Table I. A Comparison of the Rhodium Hydride Coupling Constants for the $[P_2RhH]_x$ Family of Clusters

entry	cluster	δ(Rh*H*)	$^1J_{Rh-H}$, Hz	$^2J_{P-H}$, Hz	ref
4	[(dipope)RhH]$_2$	−4.30	34.0	33–35	this work
5	$[\{(i\text{-}C_3H_7O)_3P\}_2RhH]_2$	−7.11	34.2	36.6	5
6	$[\{(CH_3O)_3P\}_2RhH]_3$	−9.56	16.5	25.0	5
2	[(dmope)RhH]$_4$	−6.52	10.7	16.1	this work

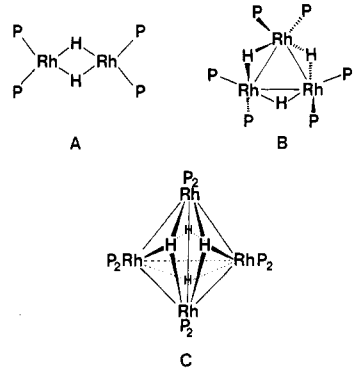

Figure 2. Structures of the $[P_2RhH]_x$ family of clusters: structures A and B have been verified crystallographically whereas structure C is tentative.

adding to the complexity in the low temperature regime.

We have also investigated the reactions of hydrogen with the (2-methylallyl)rhodium(I) complex of 1,2-bis(diisopropoxyphosphino)ethane, [η^3-(2-Me-C_3H_4)Rh(dipope)], **3**; in this case the dimeric[7] derivative [(dipope)RhH]$_2$,[9] **4**, is obtained as bright red crystals. The hydride resonance of **4** appears as a broad, unsymmetrical *septet* which upon phosphorus decoupling simplifies to a binomial *triplet*, indicating coupling with *two* magnetically equivalent rhodium nuclei ($^1J_{Rh}$ = 34.0 Hz). Because of the broadness of the phosphorus-coupled hydride pattern of **4**, we have been unable to extract an accurate phosphorus coupling constant; however, on the basis of previous work[5] with the closely related rhodium hydride dimer utilizing monodentate triisopropyl phosphite ligands, $[\{(i\text{-}C_3H_7O)_3P\}_2RhH]_2$, **5**, the observed seven-line pattern can be considered as an overlapping triplet of *quintets* which would require a phosphorus coupling constant between 33 and 35 Hz, indicating *four* magnetically equivalent phosphorus nuclei. Interestingly both the rhodium– and phosphorus–hydride coupling constants of **4** are nearly identical with those of **5** (Table I), suggesting that these binuclear complexes are isostructural: all four phosphorus atoms and two rhodium atoms coplanar as in Figure 2, structure A.[10]

The factors that determine the nuclearity of the $[P_2RhH]_x$ clusters are clearly steric in origin. In our case, the choice of the bidentate ligand $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ allows for the formation of the *tetranuclear* cluster **2**, the largest member of this family of clusters; this contrasts the use of $P(OCH_3)_3$, a monodentate ligand, which generates[5] the *trinuclear* cluster $[\{(CH_3O)_3P\}_2RhH]_3$, **6** (structure B, Figure 2). With relatively small substituents such as methoxy groups of the phosphorus donors, the bidentate $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ ligand exerts a smaller steric influence than two monodentate $P(OCH_3)_3$ ligands; with larger substituents such as isopropoxy, the steric influence of the bidentate ligand must be similar to two monodentate ligands since in both cases binuclear clusters are isolated.

