C1, and the terminal methyl carbons C2 and C3.

The geometry about the tin atoms in structure **5**, on the other hand, is distorted trigonal bipyramidal, with edge sharing between tin polyhedra provided by the bridging methylene carbon and Me_2SO oxygen atoms. The bridging methylene group occupies an equatorial position in both the Sn1 and Sn2 polyhedra while O1 is found in an apical position in both cases. The tin environments are nonequivalent: Sn1 bound to a methyl carbon, C4, and C13 in the equatorial plane, in addition to the bridging C1, while the trigonal plane about Sn2 is defined by C1 and two methyl carbons C2 and C3. As anticipated, the Sn1–C13 distance of 2.372 (4) Å is significantly shorter than the Sn1–C12 and Sn2–C11 distances, 2.434 (4) Å average, reflecting the equatorial and axial occupancies, respectively.

The crystallographically identical tin atoms in **6** enjoy pseudooctahedral geometry, with a single bridging group, the methylene carbon C5, connecting the vertex-sharing polyhedra. A noteworthy feature of the structure is the short terminal Sn–O(Me_2SO) bond length of 2.118 (6) Å (average) in contrast to bridging Sn–O(Me_2SO) distances of 2.588 (6) and 2.572 (8) Å in **4** and **5**, respectively.

In comparing the structures, the tin–tin distances increase from 3.426 (1) Å in the triply-bridged structure **4** to 3.529 (1) Å in the doubly bridged **5** to 3.760 (1) Å in the singly bridged case **6**, a trend reflected in the Sn–methylene carbon–Sn valence angle which opens from 108.5 (4)° in **4** to an exceptionally large value of 130.8 (6)° in **6**.

These results show that the composition and structure of the most readily formed complexes are strongly dependent on the number of chlorines on the tin atoms. Presumably the high Lewis acidity of the trichlorostannyl groups of **3** leads to pseudooctahedral coordination in **6**. But this occurs at the expense of expanding the Sn–C–Sn bond angle to the remarkably large value of 130.8°. In **4** a more distorted octahedral configuration is achieved by two bridging oxygens of Me_2SO molecules. But **5** finds both tins pentacoordinate. Further studies should reveal structure/composition patterns and may lead to some understanding of the driving forces involved.

Crystal Data. $Sn_2(CH_2)(CH_3)_2Cl_4(Me_2SO)_2$, **4**, crystallizes in the orthorhombic space group *Pbnm* with a = 9.821 (2) Å, b = 12.411 (2) Å, c = 15.540 (3) Å, V = 1894.2 Å^3, D_{calcd} = 2.03 g cm^{-3}, Z = 4, and μ = 34.2 cm^{-1} (Mo Kα, λ = 0.71073 Å).[8] A total of 1498 independent reflections were measured on a Nicolet R3/m diffractometer and 1109 reflections with $F_o \geq 6\sigma(F_o)$ were used in the subsequent solution and least-squares refinement, which have produced current discrepancy factors of 0.048 and 0.047 for R and R_w, respectively.

$Sn_2(CH_2)(CH_3)_3Cl_3(Me_2SO)$, **5**, crystallizes in the triclinic space group $P\bar{1}$ with a = 7.551 (2) Å, b = 7.945 (2) Å, c = 13.354 (3) Å, α = 80.63 (2)°, β = 89.13 (3)°, γ = 72.96 (2)°, and V = 755.3 Å^3 to give D_{calcd} = 2.11 g cm^{-3} for Z = 2 (μ = 39.6 cm^{-1}, Mo Kα). A total of 1932 reflections were collected as above of which 1609 with $F_o \geq 6\sigma(F_o)$ were used in the structure solution and refinement. The current discrepancy factors are R = 0.045 and R_w = 0.055.

$Sn_2(CH_2)Cl_6(Me_2SO)_4$, **6**, crystallizes in the monoclinic space group $C2/c$ with a = 20.998 (5) Å, b = 7.925 (3) Å, c = 16.535 (4) Å, β = 98.79 (3)°, and V = 2719.3 Å^3 with D_{calcd} = 1.90 g cm^{-3} for Z = 4 (μ = 27.5 cm^{-1}, Mo Kα). The structure solution and least-squares refinement are based on 1277 reflections with $F_o \geq 6\sigma(F_o)$, collected on the Nicolet R3/m diffractometer. The current residuals are 0.034 and 0.038 for R and R_w, respectively.

