr)_3(NMe_2)]$[20] and similar more recent observations.[21-23] On the other hand, the *nucleophilic* character of the metal hydride accounts for formation of the bridging hydride intermediates that precede binuclear reductive elimination of aldehydes from the reaction of various neutral metal hydrides with, for example, $[(CH_3CN)Re(C(O)R)(CO)_4]$.[24]

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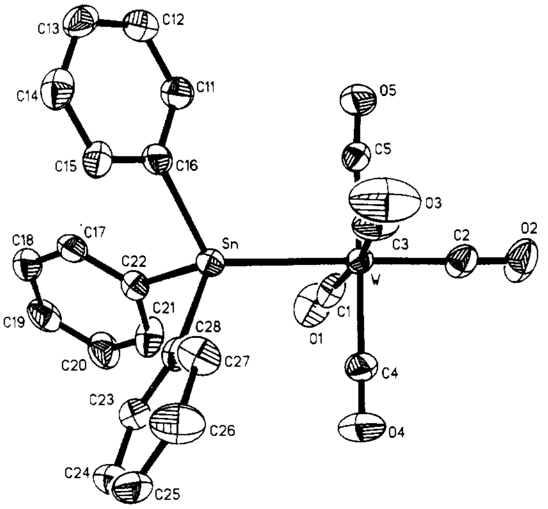

Figure 1. Thermal ellipsoid plot (50% probability) with the numbering scheme of $[Ph_3SnW(CO)_5]^-$. Hydrogen atoms have been omitted for clarity.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[PPN][Ph_3SnW(CO)_5]$

Bond Lengths			
W-C(1)	2.048 (10)	W-C(2)	1.970 (9)
W-C(3)	2.011 (11)	W-C(4)	2.032 (9)
W-C(5)	2.033 (8)	W-Sn	2.812 (1)
C(1)-O(1)	1.131 (11)	C(2)-O(2)	1.161 (11)
C(3)-O(3)	1.134 (12)	C(4)-O(4)	1.142 (10)
C(5)-O(5)	1.144 (10)	Sn-C(16)	2.209 (5)
Sn-C(22)	2.197 (5)	Sn-C(28)	2.199 (5)

Bond Angles			
C(2)-W-C(1)	93.2 (4)	C(3)-W-C(1)	171.9 (4)
C(3)-W-C(2)	94.7 (5)	C(4)-W-C(1)	91.7 (4)
C(4)-W-C(2)	93.0 (4)	C(4)-W-C(3)	89.4 (4)
C(5)-W-C(1)	91.1 (4)	C(5)-W-C(2)	88.7 (3)
C(5)-W-C(3)	87.5 (4)	C(5)-W-C(4)	176.6 (4)
Sn-W-C(1)	87.9 (3)	Sn-W-C(2)	178.2 (3)
Sn-W-C(3)	84.2 (3)	Sn-W-C(4)	85.5 (3)
Sn-W-C(5)	92.7 (2)	O(1)-C(1)-W	175.7 (8)
O(2)-C(2)-W	178.1 (10)	O(3)-C(3)-W	178.3 (9)
O(4)-C(4)-W	176.0 (9)	O(5)-C(5)-W	176.3 (8)
C(16)-Sn-W	118.2 (1)	C(22)-Sn-W	121.8 (1)
C(22)-Sn-C(16)	98.8 (2)	C(28)-Sn-W	112.1 (2)
C(28)-Sn-C(16)	104.2 (2)	C(28)-Sn-C(22)	98.6 (2)
C(11)-C(16)-Sn	118.4 (1)	C(15)-C(16)-Sn	121.4 (1)
C(17)-C(22)-Sn	119.3 (1)	C(21)-C(22)-Sn	120.6 (1)
C(23)-C(28)-Sn	118.9 (1)	C(27)-C(28)-Sn	121.1 (1)

That the nucleophilic character of the anionic hydrides in the case presented herein governs the reaction path is clear. That the electron-rich hydrogen atom of the metal hydride formally becomes a proton in the final product is, to our knowledge, a unique observation.