All the members of the $[P_2RhH]_x$ family of clusters are formally electron deficient and therefore coordinatively unsaturated. For example, the tetranuclear complex **2** is a 56-electron cluster,[11] electronically identical with the 56-electron cluster $H_4Re_4(CO)_{12}$, the structure of which is known[12] to be a tetrahedral array of rhenium atoms with face-bridging hydrides. That **2** is similar in structure to $H_4Re_4(CO)_{12}$ can only be speculation in the absence of crystallographic data; however, a comparison of the hydride coupling constants (Table I) of these clusters does provide support for **2** having structure C (Figure 2). Thus one observes a decrease in $^1J_{Rh-H}$ on going from doubly edge bridging hydrides as in **4** and **5** (structure A) to singly edge bridging for **6** (structure B). That a further decrease of $^1J_{Rh-H}$ is observed in **2** may be evidence for face-bridging hydrides and therefore structure C. We are attempting to grow suitable crystals of **2** for crystallographic studies to verify this hypothesis.

Each rhodium center in **2** and **4** is formally in the +1 oxidation state and therefore susceptible to oxidative addition. Indeed, both **2** and **4** readily exchange their hydrides with deuterium at atmospheric pressure in minutes to form the corresponding deuterides. A consequence of this facile oxidative addition of H_2 or D_2 and their inherent coordinative unsaturation is that both **2** and **4** are extremely efficient hydrogenation catalysts for simple olefins. Whether or not the integrity of the cluster is maintained[5] throughout the hydrogenation cycle is under active investigation and will be the subject of future publications.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada, Research Corp., and the President's Emergency Research Fund (UBC) are gratefully acknowledged. We also thank Mr. Peter Borda for the chemical analyses and Dr. S. O. Chan and his staff for help with the NMR experiments. The generous loan of hydrated rhodium trichloride from Johnson-Matthey is also acknowledged.

Registry No. 1, 80105-91-5; 2, 80105-92-6; 3, 80105-93-7; 4, 80126-87-0.

(9) 4: mp 153 °C dec; ^{1}H NMR (C_7D_8) P(OC*H*(CH_3)$_2$), 5.35 ppm (m, 8, J = 6.4 Hz); P(OCH(C*H*$_3$)$_2$, 1.35 and 1.45 ppm (d, 48); PC*H*$_2$, 1.49 ppm (br m, 8); Rh*H*, −4.3 ppm (br sep, 2, J_{Rh} = 34.05 Hz, J_P = 33–35 Hz); ^{31}P{^{1}H} NMR (C_6D_6, ppm relative to $P(OMe)_3$ at +141.0 ppm) 196.4 (AA′A″A‴XX′, $|^1J_{Rh} + {}^3J_{Rh}|$ = 212.4 Hz). Anal. Calcd for $C_{14}H_{33}O_4P_2Rh$: C, 39.08; H, 7.73. Found: C, 39.01; H, 7.62.

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Synthesis and ^{31}P NMR Characterization of $[W_2(CO)_{10}PPh_2]^-$, $[W_2(CO)_9(PPh_2H)PPh_2]^-$, $[W_2(CO)_8(PPh_2)_2]^{2-}$, and $W_2(CO)_8(PPh_2)_2$

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Summary: Tetrahydrofuran solutions of $(OC)_5WPPh_2H$ are converted to $[W_2(CO)_{10}PPh_2]^-$, $[W_2(CO)_9(PPh_2)(PPh_2H)]^-$,

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Table I. ^{31}P NMR[a] of Phosphido-Bridged Tungsten Carbonyls (CD_3CN)

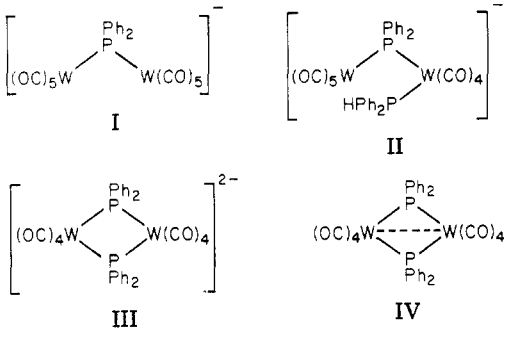
complex	δ_{PPh_2}	δ_{PPh_2H}	J_{PP}, Hz	J_{WPPh_2}, Hz	J_{WPPh_2H}, Hz
I	−63.5			168.7	
II	−61.6	7.4	19.5	163.2[b]	228.0
III	−99.2			156.0	
IV	180.0			162.0	