All data was collected on a Nicolet R3/m automated four-circle diffractometer, in the range $0° \geq 2\theta \geq 50°$, and processed on a Nova 3 computer, using local versions of the SHELXTL crystallographic computing package. Lorentz and polarization corrections and absorption corrections were carried out in the usual fashion. Details of the usual procedures may be found in ref 9 and 10.

Acknowledgment. Support of this work has been provided by the National Science Foundation (Grant CHE 750075402) and by the National Institutes of Health (partially by Grant GM22566 and funding for the diffraction from Grant GM27459). Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. 1, 79992-66-8; 2, 79992-67-9; 3, 79992-68-0; 4, 79992-48-6; 5, 79992-49-7; 6, 79992-50-0.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors are available (28 pages). Ordering information is given on any current masthead page.

(8) The alternative space group $Pbn2_1$ was discarded on the basis of the Hamilton significance test.

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(10) M. W. Bishop, J. Chatt, J. R. Dilworth, P. Dahlstrom, J. Hyde, and J. Zubieta, *J. Organomet. Chem.*, **213**, 109 (1981).

A New Organometallic Photoreaction: Interconversion of Metal–Alkylidene Geometric Isomers

Fred B. McCormick, William A. Kiel, and J. A. Gladysz*[1]
Department of Chemistry, University of California Los Angeles, California 90024

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Summary: Benzylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$ (**1**), which exists as a >99:1 mixture of anticlinal (**1t**, "thermodynamic") and synclinal (**1k**, "kinetic") Re=C bond geometric isomers at room temperature, is isomerized when irradiated between −20 and −78 °C in CD_2Cl_2, CD_3CN, or $(CD_3)_2CO$ to a (55 ± 3):(45 ± 3) **1t/1k** photostationary state. Propylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$ (**2**), which exists as a (95±1):(5±1) mixture of anticlinal (**2t**) and synclinal (**2k**) isomers at room temperature, is similarly isomerized to a (59 ± 2):(41 ± 2) photostationary state. Absorption spectra of **1t** and **2t** and unsuccessful attempts to photosensitize **1t** → **1k** (azulene, rose bengal, eosin Y) are reported. Thermal isomerization rates for **1k** → **1t**, measured between 4 °C ($t_{1/2}$ = 443 min) and 29.5 °C ($t_{1/2}$ = 17 min), yield $\Delta H^{\ddagger}$ = 20.9 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ = −3.8 ± 0.2 eu. The benzylidene complex $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHC_6H_5)]^+CF_3CO_2^-$ (**3**) decomposes upon low-temperature irradiation.

We recently reported the synthesis of a series of rhenium–alkylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=$

(1) Fellow of the Alfred P. Sloan Foundation (1980–1982) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985); after 6/30/82, address correspondence to this author at the Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

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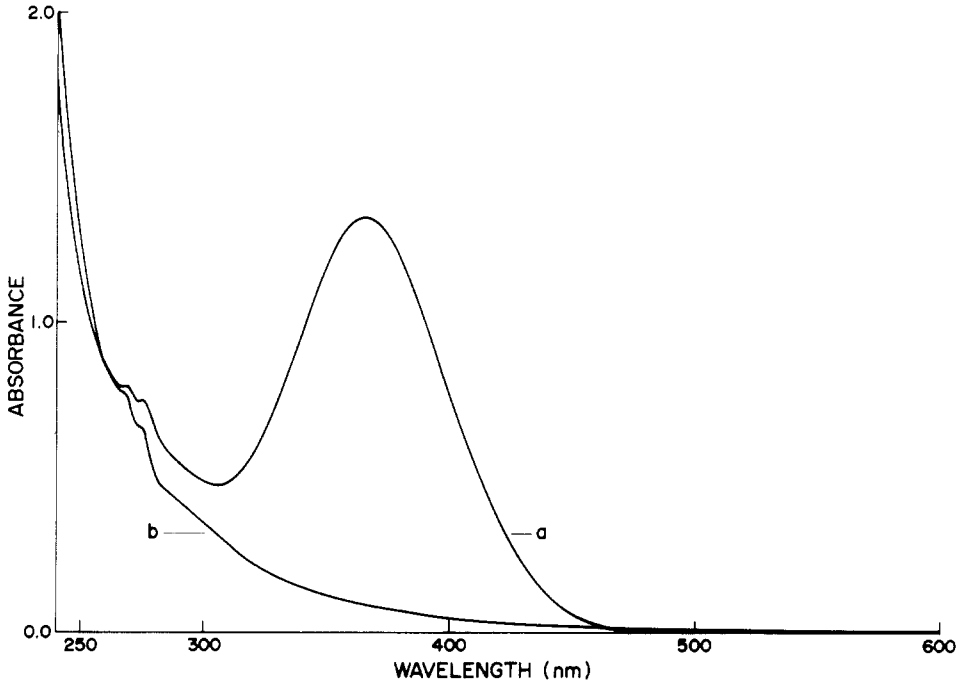
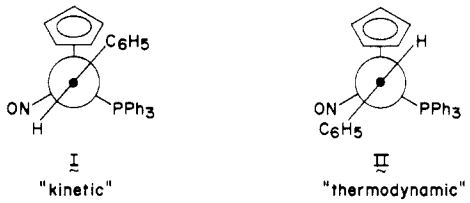


