1.18 mmol), and 40 mL of *n*-hexane in air. The solution was refluxed under nitrogen with stirring for 16 h. During this time, a yellow solid gradually precipitated. This was collected by filtration, washed with several small portions of hexane, and air-dried to give complex **5** as an air-stable yellow microcrystalline solid in 72% yield (395 mg, 0.352 mmol). The infrared spectrum of the filtrate showed only unreacted starting material. Anal. Calcd for $C_{36}H_{25}IO_6Os_2P_2$: C, 38.50; H, 2.23. Found: C, 39.06; H, 2.49. IR (CH_2Cl_2): ν_{CO} 2089 (w), 2056 (s), 2012 (vs), 1994 (ssh), 1968 (m sh) cm^{-1}. MS (EI): *m/z* 1126 (M^+, ^{192}Os), 1098 ($M^+ - CO$), 1070 ($M^+ - 2CO$), 1042 ($M^+ - 3CO$), 1014 ($M^+ - 4CO$), 986 ($M^+ - 5CO$), 960 ($M^+ - 6CO$).

Synthesis of $Os_2(\mu\text{-}PPh_2)(CH_3)(CO)_6(PPh_3)$ (6). A 100-mL Schlenk flask was charged with complex **5** (54 mg, 0.053 mmol), 20 mL of THF, and MeLi (45 μL of a 1.2 M Et_2OH solution). The reaction mixture was stirred for ca. 5 min at room temperature after which time the solvent was removed under vacuum and the residue extracted with several small portions of benzene. The benzene was removed by rotary evaporation to yield complex **6** as a yellow oil. Attempts to crystallize this oil were not successful. The product was shown to be pure by solution infrared spectroscopy and subsequently characterized by ^{31}P NMR, ^1H NMR, and mass spectroscopy. IR (THF): ν_{CO} 2074 (w), 2035 (s), 1997 (vs), 1964 (s), 1946 (m) cm^{-1}. MS (EI): *m/z* 1014 (M^+, ^{192}Os).

X-ray Diffraction Study of 1. A crystal of **1** grown from hexane was mounted on a glass fiber. Preliminary photographic work and systematic absences uniquely identified the space group as $P2_1/c$. The unit-cell parameters reported in Table I were obtained from the least-squares fit of the angular settings of 25 reflections ($20° \le 2\theta \le 30°$). An empirical absorption correction based on ψ-scans of seven close-to-axial reflections was applied to the intensity data.

Direct methods (SOLV) revealed the Os and I atom locations. The remainder of the non-hydrogen atoms were located in subsequent difference Fourier syntheses. The model used in the final refinement by a blocked-cascade routine included all non-hydrogen atoms as anisotropic contributions and hydrogen atoms as idealized (d(C–H) = 0.96 Å) isotropic contributions. The final data/parameter ratio was 11.71/1. The mean Δ/σ of the final cycle was 0.023, and the slope of a normal probability plot was 1.236. All programs and scattering factors were obtained from the SHELXTL (version 4.1) and P3 program packages (Nicolet Corp., Madison, WI). Final atomic coordinates are given in Table III.

Acknowledgment. The National Science Foundation (Grant CHE8501548) is gratefully acknowledged for support of this research and for contributing to the purchase of the X-ray diffractometer at the University of Delaware. A.W.H. thanks Loyola University of Chicago for summer support through a Faculty Development Research Grant.

Registry No. **1**, 102851-52-5; **3**, 22587-71-9; **4**, 22391-77-1; **5**, 102851-54-7; **6**, 102851-55-8; $Os_2(\mu\text{-}PPh_2)_2(CO)_6$, 102851-53-6; $Os_3(CO)_{12}$, 15696-40-9; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond lengths and angles, and calculated hydrogen atom positions for **1** (2 pages). Ordering information is given on any current masthead page.

