

Surface Organometallic Chemistry: Reactivity of Silica-Bound Rhodium Allyl Complexes and the Genesis of Highly Dispersed Supported Rhodium Catalysts

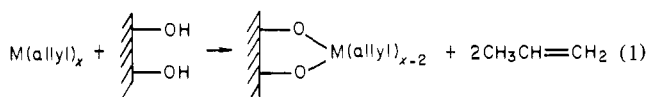
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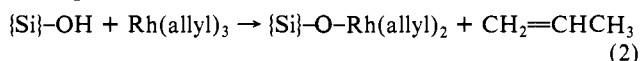
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Abstract: The surface organometallic chemistry of silica-supported diallylrhodium, {Si}-O-Rh(allyl)₂ (Si is used to indicate surface Si), was characterized by ¹H NMR, IR, and XP spectroscopy. The complex was reduced by H₂ under mild conditions, with the elimination of propene, to give highly dispersed rhodium metal aggregates. Reaction of the surface with CO led to the formation of Rh^I(CO)₂ species, formed not from the {Si}-O-Rh(allyl)₂ groups but from other groups, presumably incorporating Rh(III) ions. The reaction of {Si}-O-Rh(allyl)₂ with hydrogen was inhibited by CO bonded to these other Rh centers. Evidently the reduction of the diallyl groups by hydrogen proceeded via reduction of Rh(III) ions with spillover of hydrogen to the support, which led to further protolysis of {Si}-O-Rh(allyl)₂ and eventually to rhodium metal. The small metal aggregates, observed by transmission electron microscopy, were catalytically active for toluene hydrogenation.

One of the central challenges of catalysis is to prepare surfaces with well-defined structures for determination of relations between structure, reactivity, and catalytic activity. One of the methods of preparing well-defined supported-metal catalysts involves the protolysis reaction of a transition-metal allyl complex and the OH groups terminating the surface of an inorganic oxide:



Catalyst precursors prepared in this way have been reported by Yermakov and co-workers¹ for transition metals including Zr, Hf, Nb, Cr, Mo, W, Re, Ni, Pd, and Pt. Ward et al.^{2a} and Ward and Schwartz^{2b,c} recently reported the synthesis of a diallyl complex of rhodium anchored through a Rh-O bond to SiO₂ (and to TiO₂).³



The diallyl complex of Rh was suggested to be bound initially to only one oxygen, the suggestion being based mainly on the observed stoichiometry of the synthesis reaction (eq 2).^{2a,b,d} Reactions of the supported complex with H₂, HCl, olefins, and phosphines were investigated; structures of the resulting surface species were formulated on the basis of the observed reaction stoichiometries and infrared spectra of the surface species. The supported diallylrhodium complex was found to be a precursor of a catalyst for hydrogenation of olefins and of arenes.^{2b-d}

The objective of the research described here was to use a battery of surface spectroscopic methods, namely, FTIR, XPS, and ¹H NMR, to characterize the structures, reactivities, and catalytic activities of the silica-supported species derived from [Rh(allyl)₃]; a specific goal was to establish the nature of the catalytically active species and the chemistry of their formation from the diallylrhodium complex present initially on the surface.

Experimental Methods

Catalyst Synthesis. The silica support, Cab-O-Sil (M-5 grade, Cabot Corp.), was slurried with deionized water, dried in an oven, transferred to a fritted glass tube, heated to 200 °C under flowing oxygen for 12 h, and then dried under vacuum at 200 °C for 12 h. The calcined silica was transferred to a glovebox, where it was stored under nitrogen.

The solvents toluene and diethyl ether were refluxed over sodium/benzophenone and then distilled under nitrogen immediately prior to use.

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Table I. Comparison of Vibrational Frequencies of [Rh(allyl)₃] and {Si}-O-Rh(allyl)₂

allyl vibrations of {Si}-O-Rh(allyl) ₂ , cm ⁻¹			KBr disk of [Rh(allyl) ₃], cm ⁻¹	assignment
a	b	c		
3055	3055	3050	3061 m	A'ν(CH ₂)
2992			3000 m	A'ν(CH ₂)
2942			2960 w	
2900		3000-2800	2928 w	A' + a''ν(CH ₂)
2851			2850 vw	
			2350 vw	
			2350 w, br	
			1760 w	
1491		1490	1483 m	A'δ(CH ₂)
	1473			
1463		1460	1453 m	A'δ(CH ₂)

^a This work. ^b Reference 2a. ^c Reference 2d. ^d Reference 7.

The complexes [Rh(1,5-hexadiene)Cl]₂ and [C₃H₅MgBr] were prepared by literature methods;^{4,5} [Rh(allyl)₃] was prepared by a literature method,^{6a} slightly modified, as follows: [C₃H₅MgBr] was added to [Rh-(1,5-hexadiene)Cl]₂ under nitrogen and stirred at -78 °C, and the resultant mixture was warmed to 0 °C. A stream of air, having passed through a CaSO₄ trap at -78 °C, flowed into the solution, which was allowed to warm to room temperature. The product was purified by sublimation, and its purity was confirmed by comparison of the observed and reported infrared and ¹H NMR spectra.^{6b,7}

The silica-supported rhodium allyl complex, represented as {Si}-O-Rh(allyl)₂, was synthesized by the method of Ward et al.,^{2a} with each of the steps carried out under an inert atmosphere. In one preparation, giving the lowest loading of Rh on the surface, [Rh(allyl)₃] (0.0752 g) was dissolved in dry toluene (40 mL), and the solution was added dropwise over a 2-h period to a toluene slurry of silica. During this time, the [Rh(allyl)₃] was adsorbed onto the silica, the supernatant solution becoming colorless. The resulting golden-yellow solid was filtered and

(1) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. In "Catalysis by Supported Complexes"; Elsevier: Amsterdam, 1981.

(2) (a) Ward, M. D.; Harris, T. V.; Schwartz, J. J. *Chem. Soc., Chem. Commun.* **1980**, 357. (b) Ward, M. D.; Schwartz, J. J. *Mol. Catal.* **1981**, *11*, 397. (c) Ward, M. D.; Schwartz, J. J. *Am. Chem. Soc.* **1981**, *103*, 5253. (d) Ward, M. D. Ph.D. Dissertation, Princeton University, 1981.

(3) [Rh(π-C₃H₅)CO(PPh₃)₂] on γ-alumina has also been reported: Spek, Th. G.; Scholten, J. J. F. *J. Mol. Catal.* **1977**, *3*, 81.

(4) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(5) Crummitt, O.; Budewitz, E. P.; Chudd, C. C. *Org. Synth.* **1963**, *4*, 1748.

(6) (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 583. (b) Powell, J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1966**, 323.

(7) Andrews, D. C.; Davidson, G. J. *Organomet. Chem.* **1973**, *55*, 383.

washed successively with toluene (5×20 mL) and *n*-hexane (5×20 mL). The solid was then dried under vacuum for 12 h. Alternatively, the highest loading of Rh was obtained by the same procedure, except that 0.160 g of $[\text{Rh}(\text{allyl})_3]$ was used in 40 mL of toluene with 1.8 g of silica. After the mixture was stirred 5 h, less than all the $[\text{Rh}(\text{allyl})_3]$ had adsorbed, as indicated by the persistence of color of the supernatant solution. The sample was filtered and washed exhaustively with toluene and *n*-hexane and then dried under vacuum. The infrared spectrum of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ so obtained agrees well with those reported previously (Table I).^{2a,d} Comparison of the ^1H NMR spectra of the samples with low and high rhodium loadings provided no indication of any difference in the surface species formed. Samples were analyzed for Rh by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Rhodium loadings varied from 0.75 to 3.2 wt %.