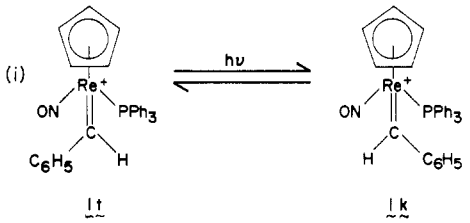
Figure 1. Absorption spectra of **1t** (trace a) and **2** (trace b) in CH_3CN.

CHR)]$^+PF_6^-$, which are capable of existing in two isomeric forms:[2] a "kinetic" isomer (**k**), which is stereospecifically generated at −78 °C by the reaction of (η-C_5H_5)Re(NO)(PPh_3)(CH_2R) alkyls (R = C_6H_5 or primary alkyl) with $Ph_3C^+PF_6^-$, and a "thermodynamic" isomer (**t**) obtained in 94–100% equilibrium yields upon warming the kinetic isomer to 10–25 °C. X-ray crystallographic[3] and theoretical[4] studies indicate these isomers to have the general structures I(**k**) and II(**t**), respectively (Newman



projections down the alkylidene–rhenium bond). Since geometric isomerism arising from metal–carbon multiple bonding is without precedent, we have undertaken additional studies of this phenomenon. In this communication, we report that these isomers can be photochemically interconverted. Photostationary states result, as has previously been observed upon olefin irradiation.[5]

Direct irradiation of CD_2Cl_2, CD_3CN, or $(CD_3)_2CO$ solutions[6] of isolated "thermodynamic" benzylidene [(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**1t**) between −20 °C and −78 °C afforded, after 3 h, clean (55 ± 3):(45 ± 3) mixtures of **1t** and **1k** (eq 1) as determined by NMR in-



tegration of the C_5H_5 proton resonances. Continued irradiation (up to 9 h) did not alter the **1t**/**1k** ratio. These solutions were allowed to relax back to thermal equilibrium in the dark (**1t**/**1k** > 99:1); a sample to which *p*-di-*tert*-butylbenzene standard had been added indicated >95% of the original **1t** to be present. Additional irradiation cycles could be conducted without noticeable sample deterioration.

Similar experiments were conducted in $(CD_3)_2CO$ with propylidene [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_3$)]$^+PF_6^-$ (**2**),[6] which exists (depending somewhat upon solvent) as a 96–94:4–6 mixture of **2t**/**2k** at room temperature. Photostationary states (**2t**/**2k**) of (59 ± 2):(41 ± 2) were obtained. Considerable sample darkening accompanied the irradiation of **2**; however, after allowing relaxation back to thermal equilibrium, ^1H NMR integration against *p*-di-*tert*-butylbenzene standard indicated >80% of the original **2** to be present.

Absorption spectra of **1t** and **2** were measured.[7] Benzylidene **1t** (yellow crystals) displayed a λ_{max} (ϵ 13000) at 365 nm in CH_3CN (Figure 1). Propylidene **2** (cream-colored) showed only a featureless tail into the visible. The absorption spectrum of pure **1k** could not be obtained; low-temperature spectra of (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$)/$Ph_3C^+PF_6^-$ reaction mixtures were complicated by starting material and byproduct (e.g., Ph_3CH) absorbances. However, a series of spectra (Figure 2) were recorded as a CH_2Cl_2 **1k**/**1t** photostationary state solution was warmed from −78 °C to room temperature. An isos-

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(6) All irradiations were conducted through Pyrex with a Hanovia 450-W lamp. Samples were contained in septum-capped 5-mm NMR tubes; those which were rigorously degassed gave results identical with those which were undegassed.

(7) (a) Spectra were obtained on a Cary 219 spectrophotometer. (b) Benzylidene **1t** does not luminesce (single crystal, 10 K). We thank Professor J. I. Zink for conducting this experiment and informing us of the results.