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Oxide-Dependent Deposition and H_2-Promoted Aggregation of Organorhodium Complexes

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Received November 13, 1985

We have recently described the chemistry of organorhodium complexes deposited on a variety of oxide surfaces, and we have demonstrated that variation in non-oxide ligation about the metal center can be used to control reactivity of the bound complex.[1] Although in previous work we had noted that a variety of oxides could be used for chemical attachment of organorhodium complexes,[2] we had not extensively studied how variation in the oxide itself affects the structure or reactivity of complexes bound thereto, and deposition control was attained only by adjusting *total* content of hydroxyl groups on the oxide. The more subtle notion was not considered that *relative* locations might vary of reactive hydroxyl groups on oxides of different structure, although this distribution of reactive sites would control deposition of 1 equiv of an organometallic with regard to another. Silica and alumina are among the most commonly used oxides for chemical attachment to reactive organometallic complexes,[3] and we have found that an interesting oxide-dependent deposition phenomenon distinguishes these two materials: although for both we have utilized samples containing a large excess of reactive hydroxyl groups relative to total rhodium deposited, we note that, for silica, deposition of rhodium complexes occurs selectively to generate *dimers*; on alumina (of comparable total surface hydroxyl group concentration), *monomers* are formed. In the course of these studies we also have found that hydrogen, a typical reagent for "activation" of oxide-bound organometallic species, enables migration of surface-"bound" organorhodium complexes and fosters the conversion of deposited "weak dimers" to aggregates.

Experimental Section

Infrared, UV-vis, and mass spectra were recorded on Digilab FTS-20C, Hewlett Packard, and AEI MS9 instruments, respectively. GC and GC/MS spectra were recorded by Hewlett Packard 5840A and 5992B instruments respectively. IR spectra of oxide-bound complexes were recorded by using self-supporting pressed disks with unreacted oxide samples in the reference beam. Oxides used were Aerosil 300 (SiO_2) and Aluminoxid C (Al_2O_3), Degussa, and were dried in vacuo prior to use. All reactions were performed at room temperature under N_2 except where noted otherwise.

Preparation of $Rh(C_3H_5)(CO)_2$ (1). $[Rh(CO)_2Cl]_2$ (0.25 g) was dissolved in dry Et_2O (15 mL) under N_2. The reaction mixture was cooled to 0 °C, and 1 equiv of C_3H_5MgCl/Et_2O was added dropwise. The reaction mixture was stirred for 30 min, and the solvent was then removed in vacuo (ca. 30 torr). The product was extracted with *n*-pentane and obtained by evacuation; it was sublimed before use.

Deposition of 1 onto Oxide Supports. Sublimed **1** was dissolved in pentane; the concentration of the solution was determined by UV–visible spectroscopy from a calibrated plot of concentration vs. absorbance at λ = 388 nm, and a measured amount of reactive solution was added to a slurry of oxide in pentane under N_2. After 24 h of stirring, excess **1** was removed by washing with pentane and was quantified by UV–visible spectroscopy.

Treatment of dried SiO_2 (Degussa Aerosil 300; dried at 200 °C (0.02 torr), 24-h period) with a pentane solution of $Rh(C_3H_5)(CO)_2$ for 24 h resulted in an off-white solid showing IR absorptions at 2107 (sh), 2091 (s), and 2033 (s) cm^{-1}. Treatment of dried Al_2O_3 (Aluminoxid C; dried at 200 °C (0.02 torr), 24–h period) with a pentane solution of $Rh(C_3H_5)(CO_2)_2$ for 24 h resulted in a pale yellow solid showing IR absorptions at 2091 (s) and 2021 (s) cm^{-1}.

Preparation of ^{13}CO-Enriched Samples. A mixture of $^{12}CO/^{13}CO$ was made up and this same mixture used for all the following reactions. The mixture contained a large excess of CO relative to the rhodium complexes.

(a) ^{13}CO-Enrichment of $[Rh(CO)_2Cl]_2$. $[Rh(CO)_2Cl]_2$ (0.5 g) was dissolved in hexane (50 mL), the solution was degassed by freeze–thaw cycles and frozen, the $^{12}CO/^{13}CO$ mixture was introduced, and the vessel was then sealed. The reactants were warmed to room temperature and stirred for 4 h. The solvent was removed in vacuo and the product