Infrared Spectroscopy. Infrared spectra of the silica-supported rhodium species were obtained with a Nicolet 7199 Fourier transform spectrometer having a globar source and a mercury/cadmium telluride cryogenic detector. The spectral resolution was 4 cm^{-1} . Samples of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ were pressed into self-supporting disks, 20 mm in diameter, held in a thermostated quartz cell connected to a portable gas-handling system.⁸

Spectra of the wafers were obtained during reactions with H_2 , D_2 , or CO . Purified gases such as N_2 , CO , and H_2 were introduced into the infrared cell with the gas-handling system. Samples could be treated under vacuum ($\sim 5 \times 10^{-5}$ torr) or at pressures as great as atmospheric. Traces of oxygen and water were removed from the reactant gases by flow through columns containing BASF copper catalyst and zeolite A, respectively.

^1H NMR Spectroscopy. Prior to the ^1H NMR experiments, the sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ was transferred into a tubular Pyrex flow reactor having an NMR tube attached as a side arm. During reactions, gas flowed over the powder sample on a glass frit; subsequently, the reactor was tilted to transfer the solid to the NMR tube for analysis. The apparatus is described elsewhere.⁹⁻¹¹

The spectrometer operated at a frequency of 56.41 MHz for the proton resonance. The magnet had an external deuterium lock, and magnetic field drift in any experiment was <0.2 ppm. The proton spectra were recorded by coaddition of 100–1000 or more transients followed by Fourier transformation.

The gas-handling system mentioned above was used for introduction of CO and H_2 ; HCl and D_2 were introduced via a Schlenk line. Reactions were carried out either statically or with flowing gaseous reactants.

X-ray Photoelectron Spectroscopy. Pressed wafer samples were analyzed with a Physical Electronics AES/XPS system (Model 550), consisting of an ultrahigh-vacuum analysis chamber and a pretreatment chamber with high-vacuum capabilities. Samples were brought in contact with hydrogen in the pretreatment chamber under slight purge conditions and then transferred into the analysis chamber without exposure to the external atmosphere. The pressure in the analysis chamber during data acquisition was typically 5×10^{-9} torr.

XP spectra were obtained with a Mg radiation source and a cylindrical mirror analyzer. Signals were multiplexed and averaged to improve the signal-to-noise ratios. The acquisition time for each spectrum was 5 min, and checks were made to ensure that charging equilibrium had been reached and that spectral shifts were not indicative of equilibration of charging. The spectral resolution was 0.5 eV. Atomic concentrations of Rh, C, and Cl were obtained using peak areas and the appropriate area sensitivities for each element;¹² these concentrations are accurate to $\pm 10\%$. Reported binding energies are referenced to the Si 2p peak at 103.4 eV; the reported binding energies are accurate to ± 0.2 eV. The peaks which were multiplexed for detailed investigation were the Rh 3d, Si 2p, C 1s, and Cl 2p peaks.

Transmission Electron Microscopy. Transmission electron microscopy was used to investigate samples of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ after reaction with hydrogen at 25 °C. Samples were prepared either by embedding in epoxy resin and microtoming into sections or by slurrying in reagent grade acetone. These samples were then either supported or deposited on a Cu grid positioned in the electron beam (80–100 keV) of a Philips EM-400T microscope.

Catalytic Hydrogenation of Toluene. A sample (250 mg) of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ powder was loaded into a tubular stainless-steel flow reactor

Table II. XPS Results: Binding Energies of Rh $3d_{5/2}$ Electrons as a Function of Time of Exposure of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to X-rays

exposure time, min	binding energy, eV (± 0.2)
5	308.9
10	308.9, 308.6
15	308.7, 308.4
20	308.6
45	308.3
90	308.0

Table III. XPS Results: Binding Energies of Rh $3d_{5/2}$ Electrons in Various Rhodium Samples

sample	binding energy, eV	ref
Rh metal	307.1, 307.0	17a,b
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	309.7, 310.2, 310.3	17a,b
Rh_2O_3	309.1	17b
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	309.5	17c
$\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$	308.9	this work

under N_2 in a glovebox. Helium carrier gas bubbled through toluene at 70 °C and then through toluene at 25 °C to give a feed stream of helium containing toluene at the saturation vapor pressure. This feed flowed over the catalyst at room temperature for 1.5 h, and then the catalysis experiment began as the helium stream was replaced by the coreactant, hydrogen.

The effluent from the reactor flowed through the gas sampling valve of a Hewlett-Packard 5150 gas chromatograph, where it was resolved in two columns in series, one packed with 5.16% DEGS/1.7% Bentone 34 Chromasorb W and the other with 5% Apiezon-L/Chromasorb W. The product stream was sampled periodically to provide a measure of the conversion of toluene as a function of time on stream.

Results and Discussion

Characterization of the Supported Rhodium Diallyl Complex. The structure of the bound complex formed from $[\text{Rh}(\text{allyl})_3]$ and silica has been inferred by Ward et al.^{2a,b,d} to be $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$. The infrared spectra observed in our work are in agreement with those reported by Ward et al. Vibrational frequencies observed for $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ and for $[\text{Rh}(\text{allyl})_3]$ are summarized with the band assignments in Table I. The IR spectra support the inference that the allyl ligands are present in the surface-bound complex.

Further structural evidence is provided by the ^1H NMR and XPS data. A ^1H NMR spectrum of the sample incorporating the diallylrhodium complex is shown in Figure 1A. There is a single resonance at δ 1.2 relative to Me_4Si (external). This resonance is assigned to the protons of the allyl groups of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$.¹³ Remarkably, the full width at half-height is only 1.7 ppm. The sharpness of this peak indicates that virtually all the allyl protons were in the same average environment, as would be expected for a unique (molecular) complex on the support surface.

Proton resonances indicating $\{\text{Si}\}-\text{OH}$ groups were not observed with this sample, presumably because the concentration of these groups was less than that detectable with the spectrometer. A sample of the calcined silica without rhodium also failed to show a signal, but when the silica was treated with deionized water and then evacuated, a resonance became evident. It was centered at 0 ppm, consistent with the results of Sheng and Gay.¹⁴ Although the T_1 for the protons of $\{\text{Si}\}-\text{OH}$ groups on silica has been reported to be approximately 20 s,¹⁵ we observed this resonance with repetition rates of 2–3 s; others¹⁴ have observed even lower values.

A test of the oxidation state of Rh in the sample prepared from $[\text{Rh}(\text{allyl})_3]$ and silica is provided by the XPS results. Accurate

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(9) Apple, T. M.; Gajardo, P.; Dybowski, C. *J. Catal.* **1981**, *68*, 103.

(10) Duncan, T. M.; Dybowski, C. *Surf. Sci. Rep.* **1981**, *1*, 157.

(11) Gajardo, P.; Apple, T. M.; Dybowski, C. *Chem. Phys. Lett.* **1980**, *74*, 306.

(12) Physical Electronics Software Package V, Perkin-Elmer Physical Electronics, Eden Prairie, MN, 1979.

(13) The resonance at δ 1.2 is assigned to protons of allyl ligands on the basis of the structural inferences drawn by Ward et al.² It is not possible from these ^1H NMR results alone to determine whether the allyls are intact π bound or σ bound. The ^1H NMR spectrum of $[\text{Rh}(\text{allyl})_3]$ in solution has several resonances corresponding to protons in different environments; the resolution of the solid-state NMR was insufficient to distinguish these.

(14) Sheng, T.-C.; Gay, I. D. *J. Catal.* **1981**, *71*, 119.

(15) Schrieber, L. B.; Vaughan, R. W. *J. Catal.* **1975**, *40*, 226.