[a] Spectra were recorded at 40.5 MHz on a Varian XL-100 100 NMR spectrometer equipped with Fourier transform and a pulsed deuterium lock. [b] See ref 7.

and $[W_2(CO)_8(PPh_2)_2]^{2-}$ upon treatment with potassium *tert*-butoxide. The dianion reacts with O_2 to form $W_2(CO)_8(PPh_2)_2$. These complexes have been isolated and characterized with ^{31}P NMR and IR spectroscopy.

The metal–metal bonded doubly bridged complexes $M_2(CO)_8(PR_2)_2$ (M = Cr, Mo, W) have been extensively studied.[1] Although most frequently synthesized from the thermal reaction of R_2PPR_2 and $M(CO)_6$,[2] they also have been prepared from the UV irradiation of $(OC)_5MPPh_2H$ or $(OC)_5MPPh_2Li$ in THF.[3] For the latter reaction, intermediates such as $[(OC)_4M(PR_2)_2M(CO_4)]^-$ or $[(OC)_4M(PPh_2)_2M(CO)_4]^{2-}$ may be proposed but neither has been verified. The change in oxidation state of tungsten from 0 to +1 requires an oxidizing agent, and it has been speculated that the reaction solvent serves that function.[3]

In this work we have investigated the reaction of $(OC)_5WPPh_2H$ with potassium *tert*-butoxide and have isolated and characterized $[PPN][W_2(CO)_{10}PPh_2]$ (I), $[PPN][W_2(CO)_9(PPh_2H)PPh_2]$ (II), $K_2[W_2(CO)_8(PPh_2)_2]$ (III), and $W_2(CO)_8(PPh_2)_2$ (IV).



Products I, II, and III were generated when equimolar quantities (2.0 mmol) of $(OC)_5WPPh_2H$, KO-*t*-Bu, and [PPN]Cl were dissolved in CD_3CN and allowed to react for 3 days at ambient temperature. They were identified in the crude reaction mixture, contained in a sealed NMR tube, by ^{31}P NMR spectroscopy (Table I).[4] Procedures were developed for isolating these products, and their structures were further substantiated by IR spectroscopy (Table II).

Compound I was obtained by refluxing equimolar quantities (1.0 mmol) of $(OC)_5WPPh_2H$, KO-*t*-Bu, and [PPN]Cl with excess $W(CO)_6$ (1.8 mmol) in THF (50 mL) for 1.0 h. Recrystallization from CH_2Cl_2/Et_2O gave the pure yellow solid (55%). It is stable in air both in the solid state and in solution (CH_2Cl_2, $CHCl_3$, CH_3CN, THF, Et_2O). Its ^{31}P NMR spectrum consists of a signal at 20.1 ppm for PPN^+ and a signal at −63.5 ppm, flanked by ^{183}W satellites (J_{WP} = 168.7 Hz). The observed intensities (1:6:1) for the anion are consistent with two tungsten atoms coupled to phosphorus. This pattern provides a useful means of distinguishing such compounds from those which have a single tungsten atom coupled to phosphorus. Although many other anionic monobridged group 6 complexes, $[M_2(CO)_{10}X]^-$ (X = Cl^-, Br^-, I^-, CN^-, NCS^-, SR^-, H^-), have been synthesized,[5] the only example in which X is PR_2^- is $[Mo_2(CO)_{10}PH_2]^-$.[6] The infrared spectrum of the carbonyl region of I shows a spectral complexity which also has been observed for other $[M_2(CO)_{10}X]^-$ systems.[5]