X-ray Crystal Structure Determination of $[PPN][Ph_3SnW(CO)_5]$. A thermal ellipsoid plot of the molecular structure of $[Ph_3SnW(CO)_5]^-$ with the numbering scheme is shown in Figure 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table III. Intramolecular distances and intramolecular angles of $[Ph_3SnW(CO)_5]^-$ are listed in Table IV. As expected, the $[Ph_3SnW(CO)_5]^-$ anion possesses an octahedral structure. The W-Sn bond distance of $[PPN][Ph_3SnW(CO)_5]$, 2.812 (1) Å, is significantly shorter than the distance of 2.837 (1) Å in the $[W(=C(H)C_6H_4Me_4)(SnPh_3)(CO)_2(Cp)]$ complex[3] and is statistically the same as the W-Sn bond length in $[PPN]^+[Me_3SnW(CO)_5]^-$ (W-Sn = 2.810 (8) Å).[4] There is some small distortion of the molecular geometry as evidenced by variation in Sn-W-CO bond angles ranging from 92.7 (2)° (Sn-W-C(5)) to 84.2 (3)° (Sn-W-C(3)). The counterion, $[Ph_3PNPPh_3]^+$, is in a bent configuration with P-N-P = 143.3 (5)°.

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Registry No. $[PPN][HW(CO)_5]$, 78709-76-9; $[PPN][Ph_3SnW(CO)_5]$, 114944-23-9; $[PPN][HCr(CO)_5]$, 78362-94-4; $[PPN][cis\text{-}HW(CO)_4P(OMe)_3]$, 82963-28-8; Ph_3SnOH, 76-87-9; $[cis\text{-}Ph_3SnW(CO)_4P(OMe)_3]^-$, 114944-24-0.

Supplementary Material Available: A thermal ellipsoid plot (50% probability) with numbering scheme (Figure 1S), bond angles (Table 1S) and bond distances (Table 2S) of $[Ph_3PNPPh_3]^+$, anisotropic displacement parameters (*U* values) (Table 3S), H atom coordinates and isotropic displacement parameters (Table 4S), a ball and stick plot of $[Ph_3SnW(CO)_5]^-$ as viewed through the W-Sn bond (Figure 2S), and atomic coordinates and equivalent isotropic displacement parameters of $[Ph_3PNPPh_3]^+$ (Table 5S) (7 pages); calculated and observed structure factor amplitudes (Table 6S) (26 pages). Ordering information is given on any current masthead page.

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Substitutional Reactivity of $Fe_2Os(CO)_{12}$

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For several years we have examined ligand and metal center effects on the substitutional reactivity of mononuclear and polynuclear complexes.[1-5] The substitutional reactivities of group 8 carbonyl complexes have indicated a cluster effect on reactivity.[4,5] The mixed-metal clusters $FeRu_2(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ undergo substitution reactions more readily than $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$, indicating that the heterometallic center affects the reactivity.[4,5] We now wish to report the kinetics of reaction of $Fe_2Os(CO)_{12}$ with the ligands PPh_3, $P(OMe)_3$, and $P(OPh)_3$.

Experimental Section

Iron pentacarbonyl (Aldrich Chemical Co.) and triosmium dodecacarbonyl (Strem Chemical Co.) were used without further purification. Triphenylphosphine was recrystallized from ethanol, and trimethyl phosphite was purified by vacuum distillation. Hexane, cyclohexane, and methylene chloride were stirred over H_2SO_4, washed with $NaHCO_3$ solution, stirred over $CaCl_2$, and distilled from CaH_2. All preparative-scale thin-layer chromatography was accomplished by using 1.0 mm thick silica gel plates.

$Fe_2Os(CO)_{12}$. Dodecacarbonyldiironosmium was prepared according to the literature procedure.[6] To a suspension of $Fe_2(CO)_9$ in heptane was added a solution of $H_2Os(CO)_4$[7] ($Fe_2(CO)_9$:$H_2Os(CO)_4$ ratio of 4:1), prepared from 1.0 g of OsO_4. The mixture was stirred at room temperature overnight under N_2. A deep purple solution and some solid were obtained. The solvent was removed under vacuum, and the purple products were extracted with CH_2Cl_2 in a drybox, leaving unreacted $Fe_2(CO)_9$ as an orange solid. The CH_2Cl_2 solution of the products was concentrated and purified by TLC (cyclohexane). This purple solution afforded $Fe_3(CO)_{12}$ (green), $Fe_2Os(CO)_{12}$ (purple, 100-150 mg), and small amounts of $H_2FeOs_3(CO)_{12}$. IR spectral data for $Fe_2Os(CO)_{12}$ and its substituted products are shown in Table I.

The kinetic reactions were accomplished under a nitrogen atmosphere in foil-wrapped vessels in darkened hoods under pseudo-first-order con-

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