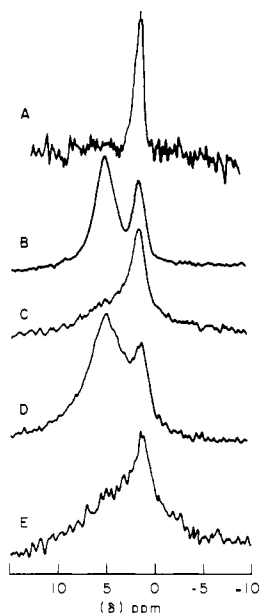


Figure 1. ^1H NMR spectra of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ (3.2 wt % Rh) during reactions with H_2 and HCl : A, $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ before reaction (spectrum is the product of 100 coadditions); B, after reaction with flowing H_2 (760 torr, 25 °C; 1000 coadditions); C, subsequent evacuation (1×10^{-3} torr, 25 °C; 1000 coadditions, intensity multiplied by 2.0 vs. spectrum B); D, after reaction with HCl (760 torr, 25 °C; 1000 coadditions, intensity multiplied by 2.0 vs. spectrum B); E, subsequent evacuation (1×10^{-3} torr, 25 °C; 1000 coadditions, intensity multiplied by 3.0 vs. spectrum B).

Table IV. Infrared Spectra of Supported $\text{Rh}(\text{CO})_2$ Species in the Carbonyl Region

band locations, cm^{-1}	species assigned	ref
2101, 2035	$\text{Rh}(\text{CO})_2/\text{Al}_2\text{O}_3$	19a
2101, 2031	$\text{Rh}(\text{CO})_2/\text{Al}_2\text{O}_3$	19b
2090, 2031	$\text{Rh}(\text{CO})_2-\text{L}-\text{SiO}_2$	19c
2105, 2091, 2035	$\text{Rh}(\text{CO})_2/\text{SiO}_2$	19d,e
2105 (w, sh), 2090 (vs), 2035 (vs)	$\text{Rh}(\text{CO})_2/\text{SiO}_2$	this work

XPS data were acquired in 5 min with a sample containing 3.2% Rh at -80 °C.¹⁶ The initial binding energy of the Rh $3d_{5/2}$ electrons in this sample is estimated to be 308.9 eV (Table II); the binding energy of the Rh $3d_{5/2}$ electrons in Rh_2O_3 is reported to be 309.1 eV.¹⁷ This comparison and others (Table III) provide evidence of Rh(III) in the sample, as expected from the stoichiometry of the synthesis (eq 2).^{2a,b,d} We caution, however, that there is a wide range of Rh 3d binding energies spanned by Rh(I) and Rh(III) complexes and that it is impossible to assign the valence state exactly.^{17d} A shift of the Rh $3d_{5/2}$ peak to lower binding energies occurred during irradiation (Table II)—an expected result^{17d} which suggests the formation of rhodium in lower oxidation states and decomposition of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$.¹⁸

Reaction of Supported Rhodium Complexes with CO. In an investigation of the reactivity of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with the probe

(16) Samples with low rhodium concentrations ($<1\%$ Rh) required long collection times (>20 min), since the signal-to-noise ratio was low, and accurate binding energies of the Rh $3d_{5/2}$ peaks could not be determined. Further, when the analysis was conducted at room temperature with the sample containing 3.2 wt % Rh, severe decomposition occurred within 5 min. The Rh $3d_{5/2}$ binding energy shifted from 308.9 to 308.0 ± 0.2 eV during this period.

(17) (a) Imanka, T.; Kaneda, K.; Teranishi, T.; Terasawa, M. *Proc. Int. Congr. Catal.*, 6th 1976, 509. (b) Contour, J. P.; Mouvier, G.; Hoogewijs, M.; Leclere, C. *J. Catal.* 1977, 48, 217. (c) Anderson, S. L. T.; Watters, K. L.; Howe, R. F. *Ibid.* 1979, 59, 340. (d) Anderson, S. L. T.; Watters, K. L.; Howe, R. F. *Ibid.* 1981, 69, 212.

(18) We infer that the shift of the Rh $3d_{5/2}$ peak did not result from charging of the sample surface, since there was no concomitant shift of the Si 2p peak(s).

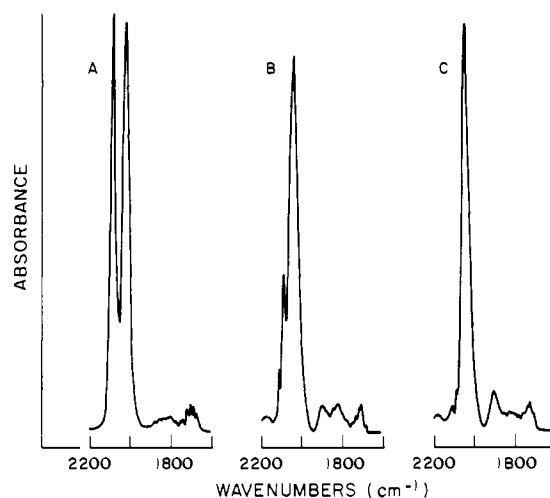


Figure 2. Infrared spectral changes during reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with CO and H_2 : A, after CO exposure (760 torr, 25 °C); B, subsequent treatment with flowing H_2 (760 torr, 100 °C); C, subsequent treatment with flowing H_2 (760 torr, 150 °C).

molecule CO , a wafer of the fresh sample was evacuated in the infrared cell at room temperature for 30 min, exposed to CO at 1 atm for 15 min, and then evacuated. Three bands appeared in the terminal carbonyl region of the infrared spectrum, at 2105 (w, sh), 2090 (vs), and 2035 (vs) cm^{-1} . To improve the quality of the spectrum, the absorption of the SiO_2 support was subtracted; there was no evidence of bridging carbonyls (Figure 2A). The two strong bands are assigned as a doublet indicative of a $\text{Rh}^{\text{I}}(\text{CO})_2$ species, consistent with numerous assignments of surface-bound dicarbonyl rhodium species (Table IV).¹⁹ It is significant that the observed carbonyl bands are not in the range expected for a $\text{Rh}^{\text{III}}(\text{CO})_2$ complex.^{19f}

Treatment of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with CO led to an instantaneous color change from yellow to white; an ^1H NMR spectrum of the sample after 12 h of exposure to CO displayed the aforementioned allyl resonance at δ 1.2, with unchanged intensity. The spectra clearly indicate that bringing the surface-bound diallyl complex in contact with CO for 12 h neither reduced nor shifted the allyl resonances, which implies that the allyl groups were not displaced by CO .²⁰ If reaction had occurred with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to generate $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2(\text{CO})_2$, then we would expect this complex to have undergone rapid reductive coupling of the allyl ligands, to eliminate volatile 1,5-hexadiene and to generate $\{\text{Si}\}-\text{O}-\text{Rh}(\text{CO})_2$. Support for this expectation is based upon the observation that soluble group 8 transition-metal allyl complexes react with nucleophiles with the elimination of 1,5-hexadiene.²⁰ If $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2(\text{CO})_2$ had formed and were stable toward reductive coupling and elimination of the allyl ligands, then we would expect the infrared spectrum of this species to be considerably different from that reported for $\text{Rh}^{\text{I}}(\text{CO})_2$. Since the infrared spectrum observed for the product of the reaction with CO matches that reported for $\text{Rh}^{\text{I}}(\text{CO})_2$, we exclude the possibility that CO reacted with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to form $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2(\text{CO})_2$. Since our ^1H NMR results also indicate that no reaction had occurred with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ groups, even after exhaustive reaction with CO , we conclude that CO reacted with other rhodium species on the surface.²¹

(19) (a) Yates, J. T.; Worley, S. D.; Duncan, T. M.; Vaughan, R. W. *J. Chem. Phys.* 1979, 70, 1219. (b) Yates, J. T.; Worley, S. D.; Duncan, T. M.; Vaughan, R. W. *Ibid.* 1979, 70, 1225. (c) Knözinger, H.; Thornton, E. W.; Wolf, M. *J. Chem. Soc., Faraday Trans. 1*, 1979, 75, 1888. (d) Theolier, A.; Smith A. K.; Leconte, M. J.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* 1980, 191, 415. (e) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. *J. Organomet. Chem.* 1978, 153, 73. (f) Primet, M.; Vedrine, J. C.; Naccache, C. *J. Mol. Catal.* 1978, 4, 411.