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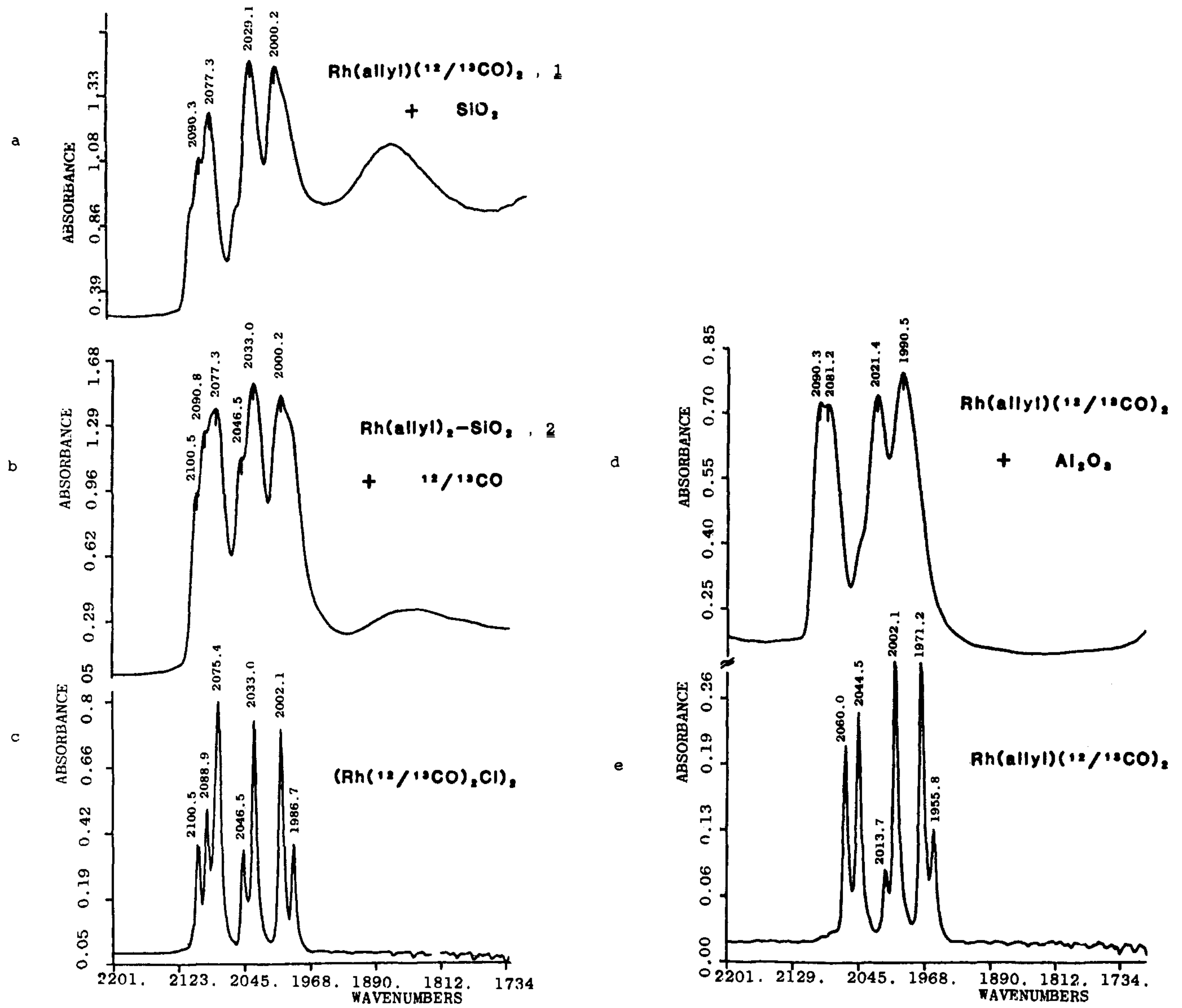


Figure 1. Infrared spectra of $^{12}CO/^{13}CO$-labeled rhodium complexes: (a) reaction of (allyl)Rh$(CO)_2$ with silica; (b) reaction of silica-supported diallylrhodium with $^{12}CO/^{13}CO$; (c) Rh$(^{12}CO/^{13}CO)_2Cl)_2$; (d) reaction of (allyl)Rh$(^{12}CO/^{13}CO)_2$ with alumina; (e) Rh(allyl)$(^{12}CO/^{13}CO)_2$.

examined as a hydrocarbon solution by infrared spectroscopy (Figure 1c).

(b) Preparation of ^{13}CO-Enriched 1. The sample of $[Rh(CO)_2Cl]_2$ used above was converted to **1** by reaction with C_3H_5MgCl/Et_2O. The isotopic enrichment level of $[Rh(CO)_2Cl]_2$ and **1** was determined by mass spectrometry as 35% ± 2% (Figure 1e).

Synthesis of [SiO]Rh(allyl)$_2$ (2). Degussa Aerosil 300 (1.5 g, dried at 200 °C (0.02 torr), 24-h period) was placed in a 100-mL Schlenk flask containing a magnetic stirring bar. Triallylrhodium[2] (60 mg, 0.23 mmol) was added to the flask in 40 mL of toluene. The flask was quickly capped, and the mixture was stirred at ambient temperature for 24 h. Volatiles were then completely removed in vacuo (10^{-6} torr) through a series of traps (−78, −196 °C). The evolved propylene was quantified in a calibrated PV manometer (typically >0.90 equiv of Rh) and verified by GC and GC/MS analysis. Species **2** was then washed with excess pentane, and excess solvent was removed in vacuo at 10^{-6} torr.

