mediates in olefin metathesis[14] (and possibly in some olefin polymerizations),[15] a new type of photochemical effect upon metal-catalyzed reactions may be possible: both olefin metathesis and polymerization can exhibit high stereoselectivity, which conceivably could be altered if the alkylidene intermediates were photoisomerized to new geometric isomers. Second, it is possible that the excited states of **1** and **2** might, like their ground-state counterparts, exist in two isomeric forms. These and related photochemical and photophysical questions are presently under investigation.

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Registry No. 1k, 74540-78-6; **1t**, 74561-64-1; **2k**, 74540-85-5; **2t**, 74561-68-5; **3**, 80387-86-6.

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Coordinatively Unsaturated Clusters of Rhodium Incorporating Chelating Bidentate Ligands. Synthesis of $[\{(CH_3O)_2PCH_2CH_2P(OCH_3)_2\}RhH]_4$ and $[\{(i\text{-}C_3H_7O)_2PCH_2CH_2P(O\text{-}i\text{-}C_3H_7)_2\}RhH]_2$

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Summary: The reaction of (1,2-bis(dimethoxyphosphino)ethane)(2-methylallyl)rhodium(I), $[\eta^3\text{-}(2\text{-}MeC_3H_4)Rh(dmope)]$, **1**, and (1,2-bis(diisopropoxyphosphino)ethane)(2-methylallyl)rhodium(I), $[\eta^3\text{-}(2\text{-}Me\text{-}C_3H_4)Rh(dipope)]$, **3**, with hydrogen produces, respectively, $[(dmope)RhH]_4$, **2**, and $[(dipope)RhH]_2$, **4**. The hydride resonance of **2** is an overlapping quintet of nonets, while for **4**, a broad, overlapping triplet of quintets is observed. The solution structures of these new rhodium hydride clusters are discussed in terms of the rhodium– and phosphorus–hydride coupling constants which suggest that **2** may have a tetrahedral array of rhodium atoms with face-bridging hydrides.

Our interest in the effect of chelating ligands[1] on the reactivity of metal complexes has recently turned to didentate phosphine and phosphinite derivatives of rhodium(I).[2,3] Specifically we have undertaken a study of the use of (2-methylallyl)rhodium(I) complexes incorporating chelating ligands as catalyst precursors[4] for the hydrogenation of unsaturated substrates. Herein we report the synthesis and characterization of two new catalytically active hydridorhodium derivatives that belong to the class of coordinatively unsaturated clusters of the general formula $[P_2RhH]_x$[5].

(1) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592.
(2) Fryzuk, M. D., submitted for publication in *Inorg. Chem.*
(3) Fryzuk, M. D. *Inorg. Chim. Acta* **1981**, *54*, L265–266.
(4) The use of allylrhodium(I) complexes of monodentate phosphines and phosphites as hydrogenation catalyst precursors is known.[5]
(5) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

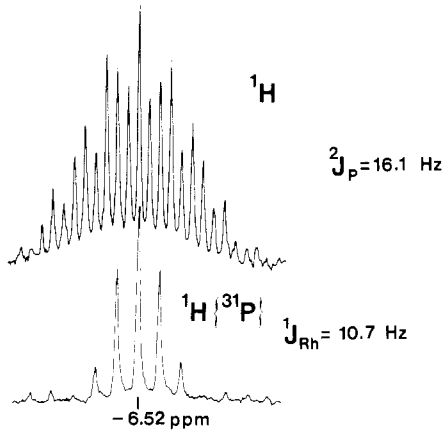
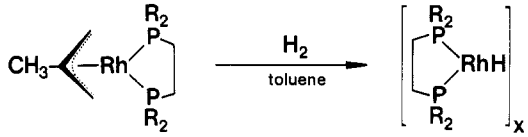


Figure 1. Hydride resonance of $[\{(CH_3O)_2PCH_2CH_2P(OCH_3)_2\}RhH]_4$, **2**; a binomial quintet (lower spectrum) is obtained when phosphorus decoupled.

When bright yellow toluene solutions of the (2-methylallyl)rhodium(I) complex of 1,2-bis(dimethoxyphosphino)ethane, $[\eta^3\text{-}(2\text{-}Me\text{-}C_3H_4)Rh(dmope)]$[2], **1**, are exposed to medium pressures of hydrogen, a slow color change to deep, black-red is observed; from these solutions, dark maroon crystals of the formula [(dmope)RhH][6] can be isolated in 60–70% yield. On the basis of ^1H NMR studies and a solution molecular weight determination[7] we formulate this complex as the tetramer $[(dmope)RhH]_4$, **2**. At room temperature the hydride resonance appears



2 : R= OCH_3, x=4
4 : R= O-i-C_3H_7, x=2

as a beautifully symmetric 23-line multiplet which simplifies to a binomial *quintet* when phosphorus is decoupled (Figure 1). This quintet is due to the coupling of *four* magnetically equivalent rhodium nuclei (^{103}Rh, 100% abundance, spin $^1/_2$) with the four equivalent hydrides. Thus the fully coupled spectrum is in fact an overlapping quintet of *nonets* due to the additional coupling of *eight* magnetically equivalent phosphorus nuclei. One must invoke a fluxional process which might involve rapid hydride migration about the cluster on the NMR time scale to explain the apparent symmetry in solution. Indeed, as the temperature is lowered, the 23-line multiplet broadens until finally, at −90 °C, a very broad triplet is observed which collapses to a broad singlet with phosphorus decoupling; in addition, the methoxy protons appear as a doublet at ambient temperatures, but a −90 °C, three doublets (phosphorus coupled) in the ratio 2:1:1 are observed. We are at present unable to account for this temperature-dependent behavior but note that freezing out the conformational flipping of the chelate ring may be

(6) **2**: mp 183 °C dec; ^1H NMR (C_6D_6) $P(OCH_3)$, 3.83 ppm (d, 48, J_P = 11.7 Hz); PCH_2, 1.51 ppm (br d, 16, J_P = 21.0 Hz); Rh*H*, −6.52 ppm (q of nonets, 4, J_{Rh} = 10.7 Hz, J_P = 16.1 Hz). Anal. Calcd for $C_6H_{17}O_4P_2Rh$: C, 22.66; H, 5.39. Found: C, 22.25; H, 5.27.
(7) The molecular weights of both **2** and **4** were determined via isothermal distillation using the Signer method.[8] Accurately made up solutions (C_6D_6) of the cluster and a standard were prepared and maintained at 24.9 °C for 7–10 days in an inverted U-tube assembly under vacuum. Molecular weight found for **2**: 1280 ± 50 (theoretical 1272). Molecular weight found for **4**: 830 ± 30 (theoretical 861). Analysis by ^1H NMR immediately after the determination showed no measurable decomposition.
(8) (a) Signer, R. *Justus Liebigs Ann. Chem.* **1930**, *478*, 246. (b) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

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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

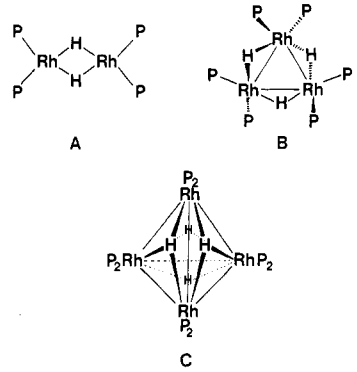

Figure 2. Structures of the $[P_2RhH]_x$ family of clusters: structures A and B have been verified crystallographically whereas structure C is tentative.

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.

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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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(12) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687.

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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