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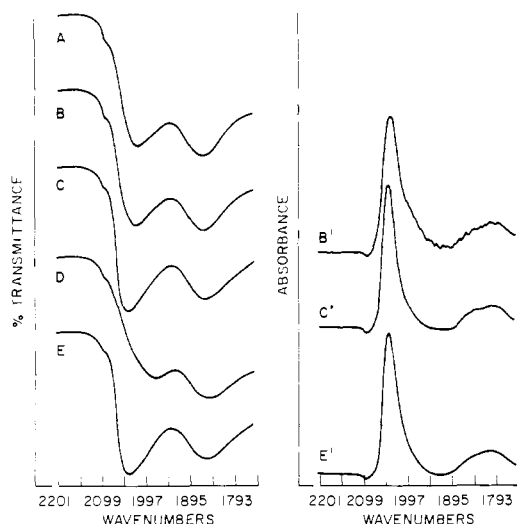
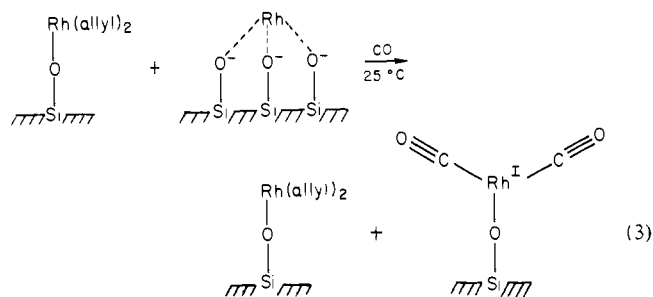


Figure 3. Infrared spectral changes during reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 : A, $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ after 30 min evacuation (1×10^{-4} torr, 25°C); B, after reaction with H_2 for 30 min (760 torr, 25°C); B', spectrum B after subtraction of SiO_2 bands; C, after reaction with H_2 for 240 min (760 torr, 25°C); C', spectrum C after subtraction of SiO_2 bands; D, subsequent evacuation (1×10^{-4} torr, 25°C); E, after reexposure to H_2 for 30 min (760 torr, 25°C); E', spectrum E after subtraction of SiO_2 bands.

Although the exact nature of these other rhodium species is unknown, we suggest that prior to reaction with CO, they incorporate Rh(III) ions generated by further protolysis of the rhodium allyl complexes on the surface. We suggest that Rh(III) ions, so generated, are likely the species which react with CO, being reduced to the $\text{Rh}^{\text{I}}(\text{CO})_2$ species indicated by the IR spectra. The reduction of Rh(III) ions by CO to give $\text{Rh}^{\text{I}}(\text{CO})_2$ has been reported to occur slowly in solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and the reduction is promoted in the presence of H_2O .²² We would expect this reduction to occur rapidly with Rh(III) ions on the support, especially if no ligands (other than surface oxygen ions) were formally bound to the rhodium. Presumably, CO_2 is also formed in this reaction, but this suggestion is untested. To summarize, the overall reaction with CO is represented schematically as in eq 3. With this reaction, the whole set of spectroscopic data is



now accounted for.

Reaction of Supported Rhodium Complexes with H_2 and HCl.

The reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 was investigated with

(21) An XP spectrum of the $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ after exposure to CO for 90 min, followed by evacuation, showed a binding energy of 309.4 eV and a C:Rh atomic ratio of 7:1. This binding energy is 0.5 eV higher than that of the untreated sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$. Although this result might be interpreted as evidence of reaction of CO with the diallyl complex, we discount the possibility on the basis of the IR and NMR results stated above and on the basis of the XPS result showing that the 7:1 C:Rh ratio after reaction of the sample with CO was essentially unchanged, which confirms the conclusion that allyl ligands were not displaced.

(22) (a) James, B. R.; Rempel, G. L. *J. Chem. Soc. A* **1969**, 78. (b) James, B. R.; Rempel, G. L.; Ng, F. T. T. *Ibid.* **1969**, 2454.

the battery of spectroscopic methods. After evacuation of a fresh sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ for 30 min at 25°C , the infrared spectrum A of Figure 3 was recorded. After flow of H_2 over the sample for 30 min, spectrum B was obtained (Figure 3). Spectrum B' resulted from subtraction of the bands of the SiO_2 support and showed that two new bands had appeared, at 2038 and 1812 cm^{-1} ; these are assigned as terminal and bridging rhodium hydride bands, respectively.²³ Further reaction in flowing H_2 led to an increase in the intensities of these bands (Figure 3). Evacuation at room temperature led to a rapid reduction in the intensity of the band at 2038 cm^{-1} (Figure 3) while the intensity of the bridging band was not reduced.²⁴ Reexposure of the sample to H_2 led to a complete restoration of the band at 2038 cm^{-1} within 30 min. The intensity of the restored band was equal to what it had been after the first 4 h of exposure to H_2 . Exposure to H_2 for an additional hour at 25°C produced no further changes in the intensities of the rhodium hydride bands.

In summary, these results demonstrate clearly that H_2 adsorption on the sample was reversible. The reversible nature of the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 has not been previously reported. However, the reversible chemisorption of hydrogen on metals has been studied by infrared spectroscopy.²³ These studies have shown that hydrogen is chemisorbed on supported metals in two different forms. One form is loosely bound in a terminal mode and is readily desorbed. The second form is strongly bound in a bridging mode and is not readily desorbed. The different bonding modes, terminal vs. bridging, for these hydrogens are assigned on the basis of the positions of the infrared bands that they display. The terminally bound hydrogen displays an infrared band at higher energy than the bridge-bound hydrogen.

The reversibility of the reaction of hydrogen with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ is directly analogous to that observed with supported metals. Specifically, evacuation at 25°C of a sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$, previously exposed to hydrogen, results in a drastic reduction of the intensity of the band assigned to the terminally bound hydride and little or no change in that assigned to the bridge-bound hydride. Reexposure of the sample to hydrogen results in a restoration of the intensity of the band assigned to the terminally bound hydride. On the basis of the close similarity of these results for the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen to results for the simple reversible chemisorption of hydrogen on a supported metal, we suspected that rhodium metal aggregates might be forming. This suspicion was further supported by the blackening of the sample during the course of these experiments. Such a color change from golden yellow to black would be expected if the Rh(III) center of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ were undergoing an overall reduction in oxidation state to Rh(0) and forming aggregates. Further experiments, mentioned below, were conducted which confirmed that rhodium aggregates were indeed formed during reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen.

Infrared spectroscopy was also used to characterize the reaction of the supported rhodium complexes with D_2 . After 1.5 h of exposure of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to flowing D_2 , a strong O-D band had developed at 2550 cm^{-1} , at the expense of the O-H band. A band also developed at 2038 cm^{-1} , indicative of the aforementioned rhodium hydride, the hydrogen presumably being transferred from $\{\text{Si}\}-\text{OH}$ groups. The 2038-cm^{-1} band was removed by evacuation

(23) For results of infrared spectroscopic investigations of hydrogen chemisorption on supported metals, see the following references: (a) Pliskin, W. A.; Eischens, R. P. *Z. Phys. Chem.* **1960**, *24*, 11. (b) Darenbourg, D. J.; Eischens, R. P. *Proc. Int. Congr. Catal.*, *5th* **1973**, 371. (c) Smith, W. H.; Eckstrom, H. C.; Baer, F. *J. Phys. Chem.* **1968**, *72*, 369. (d) Buzon-Verduraz, F.; Contour, J.-P.; Pannetier, G. C. *R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *269C*, 1436. (e) Primet, M.; Basset, J. M.; Mathieu, M. V.; Prette, M. *J. Catal.* **1973**, *28*, 368. (f) Dixon, L. T.; Barth, R.; Gryder, J. W. *Ibid.* **1975**, *37*, 368. (g) Contour, J. P.; Pannetier, G. *Ibid.* **1972**, *24*, 434. (h) Candy, J. P.; Fouilloux, P.; Primet, M. *Surf. Sci.* **1978**, *72*, 167.