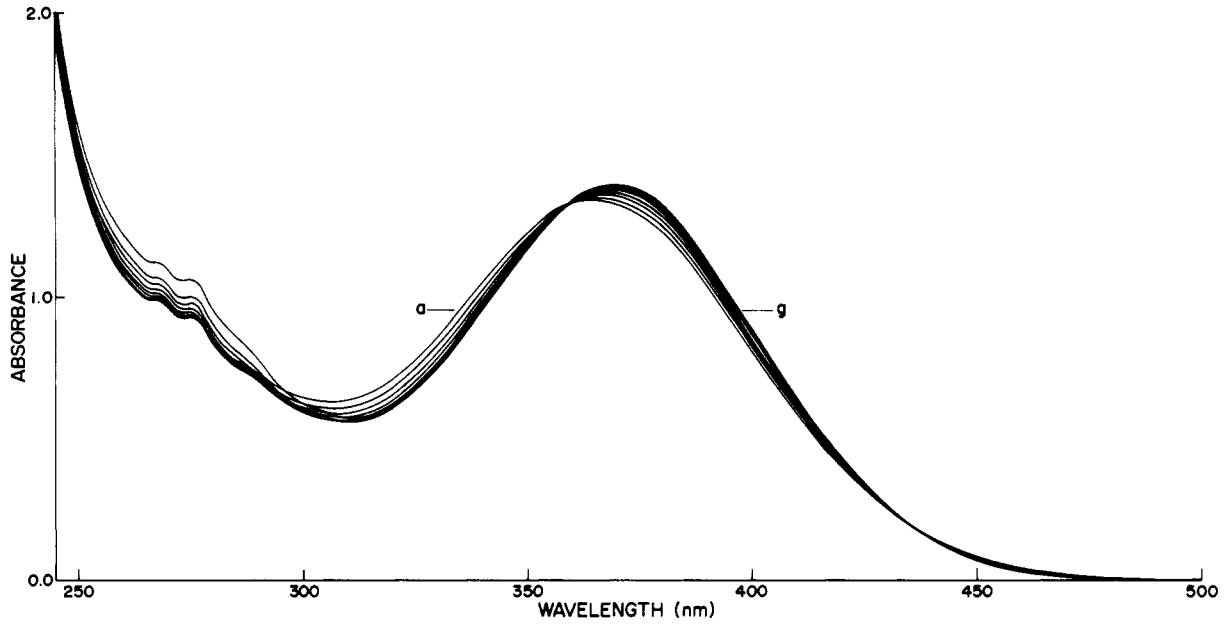

Figure 2. Absorption spectra recorded as a (55 ± 3):(45 ± 3) **1t**/**1k** mixture in CH_2Cl_2 (prepared by photolysis at −78 °C) was warmed to room temperature: initial spectrum, trace a; final spectrum, trace g.

Table I. Rate Constants for the Re=C Bond Rotation **1k** → **1t** in CD_2Cl_2[a]

entry	temp, ±0.1 °C	$10^5 k_{obsd}$, s^{-1}
1	29.5	69.2 ± 0.6
2	24.0	37.6 ± 0.6
3	19.0	20.5 ± 0.2
4	19.0	19.2 ± 0.2
5[b]	19.0	20.9 ± 0.3
6	14.0	11.5 ± 0.2
7	10.0	4.81 ± 0.10
8	10.0	6.93 ± 0.10
9	4.0	2.61 ± 0.03

[a] $[1k]_0$ = 0.038 − 0.042 M; generated in situ from (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) and $Ph_3C^+PF_6^-$ at the temperature of measurement unless noted. Entries 1-5 were followed through $>2t_{1/2}$, others were followed through at least one $t_{1/2}$. [b] **1k** photochemically generated at −78 °C.

bestic point is evident as **1k** isomerizes to **1t**, and it can be concluded that λ_{max} for **1k** is at shorter wavelength than that for **1t**.[8]

Since photoisomerization of **1t** offered the only means of generating **1k** without significant quantities of byproducts, the first-order rate constant for equlibration back to **1t** (in CD_2Cl_2) was measured by ^1H NMR at 19 °C (entry 5, Table I). The k_{obsd} determined was in good agreement with the k_{obsd} obtained (19 °C) from **1k** prepared in situ from (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) and $Ph_3C^+PF_6^-$ (entries 3 and 4, Table I). Hence, data obtained by the latter route can reliably be used to calculate activation parameters for rotation about rhenium–alkylidene bonds. Rate constants for **1k** → **1t** were measured from 4 °C ($t_{1/2}$ = 443 min) to 29.5 °C ($t_{1/2}$ = 17 min), as summarized in Table I; these yielded $\Delta H^\ddagger$ = 20.9 ± 0.4 kcal/mol and $\Delta S^\ddagger$ = −3.8 ± 0.2 eu.