(a) Reaction of 2 with CO. A small sample of **2** was pressed into a pellet suitable for IR analysis. The pellet was placed in a flask under an atmosphere of CO for 12 h. After evacuation of the flask for 1 h, IR analysis showed the formation of [SiO]Rh$(CO)_2$ (**3**). ν_{CO} = 2106 (sh), 2089 (s), 2031 (s) cm^{-1} (see Figure 2c).

(b) Reaction of 2 with $^{13}CO/^{12}CO$. Species **2** was exposed to the $^{13}CO/^{12}CO$ gas mixture for 4 h. The resultant volatile product mixture (1,5-hexadiene and CO) was removed in vacuo to give **3** (see Figure 1b).

(c) Synthesis of [SiO]RhH$_2$ (4) from [SiO]Rh(allyl)$_2$ without Using H$_2$. Species **2** was placed in a 100-mL Schlenk flask containing 20 mL of freshly distilled *n*-octane. The mixture was heated to reflux for 20 h. The solvent was removed by vacuum distillation, and the solid was washed with excess pentane to yield olive drab **4**. ν_{Rh-H} = 2089 (s), 2025 (s), 1855 (w, br) cm^{-1} (see Figure 2a).

(d) Reaction of [SiO]RhH$_2$ Prepared from Octane with H$_2$. Species **4** (0.122 mmol) was placed in a 100-mL flask and treated with 1 atm of H_2 for 5 days. Evacuation for 1 h gave **5**. ν_{Rh-H} = 2029 (s), 1875 (s, br) cm^{-1} (see Figure 2b). A small amount of C_3 equivalents (ca. 10%) was also recovered, indicating that **4** had been obtained in ca. 90% yield from **2**.

(e) Reaction of 4 with CO. A pellet suitable for IR analysis of **4** was placed in a 50-mL flask under an atmosphere of CO for 12 h. Evacuation of the flask for 1 h yielded **3** (see Figure 2d).

(f) Carbonylation of Hydrogenated [SiO]RhH$_2$. The IR pellet of **5** was placed in a 50-mL flask under an atmosphere of CO for 12 h; upon evacuation for 1 h, **6** was formed. ν_{CO} = 2045 (s), 1875 (m, br) cm^{-1} (see Figure 2e).

(g) Reaction of 3 with H$_2$. Species **3** (0.19 mmol) was placed in a 50-mL flask under H_2 (1 atm) for 5 days. Evacuation for 1 h yielded **6**, which was slightly contaminated with residual **3**.

Results and Discussion

Rh$(C_3H_2)(CO)_2$ and SiO$_2$. The similarity of the spectrum obtained from reaction between the title compounds and that observed for $[Rh(CO)_2Cl]_2$ suggested a possible dimeric structure for the silica-bound rhodium dicarbonyl. To probe this, a sample of ^{13}CO-enriched $[Rh(CO)_2Cl]_2$ was prepared, examined by IR methods (Figure 1c), and converted into $Rh(C_3H_5)(CO)_2$ (Figure 1e). An aliquot was used to prepare a SiO_2-supported carbonyl **3** (Figure 1a). Comparison of spectra for the supported sample with those of ^{13}CO-enriched $[Rh(CO)_2Cl]_2$ and $Rh(C_3H_5)(CO)_2$ clearly shows the *monomeric* nature of the latter and the *dimeric*