(24) After brief exposure of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to H_2 at 25°C , two bands with nearly equal intensities were observed in the infrared spectrum, at 2040 and 1802 cm^{-1} . Further exposure to H_2 resulted in a large increase in intensity of the band at 2040 cm^{-1} while the band at 1802 cm^{-1} did not increase in intensity, but remained as a shoulder; a band also appeared at 1802 cm^{-1} . The bands at 2040 and 1802 cm^{-1} are assigned to terminal and bridging hydride species, respectively. The band at 1802 cm^{-1} is assigned to the SiO_2 support.

Table V. XPS Results: Changes in Rh 3d_{5/2} Peaks during Treatment of {Si}-O-Rh(allyl)₂ with H₂

time of exposure of sample to H ₂ at 25 °C, h	binding energy of Rh 3d _{5/2} electrons, eV (±0.2)	C:Rh atomic ratio (±20%)
0	308.9	8.5
3	308.9 (sh: 307.6, 309.4)	10.8
5	307.8 (sh: 308.4)	4.7
120	307.6	

Table VI. XPS Results: Binding Energies of Rh 3d_{5/2} Electrons

sample	binding energy, eV (±0.2)	Cl:Rh atomic ratio (±20%)
{Si}-O-Rh(allyl) ₂ after treatment with H ₂ for 2 days followed by HCl for 4 days, 25 °C	309.6	2.0
after 15 min X-ray exposure	309.1	2.0
after 30 min X-ray exposure	308.8	1.4
after 90 min X-ray exposure	308.3	1.2

at 25 °C, and it reappeared upon reexposure of the sample to D₂ at 1 atm and 25 °C for 1 h. An additional 3 h of exposure to D₂ caused a further increase in the intensity of the O-D band located at 2550 cm⁻¹. Evacuation once again led to removal of the band at 2038 cm⁻¹. Exposure to flowing H₂ for 5 min at 25 °C led to a rapid restoration of the original O-H band at 3500 cm⁻¹ and a drastic collapse of the O-D band at 2550 cm⁻¹. The band at 2038 cm⁻¹ was unchanged. (The strong absorption of the SiO₂ support prevented observation of any Rh-D band, even after subtraction of the SiO₂ bands.) The maintenance of the rhodium hydride band is attributed to continuing exchange between the reservoir of protons of the support and the deuterium from the gas phase, which was presumably dissociated on rhodium metal centers. After this experiment, the sample was black, indicating that the rhodium had been reduced to metal.

The reaction of {Si}-O-Rh(allyl)₂ with H₂ at 25 °C was also investigated by XPS. The results show that upon reaction there was a shift of the Rh 3d levels to lower binding energy. The Rh 3d_{5/2} peak of the untreated sample had a shoulder at 307.6 eV after 3 h of exposure to H₂ at 25 °C. This band became the prominent feature of the spectrum after 5 h of exposure to H₂ (Table III). There was an accompanying color change from the initial golden yellow to greenish-brown (after 3 h) and to black (after 5 h). The shift to lower binding energy of the Rh 3d_{5/2} peak upon treatment of the sample with H₂ is consistent with reduction of the rhodium in {Si}-O-Rh(allyl)₂. Deconvolution of the Rh 3d_{5/2} peak at 307.6 eV gave two peaks, one located at 307.1 and one at 308.2 eV, the former approximately matching that observed for rhodium metal (Table V). Therefore, we infer that reaction of the diallyl complex with H₂ resulted in reduction of Rh(III) to Rh(0), in agreement with the results stated above. The C:Rh atomic ratio initially (and after 3 h of exposure to flowing H₂) was approximately 9:1, but after 5 h, it decreased to 5:1, consistent with the removal of allyl ligands from the surface; these results are regarded as qualitative and insufficient for structure determination.

A sample of {Si}-O-Rh(allyl)₂ which had been exposed to H₂ at 1 atm and 25 °C for 2 days was treated with HCl at 25 °C for 4 days. The sample color changed from gray-black to red-brown. A new band appeared in the infrared spectrum at 2133 cm⁻¹. A Rh 3d_{5/2} peak appeared in the XP spectrum at 309.6 eV (Table VI). The binding energy and color change are consistent with the oxidation of Rh(0) by HCl to Rh(III) associated with chloride. The data of Table VI also show that prolonged exposure of this HCl-treated sample to X-rays led to a decrease in the binding energy of the Rh 3d_{5/2} electrons, as was observed for the diallylrhodium complex. The Cl:Rh ratio decreased with increasing time of exposure to X-rays.

Proton NMR spectra were also obtained during reaction of {Si}-O-Rh(allyl)₂ with H₂. Spectrum A of the initial {Si}-O-Rh(allyl)₂ complex is compared in Figure 1 with spectra of the

Table VII. Summary of Surface ¹H NMR Results

sample	δ			
	CH ₃ -CH=CH ₂ (P _{total} 400 torr)	CH ₃ -CH ₂ CH ₃ (P _{total} 400 torr)	H ₂ O	CH ₃ CH=CH ₂ : H ₂ = 4:3 (P _{total} 700 torr)
silica	4.1, 0.6 (1:1)	0.3	4.1	4.1, 0.6 (1:1)
{Si}-O-Rh(allyl) ₂ 0.75 wt % rhodium	4.1, 0.6 (1:1)	0.3	4.1	0.3
{Si}-O-Rh(allyl) ₂ 1.4 wt % rhodium	4.6, 1.0 (1:1)	0.3	4.1	0.3

sample after exposure to H₂. Two resonances are evident in spectrum B, one representative of the unreacted diallyl complex at δ 1.2, and a new one at δ 5.4.²⁵ This downfield resonance was readily removed by evacuation of the sample at 10⁻³ torr and 25 °C (Figure 1C). This result leads us to identify the new resonance at δ 5.4 with an easily desorbed species. Exposure of the evacuated sample to HCl led to spectrum D of Figure 1. Again two resonances were observed, the one at δ 1.2 indicating the allyl protons of the diallyl complex; the downfield resonance, at δ 5.4, had the same chemical shift as the resonance originating from the reaction of the diallyl complex with hydrogen. This result implies that the same product was formed in the reaction with HCl as in the reaction with H₂. Evacuation of the sample to 1 × 10⁻³ torr at 25 °C removed the species giving rise to this resonance (Figure 1E). Throughout the course of these experiments the intensity of the resonance attributed to the allyl protons of {Si}-O-Rh(allyl)₂ decreased significantly, consistent with the suggestion that reaction with H₂ occurred.

To identify the products of the reaction with hydrogen, a stream of H₂ was passed over a sample of {Si}-O-Rh(allyl)₂; the effluent gas stream flowed through a liquid nitrogen trap, where the volatile products were collected. Proton NMR spectra of the solid sample were recorded periodically, confirming the changes described above. A mass spectral analysis of the trapped products showed them to be propane and propene, the former being in excess. These results suggest that the new resonance observed at δ 5.4 during the reaction with H₂ might be associated with adsorbed propene.

In two separate experiments, H₂ flowed over samples of {Si}-O-Rh(allyl)₂ having low rhodium loadings, namely, 0.75 and 1.4 wt % (the sample used to generate the spectra in Figure 1 contained 3.2 wt % Rh). With the sample containing 1.4 wt % Rh, treatment with H₂ at 25 °C resulted in a new resonance in the ¹H NMR spectrum at δ 4.6, whereas with the sample containing 0.75 wt % Rh, treatment with H₂ resulted in a new resonance at δ 4.1. Proton NMR spectra of these H₂-treated samples after evacuation to 1 × 10⁻³ torr at 25 °C did not show this new resonance, which implies that the product of the reaction with H₂ was easily desorbed. Further treatment of the samples with H₂ resulted in the reappearance of the resonances at the same positions as had been observed initially. Subsequent evacuation again led to a reduction of the intensity of each of these resonances. With each of these samples, the reaction with H₂ was taken to completion by allowing H₂ to flow over the samples for an extended period—beyond the time when the reaction product and the allyl resonance were still observed in the ¹H NMR spectrum.