The possibility that geometric isomerization of L_nM=C(X)Y complexes might be a general photoreaction was considered. However, isomerization would be degenerate for substrates in which the =CXY plane is bisected by a L_nM fragment mirror plane such as octahedral group 6B carbonyls $(CO)_5M$=C(X)Y (for which some photochemical studies have been reported).[9] A second consideration is that there must be a sufficient activation energy barrier to prevent rapid thermal isomerization of the less stable geometric isomer to the more stable one. However, these barriers are generally much lower than that measured for **1k** → **1t**. For instance, $\Delta G^\ddagger$ for methylidene rotation in $[(\eta\text{-}C_5H_5)Fe[P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2](=CH_2)]^+CF_3SO_3^-$ is only 10.4 ± 0.1 kcal/mol over the temperature range of −65 to −14 °C;[10] furthermore, this $\Delta G^\ddagger$ is likely higher than normal because of the strong donor ligands (and absence of good π-accepting ligands) on the iron. Nonetheless, we attempted a similar photolysis with the Brookhart benzylidene complex $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHC_6H_5)]^+CF_3CO_2^-$ (**3**).[11] Irradiation of **3** generated from (η-C_5H_5)Fe(CO)(PPh_3)[CH(OCH_3)C_6H_5] and 3.5 equiv of CF_3CO_2H in degassed CD_2Cl_2 at −78 °C resulted (over the course of 30 min) in complete disappearance of the benzylidene ^1H NMR resonance (δ 17.30). The color of the sample turned from deep red to green-brown, and no new low-field ^1H NMR resonances appeared. Thus **3** is not stable to conditions which photoisomerize **1t** and **2**.

In summary, this study has shown that alkylidene complexes can exhibit a heretofore totally unexpected mode of photoreactivity. The closest analogy of which we are aware is the photoequilibration of endo/exo iron and ruthenium π-allyl isomers.[12] Two speculative extensions of our observations merit note. First, photoinitiation of transition metal mediated catalysis is well documented.[13] However, since metal alkylidenes are propagating inter-

(8) Studies are in progress to determine the nature of the photoreactive state for the conversion **1t** → **1k**. The following attempts at triplet sensitization ($(CD_3)_2CO$ solutions, −78 °C) have been unsuccessful: azulene, 1.2 equiv, 574-nm Corning 2-73 filter; rose bengal, 1.0 equiv, 514-nm Corning 3-69 filter; eosin Y, 1.0 equiv, 514-nm Corning 3-69 filter.

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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.

Acknowledgment. We are grateful to the Department of Energy and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Professors J. I. Zink and M. A. El-Sayed for helpful discussions and the Regents of the University of California for a fellowship (W.A.K.).

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 $[\{(i\text{-}C_3H_7O)_2PCH_2CH_2P(O\text{-}i\text{-}C_3H_7)_2\}RhH]_2$

Michael D. Fryzuk

Department of Chemistry, University of British Columbia Vancouver, British Columbia, Canada V6T 1Y6

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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].

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(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.

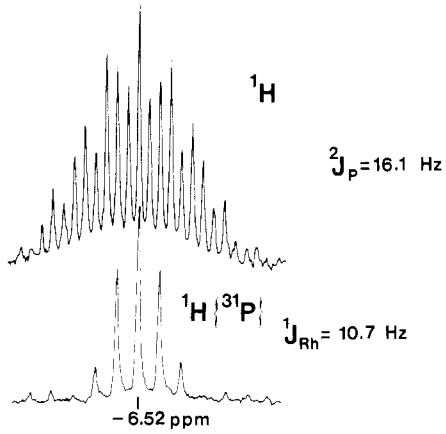
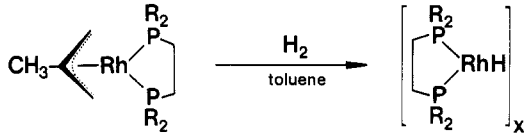


Figure 1. Hydride resonance of $[\{(CH_3O)_2PCH_2CH_2P(OCH_3)_2\}RhH]_4$, **2**; a binomial quintet (lower spectrum) is obtained when phosphorus decoupled.

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.
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