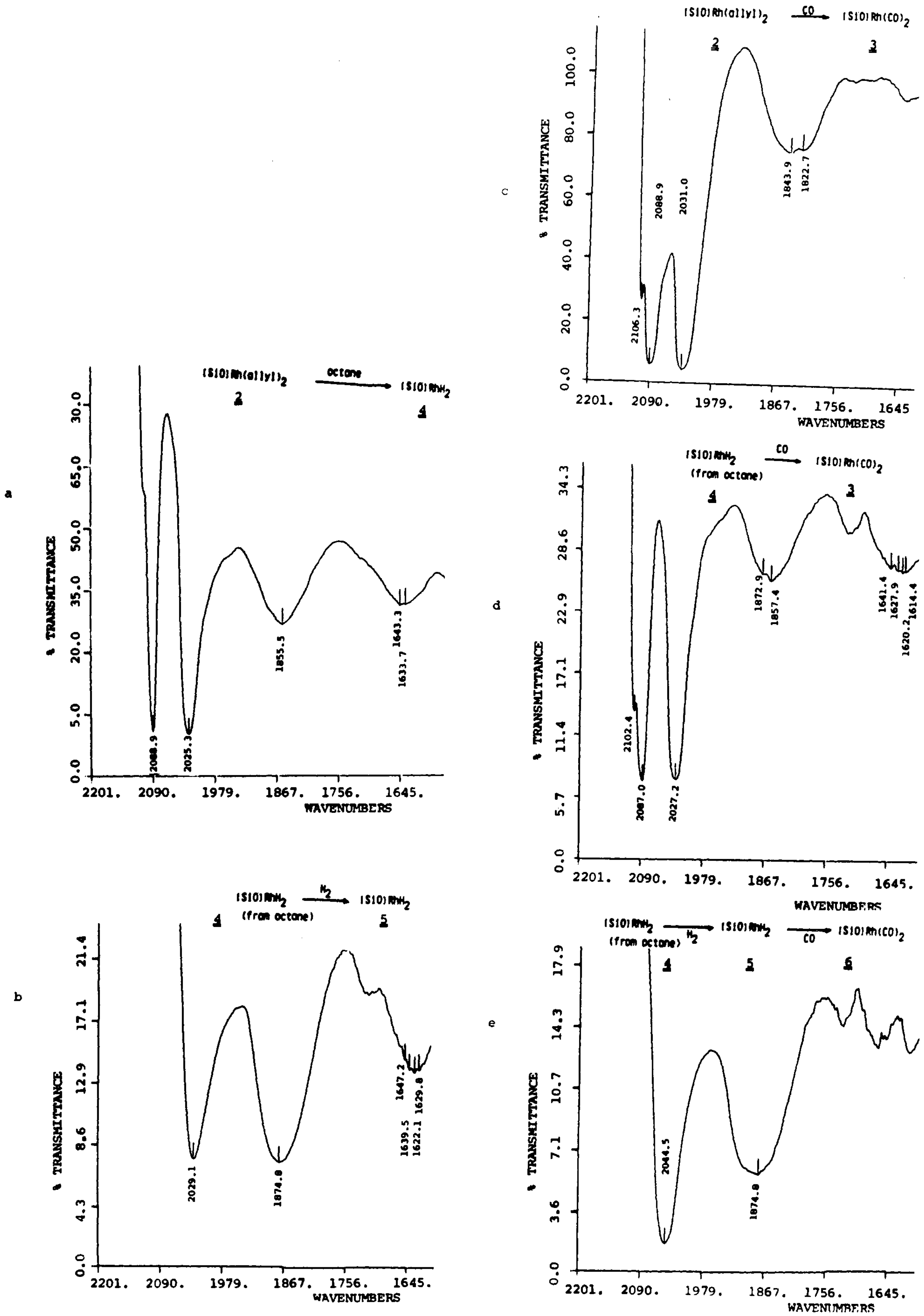
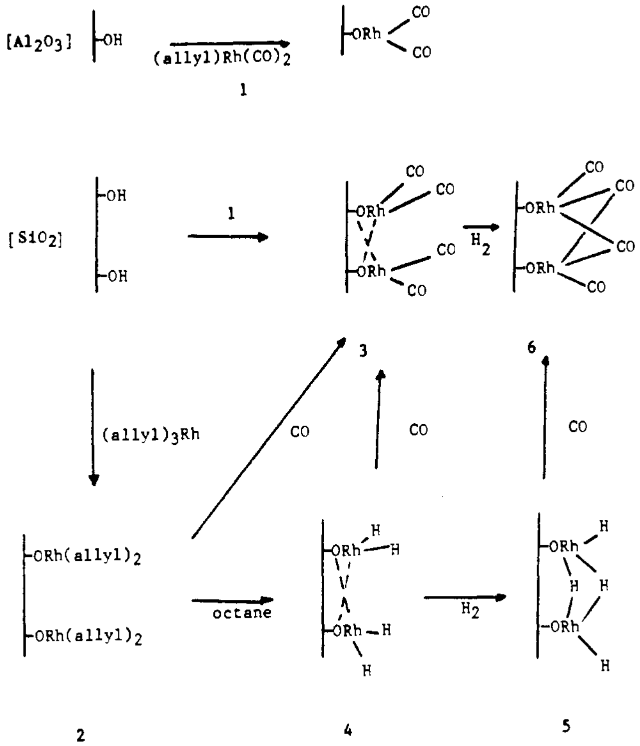


Figure 2. Infrared spectra of silicon-supported rhodium complexes before and after treatment with H_2: (a) reaction of silica-supported diallylrhodium with octane; (b) reaction of silica-supported rhodium dihydride (prepared in octane) with H_2; (c) reaction of silica-supported diallylrhodium with CO; (d) reaction of silica-supported rhodium dihydride (prepared in octane) with CO; (e) reaction of hydrogenated, silica-supported rhodium dihydride with CO.