In an effort to confirm the identities of the products of the reaction {Si}-O-Rh(allyl)₂ with H₂, ¹H NMR spectra were obtained for propene, propane, and H₂O adsorbed on the calcined silica support and on the samples containing 0.75 and 1.4 wt % rhodium—following completion of the reaction with hydrogen.

(25) The phenomenon of hydrogen spillover has been discussed extensively in the catalysis literature: (a) Sermon, P. A.; Bond, G. C. *Catal. Rev.* **1973**, *8*, 211. (b) Primet, M.; Basset, J. M.; Mathieu, M. V.; Prettre, M. J. *Catal.* **1973**, *28*, 368. (c) Anderson, J. R.; Foger, K.; Breakspere, R. J. *Ibid.* **1979**, *57*, 458. (d) Kramer, R.; Andre, M. *Ibid.* **1979**, *58*, 287. (e) Menon, P. G.; Froment, G. F. *Ibid.* **1979**, *59*, 138.

The results of these adsorption experiments are shown in Table VII. Propene adsorbed on the calcined silica support displayed two resonances with equal peak areas. The downfield resonance at δ 4.1 is assigned to the combined resonances of the methylene and methyne protons of the double bond unit, and the upfield resonance at δ 0.6 is assigned to the protons of the methyl group. These chemical shifts are in agreement with what one would expect for protons in these environments. The resonances attributed to propene adsorbed on the sample containing 0.75 wt % Rh have the same chemical shifts as the resonances of propene adsorbed on SiO_2 . The resonances of the propene on the sample containing 1.4 wt % Rh are shifted 0.5 ppm to lower field. To repeat: the downfield resonance of propene shifts to lower field with increased rhodium loading. This behavior parallels that observed for the product resonance formed during the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen. Furthermore, the downfield resonance of propene adsorbed on samples containing 0.75 and 1.4 wt % Rh appears at the same position as the new resonance identified with the product of the reaction $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen. We therefore infer that this adsorbed product was propene.

Since propane has also been identified as a product of the reaction of hydrogen with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$, propane was adsorbed on the reduced samples and ^1H NMR spectra were collected. As shown in Table VII, propane shows one resonance centered at δ 0.3, which we assign to both the methyl and methylene hydrogens. The resonance observed for propane did not shift with increasing rhodium loading. Therefore, we conclude that it is unlikely that we observed adsorbed propane under the conditions used during the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen. This result is consistent with expectation for the weakly adsorbed alkane.

We recognize that water could also have been a side product formed during the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen. Introduction of water to the calcined silica and to samples of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ which had been exhaustively reduced resulted in a single ^1H NMR resonance at δ 4.1 (Table VII). The ^1H NMR resonance indicative of water does overlap that of the downfield resonance of adsorbed propene and that of the product resonance observed during the reaction of hydrogen with the $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ samples. With the sample having the highest rhodium loading (3.2 wt %), however, the product resonance observed during reaction with hydrogen was farther downfield, at δ 5.4—a shift which would be expected for adsorbed propene but not observed for water. Thus it is likely that the ^1H NMR resonance observed for the volatile product of the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen is associated largely with propene—but the possibility of water is not entirely negligible. It is plausible that propene and water were formed by the reaction of protons, generated during the reduction of Rh(III) to Rh(0), with the allyl ligands of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ and surface hydroxyl groups, respectively. This suggestion is supported by the observation that hydrogen flowing for 2 h over a sample of pre-reduced $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ did not lead to any resonance attributable to water in the ^1H NMR spectrum. Clearly, if water were present, it must have been formed during the reduction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$.

Propane was observed by GC-mass spectrometry to be a major product of the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen. To understand this result, we conducted the following *in situ* ^1H NMR experiments. With the samples listed in Table VII (calcined silica and two $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ samples, containing 0.75 and 1.4 wt % Rh, respectively, each of the latter two after exhaustive exposure to H_2), propene and hydrogen were introduced separately and sequentially, and during the period of the introduction the surface ^1H NMR spectrum was monitored. Propene at 400 torr was introduced into the chamber containing the silica sample. Two resonances were observed, as noted previously, one at δ 4.1 and one at δ 0.6. Hydrogen was then introduced, bringing the total pressure up to 700 torr. The ^1H NMR spectrum recorded at this time indicated no change (Table VII). The same sequence of experiments was performed with each of the rhodium-containing samples. Introduction of propene at 400 torr resulted in a ^1H NMR spectrum displaying the resonances for propene (Table VII

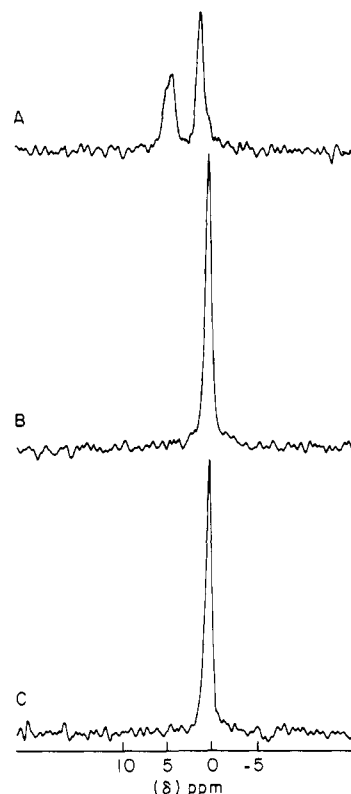


Figure 4. ^1H NMR spectra during hydrogenation of $\text{CH}_3\text{CH}=\text{CH}_2$ on reduced $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ (0.75 wt % Rh): A, $\text{CH}_3\text{CH}=\text{CH}_2$ on the reduced sample (400 torr, 25 °C; 250 coadditions); B, after introduction of H_2 to sample preexposed to $\text{CH}_3\text{CH}=\text{CH}_2$ (700 torr, 25 °C; 250 coadditions); C, after subsequent evacuation of sample (1×10^{-3} torr, 25 °C) and exposure to $\text{CH}_3\text{CH}_2\text{CH}_3$ (400 torr, 25 °C; 250 coadditions).

and Figure 4A). Hydrogen was then admitted, bringing the total pressure to 700 torr. The ^1H NMR spectrum of the sample now displayed one resonance at δ 0.3 (Table VII and Figure 4B). Evacuation of the sample (1×10^{-3} torr, 25 °C) and introduction of propane at 400 torr resulted in a ^1H NMR spectrum also showing only one resonance at δ 0.3 (Table VII and Figure 4C). This result clearly confirms that propene hydrogenation occurred on the surface of the rhodium-containing samples. Introduction of H_2 at 100 torr, followed by propene to give a total pressure of 400 torr, led to the same result, namely, one resonance in the ^1H NMR spectrum occurring at δ 0.3. Reversing the order of reagent introduction had no effect on the ultimate hydrogenation reaction of the propene. We suggest that the hydrogenation reaction of propene was catalytic, involving the Rh.

A broad resonance beneath that attributed to the allyl protons became evident in the ^1H NMR spectrum upon reaction of the sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 (Figure 1). The treatment of the sample with H_2 in these experiments caused it to become brown and then black, as it had during the reduction experiments mentioned above. The ^1H NMR spectrum of the sample obtained after extensive reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 at 25 °C is compared in Figure 5 with a spectrum of the calcined silica after treatment with distilled water and evacuation to 10^{-3} torr. These two resonances are in the same position; they are therefore assigned to protons in $\{\text{Si}\}-\text{OH}$ groups. This result is in good agreement with previous work.¹³ No other resonances were observed, either upfield or downfield of this resonance.