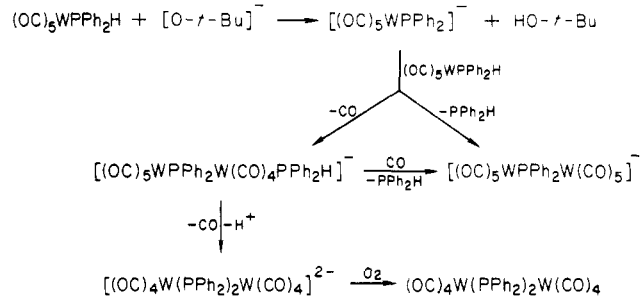
When equimolar quantities of $(OC)_5WPPh_2H$, KO-*t*-Bu, and [PPN]Cl were heated under reflux in THF for 3 h, KCl precipitated from solution, and upon evaporation of the filtrate, II was precipitated. Recrystallization of II from CH_2Cl_2/Et_2O gave pure yellow solid (39%). The ^{31}P spectrum of II consisted of a doublet at −61.6 ppm (J_{PP} = 19.5 Hz, J_{WP} = 163.2 Hz), attributed to bridging PPh_2[7] and a doublet at 7.4 ppm (J_{PP} = 19.5 Hz, J_{WP} = 228.0 Hz) which was assigned to coordinated PPh_2H. The magnitude of J_{PP} is consistent with a cis arrangement of phosphorus atoms.[8] A proton-coupled ^{31}P spectrum revealed the expected phosphorus–hydrogen coupling ($^1J_{PH}$ = 325.2 Hz, $^3J_{PH}$ = 6.4 Hz). The IR spectrum can be seen as a superimposition of absorptions for $W(CO)_4$ and $W(CO)_5$ moieties and provides further confirmation of the structure. II slowly decomposes in solution to give I and III.

Table II. Infrared Data[a] of Bridged Complexes

complex	metal carbonyl stretching freq cm^{-1}
I[b]	2064 (w), 2051 (m), 1963 (sh), 1934 (vs), 1901 (s), 1877 (s)
II[b]	2056 (m), 2004 (m), 1960 (w), 1924 (vs), 1874 (s), 1832 (m)
III[c]	1923 (m), 1880 (s), 1840 (m), 1793 (m)
IV[b]	2034 (s), 1957 (vs)

[a] Spectra were recorded with a Perkin-Elmer 337 infrared spectrometer and expanded with an E-H Sargent recorder. [b] CH_2Cl_2. [c] CH_3CN.

Scheme I



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Refluxing a THF solution of $(OC)_5WPPh_2H$ (1.0 mmol) and KO-*t*-Bu (1.0 mmol) for 6 h resulted in the precipitation of III (10%). The ^{31}P NMR spectrum of III shows signals at −99.2 ppm (J_{WP} = 156.0 Hz). The infrared spectrum of III, consisting of three medium and one strong absorption, matches in appearance that reported for $[Cr_2(CO)_8(PMe_2)]_2^{2-}$, an anion previously obtained electrochemically.[9] The yellow anion, III, reacts rapidly with air to give red IV but is stable in oxygen-free dry THF or CH_3CN. The infrared spectrum of IV is in agreement with literature reports.[2] ^{31}P resonance occurs at 180.0 ppm (J_{WP} = 162 Hz).

A reasonable reaction sequence for the production of I, II, III, and IV is presented in Scheme I.

Of particular interest is the dramatic change in the ^{31}P chemical shift which accompanies formation of a metal–metal bond. Thus our work adds further support to the notion that ^{31}P chemical shifts diagnose the presence or absence of metal–metal bonds in phosphido bridged complexes.[10]

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Registry No. I, 80049-78-1; II, 80049-80-5; III, 80049-81-6; IV, 80049-82-7; $(OC)_5WPPh_2H$, 18399-62-7.