Scheme I



nature of supported carbonyl complex **3**. The good agreement of the spectra indicates that the surface species is a close structural analogue[4] of $[Rh(CO)_2Cl]_2$.

$[SiO]Rh(allyl)_2$ reacted with CO to generate 1,5-hexadiene and supported carbonyl complex **3**. For comparison purposes, a sample of $[SiO]Rh(allyl)_2$ was treated with the same $^{12}CO/^{13}CO$ mixture; here, too, a *dimeric* structure was indicated for **3** (Figure 1b).

$Rh(C_3H_5)(CO)_2$ and Al_2O_3. An aliquot of the same ^{13}CO-enriched sample of $Rh(C_3H_5)(CO)_2$ used for deposition onto SiO_2 gave an alumina-supported product showing a relative intensity pattern (Figure 1d) analogous to that of its monomeric allyl dicarbonyl precursor (Figure 1e). An overall shift to higher frequency was detected. The observation of a *monomeric* dicarbonyl on this support is in agreement with the product derived from rhodium carbonyl cluster precursors.[5]

Migration of Complexes "Deposited" on Silica under H_2. Hydrogenation of oxide-bound organometallics is a commonly used means for their "activation" as catalyst materials,[6] and although stoichiometries of such transformations have been discussed, the role of hydrogen in facilitating migrations of such species has not been noted. Since hydrogenation of oxide-bound metal complexes can yield particulate metals,[6] the possibility that hydrogen might enable clustering of deposited complexes prior to their reduction must be considered.

Long-chain alkanes are good substrates for organorhodium complex catalyzed H/D exchange with D_2 gas.[7] In this process, an intermediate has been proposed that consists of the organorhodium complex, olefin, and "heterolytically" activated H_2. Thus, long-chain alkanes might serve as sources of "activated" H_2 for metal-ligand cleavage in these oxide-bound complexes, as they have been suggested[8,9] to do for a range of soluble organometallics. The reaction between **2** and octane gives the rhodium dihydride species, **4**, for which IR analysis (Figure 2a) suggests the preponderance of terminal rhodium hydride ligation, and only a small amount of bridging hydride ligation was detectable. Indeed, carbonylation of this dihydride (Figure 2d) yielded the same dicarbonyl (**3**) prepared from either **1** (plus silica) or **2** (plus CO) directly (Figure 2c). Treating **4** with hydrogen under mild conditions gave a new material, **5**, for which IR analysis (Figure 2b) showed a complete pattern change, specifically with greatly enhanced intensity for bridging hydride ligation. Interestingly, carbonylation of **5** yielded a new rhodium carbonyl, **6**, for which IR analysis (Figure 2e) also revealed a pattern change in the terminal CO region and greatly enhanced intensity in the bridging CO region. Carbonyl complex **6** could also be obtained from **3** under H_2. Thus, apparently, hydrogen enables conversion of "weak dimers" to more strongly ligand-bridged aggregates (the nuclearity of **5** and **6** may be higher than that which is shown in Scheme I) and may participate in this migration process by acting as a source of mobile protons[10] in processes whereby Si–O–Si groups are converted to reactive Si–OH ones.

The aggregation of silica-"bound" metal complexes abetted by H_2 may be a general phenomenon, and the migratory ability of nonzerovalent oxide-"bound" metal *complexes* in the presence of hydrogen may be an important consideration in degradative processes for these species.[11] We are now studying details of deposition and H_2-dependent migration of metal complexes "bound" to other oxides of varying basicities.

Acknowledgment. We acknowledge support for this work provided by ARCO, Sun Oil Foundation, and the National Science Foundation.

Registry No. **1**, 33292-30-7; $[Rh(CO)_2Cl]_2$, 14523-22-9; CO, 630-08-0; H_2, 1333-74-0; *n*-octane, 111-65-9.

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