One might be tempted to assign this resonance to a rhodium hydride species rather than to $\{\text{Si}\}-\text{OH}$ groups; however, upon introduction of propene and subsequent evacuation, this resonance was not decreased in intensity. A hydride of rhodium would be expected to react rapidly with propene under these conditions, and any hydride resonance would be expected to disappear. This result, combined with the spectrum of the authentic sample containing $\{\text{Si}\}-\text{OH}$ groups, therefore confirms the inference that the broad resonance is indicative of protons in $\{\text{Si}\}-\text{OH}$ groups.

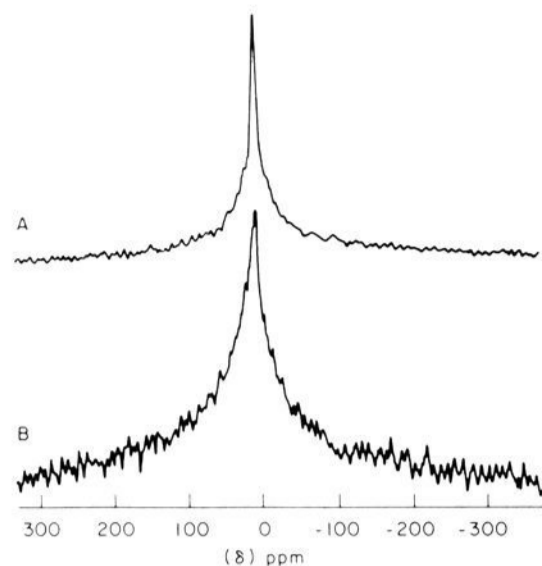


Figure 5. ^1H NMR spectra of surface hydroxyl groups: A, after prolonged reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with flowing H_2 (760 torr, 25°C ; 100 coadditions); B, $\{\text{Si}\}-\text{OH}$ protons on the calcined support surface after exposure to H_2O (20 torr; 1000 coadditions, intensity multiplied by 2.5 vs. spectrum A).

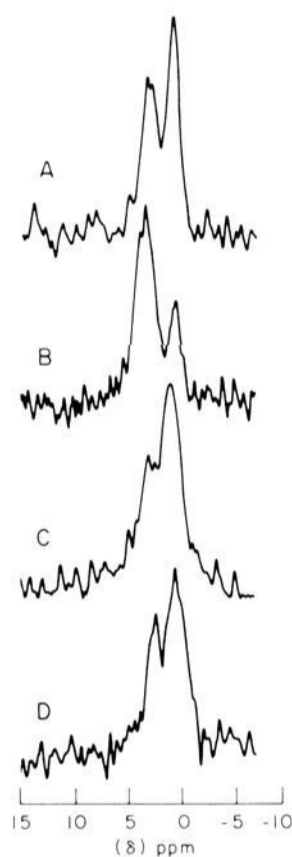


Figure 6. ^1H NMR of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ (0.75 wt % Rh) during reaction with D_2 : A, after reaction with flowing D_2 for 30 min (760 torr, 25°C ; 500 coadditions); B, after reaction with D_2 for 48 h (760 torr, 25°C ; 500 coadditions); C, subsequent evacuation of sample (1×10^{-3} torr, 25°C ; 2500 coadditions, intensity multiplied by 2.25 vs. spectrum A and B); D, after reexposure to D_2 for 60 min (500 torr, 25°C ; 2500 coadditions, intensity multiplied by 2.25 vs. spectra A and B).

The assignment to $\{\text{Si}\}-\text{OH}$ groups of the broad resonances in the ^1H NMR spectrum of the samples exposed to H_2 is supported by results of an experiment carried out with D_2 . As shown in Figure 6, treatment of a sample having a low rhodium loading (0.75 wt %) with D_2 led to the spectral changes expected on the basis of the results obtained with H_2 . First, a downfield resonance attributed to propene grew in, which was readily removed by evacuation and which continued to form upon subsequent exposure to D_2 . The notable difference between these spectra and those obtained during treatment with H_2 is that the broad resonance attributed to the $\{\text{Si}\}-\text{OH}$ groups was not present (Figure 6), as expected, since $\{\text{Si}\}-\text{OD}$ species are proton NMR silent.

The ^1H NMR results also show that exposure of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to CO at 25°C followed by exposure to H_2 at 25°C led neither to the formation of propane or propene nor to the formation of $\{\text{Si}\}-\text{OH}$ groups. We conclude that CO inhibited the reduction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to rhodium metal by H_2 at 25°C . The CO inhibition demonstrates that the otherwise facile reduction by H_2

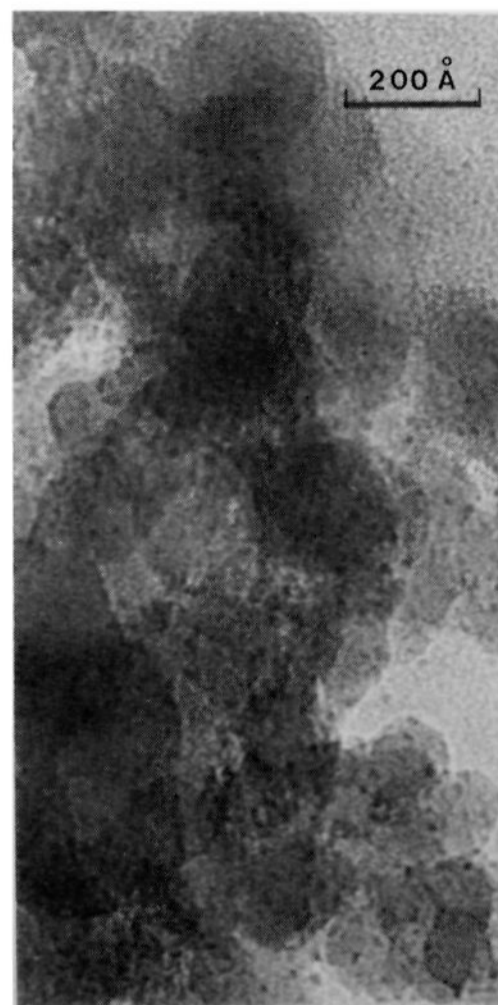


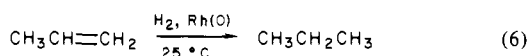
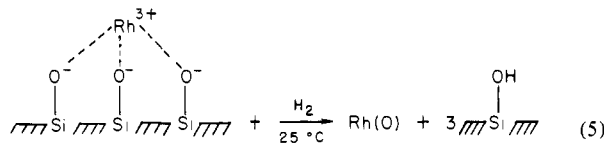
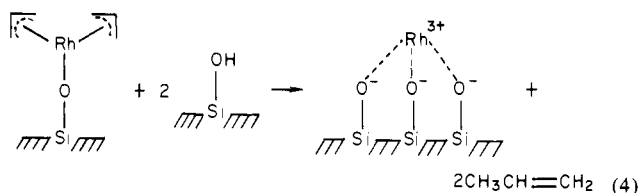
Figure 7. Transmission electron micrograph of a sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ after reduction in hydrogen at 25°C . Particles of Rh are discernible and have dimensions from 10 to 30 Å.

involved the rhodium sites which adsorb CO ; these same [presumably $\text{Rh}(\text{III})$] sites are probably responsible for the initial adsorption of H_2 .

All the spectroscopic results indicated that rhodium metal was forming during the reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with H_2 at 25°C . To characterize the reduced rhodium, transmission electron micrographs were obtained of a sample of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ (0.75 wt % Rh) which had reacted with hydrogen (in the H_2/D_2 exchange experiment) at 25°C . A micrograph of this sample is displayed in Figure 7. There is a fairly uniform distribution of rhodium aggregates ranging in size from 10 to 30 Å. The micrographs confirm the conclusion drawn from the spectroscopic results, namely, that rhodium aggregates had formed under mild reducing conditions, i.e., in flowing hydrogen at 25°C .