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Role of Heteroatoms in the Formation of Higher Nuclearity Transition-Metal Carbonyl Cluster Compounds. The Condensation of Small Clusters

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Summary: The molecules $HOs_3(\mu_3\text{-S})(\mu\text{-HCNR})(CO)_9$, R = C_6H_5, Ia, and *p*-C_6H_4F, Ib, lose carbon monoxide when heated and condense to form the higher nuclearity carbonyl clusters $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=NR})_2(CO)_{17}$, R = C_6H_5, IIa, and *p*-C_6H_4F, IIb, and $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=NR})_2(CO)_{16}$, R = C_6H_5, III. The compounds have been characterized by IR and ^1H NMR spectroscopies, and IIb and III have also been characterized by X-ray crystallographic methods. For IIb: space group $P\bar{1}$ at 28 °C; a = 9.865 (7) Å, b = 14.735 (6) Å, c = 15.926 (10) Å, α = 69.08 (5)°, β = 79.63 (6)°, γ = 86.40 (6)°, Z = 2, ρ_{calcd} = 3.01 g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques. Refinement on 3584 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.032 and R_2 = 0.030. For III: space group $P2_1/n$ at 28 °C; a = 10.506 (4) Å, b = 23.145 (12) Å, c = 16.933 (5) Å, β = 97.60 (3)°, Z = 4, ρ_{calcd} = 3.03 g/cm^3. This structure was solved by a combination of direct methods and difference Fourier techniques. Refinement on 2347 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.052 and R_2 = 0.043. IIb contains two groups of "open" clusters of three metal atoms linked by a tetracoordinate bridging sulfur atom. The metal–metal bonding in each of the "open" cluster groups is analogous to that in the molecules I. In III the metal atoms are arranged in groups of four and two with the two groups linked by a tetracoordinate bridging sulfur atom. It is believed that III is formed by the decarbonylation of IIa. A reorganization of the metal–metal bonding then occurs in which an $Os(CO)_3$ unit is shifted from one group of three to the other.

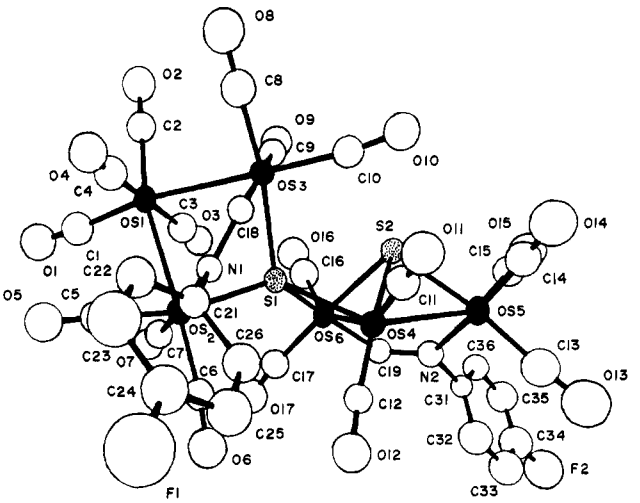
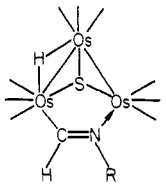


Figure 1. An ORTEP drawing of $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=N-}p\text{-}C_6H_4F)_2(CO)_{17}$, IIb, showing 50% electron density probability ellipsoids.

The decarbonylation of metal carbonyl compounds is the most successful and widely used method for the preparation of high nuclearity transition-metal carbonyl cluster compounds.[1] In this process, metal–metal bonds replace the metal–carbon bonds of the eliminated ligands. It is well-known that heteronuclear bridging ligands will enhance the stability of polynuclear metal complexes.[2] Recently it has been proposed that these heteronuclear bridging ligands can play an important role in the systematic synthesis of higher nuclearity cluster compounds.[3]

We wish to report that we have now observed an example of the aggregation of two transition-metal clusters which unequivocally shows the importance and role of the heteronuclear bridging ligand in preliminary cluster condensation and the eventual reorganization of the metal–metal bonds within the clusters.

We have recently reported the synthesis of the cluster compounds $HOs_3(\mu_3\text{-S})(\mu\text{-HC=NR})(CO)_9$, R = C_6H_5, Ia, and *p*-C_6H_4F, Ib.[4] When heated to reflux in octane solvent



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