From the combined spectroscopic and microscopic results, it is clear that reaction of $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ with hydrogen results in reduction of rhodium to the metal and formation of propene; this process requires cleavage of the $\text{Rh}-\text{O}$ bond. We propose that H_2 is initially adsorbed at the same sites that initially adsorb CO , namely, the $\text{Rh}(\text{III})$ ions. This adsorption of H_2 at the $\text{Rh}(\text{III})$ ions leads to reduction to $\text{Rh}(0)$ and spillover of protons to the support.²⁵ These protons are available to react with $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$, generating, we propose, more propene and $\text{Rh}(\text{III})$ ions. Further reaction with H_2 results in more reduction to rhodium metal and hydrogenation of propene to give propane. This proposal is supported by the experimental observation that, in the presence of D_2 , protons on the support are exchanged with deuterons. Presumably this hydrogen-deuterium exchange proceeds by a mechanism like that outlined above for the reaction of the rhodium complex with hydrogen, namely, via an initial heterolytic cleavage of deuterium. Further support for the intermediacy of alternate rhodium sites comes from the observation that prior reaction with CO inhibited the reaction with H_2 . This observation can be explained readily since CO reacts with these $\text{Rh}(\text{III})$ ions to generate $\text{Rh}^1(\text{CO})_2$ groups, as proposed above, rendering them unavailable for activation of H_2 and subsequent adsorption; thus, when CO is preadsorbed, hydrogen is not cleaved, protons are not spilled over to the support, and the reaction with H_2 is inhibited. Summarizing these results, we propose that the reaction with H_2 leads to elimination of propene, cleavage of the

Rh-O bond, reduction of Rh(III) ions to Rh(0), and hydrogenation of propene to propane:



Reaction of Supported Rhodium Complexes with CO and H₂.

Reaction of the supported rhodium complex with CO after H₂ treatment and vice versa were also investigated.

To elucidate the nature of the rhodium in the H₂-treated sample, it was exposed to CO at 1 atm and 25 °C. The resulting sample had an infrared spectrum with carbonyl bands at 2109, 2090, 2055, 2035, and 1880–1845 cm⁻¹. The bands at 1880–1845 cm⁻¹ and that at 2055 cm⁻¹ are attributed to a bridging CO species and a terminal monocarbonyl species, respectively;^{19a-d} these results indicate that during the reaction with H₂, aggregation of the metal had occurred. As expected, the sample was black after the experiment.

The ¹H NMR spectra had already shown that exposure to CO inhibited the reaction with H₂ at 25 °C. With this in mind, we investigated reaction of the CO-exposed material with H₂ at elevated temperatures. After {Si}-O-Rh(allyl)₂ had been exposed to CO, it was exposed to H₂ at 1 atm and 25 °C for 15 min; there was no observable change in the infrared spectrum. Subsequent heating of the sample to 100 °C under flowing H₂ led to a marked decrease in the intensities of the carbonyl bands at 2105 and 2090 cm⁻¹ relative to the band at 2035 cm⁻¹ (Figure 2B). Reaction with H₂ at 100 °C for 30 additional minutes produced no further change in the spectrum. Heating to 150 °C under H₂ caused the bands at 2105 and 2090 cm⁻¹ to decrease further in intensity and the band at 2031 cm⁻¹ to broaden and shift to 2055 cm⁻¹ (Figure 2C). Exposure of the sample to H₂ for an additional 30 min at 150 °C led to no further change in the spectrum. After evacuation of the sample at 150 °C for 30 min, all the carbonyl bands were reduced to very low intensity. The sample removed from the cell was black, which suggests that Rh metal had formed. The decrease in intensity of the band at 2090 cm⁻¹ (attributed to the dicarbonyl rhodium species) is consistent with the suggestion of metal agglomeration in these experiments. The shift and broadening of the band originally located at 2035–2055 cm⁻¹ is also consistent with this suggestion, since it can be explained by the growth of a new terminal monocarbonyl.

The conclusion that the rhodium agglomerated is supported by XPS results. A sample of {Si}-O-Rh(allyl)₂, after exposure to CO, was heated from 25 to 150 °C in H₂ and held at 150 °C for 10 min, after which the sample blackened and the Rh 3d_{5/2} peak was observed at 307.4 eV. The intensity of the Rh peak decreased 5-fold relative to the intensities of the Rh peaks of the untreated and CO-treated samples; this result supports our contention that the rhodium aggregated into crystallites, since it indicates that a decreasing fraction of the Rh atoms were present on a surface, accessible to the X-rays. Further, deconvolution of the broad peak at 307.4 eV gave rise to two peaks (at 307.0 and 308.1 eV), consistent with partial reduction of the sample to rhodium metal (Table III).

Summary of Surface Organometallic Chemistry and Genesis of the Supported Metal Catalyst

Reduction of the Rhodium. In summary, the spectroscopic results and transmission electron micrographs lead to the con-

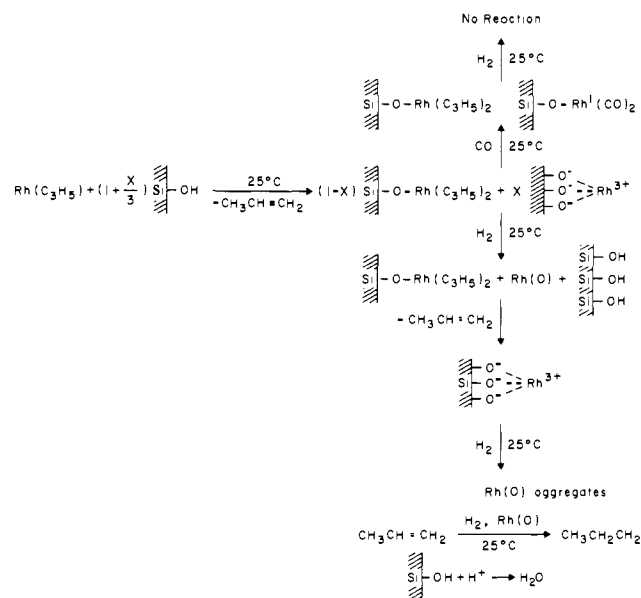


Figure 8. Proposed scheme of reactions for {Si}-O-Rh(allyl)₂ with CO and H₂.

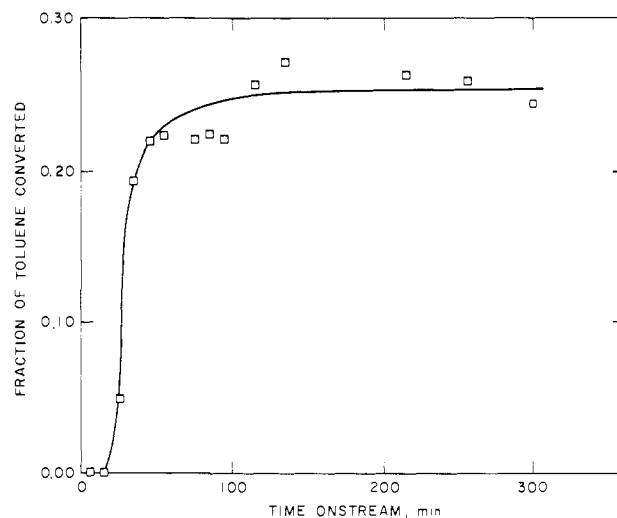
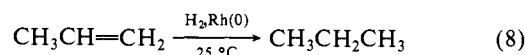
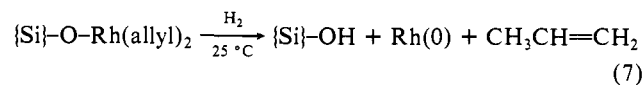


Figure 9. Transient catalytic hydrogenation of toluene in a flow reactor at 25 °C. The initial form of the catalyst was {Si}-O-Rh(allyl)₂; the catalytically active species is inferred to be rhodium metal.

clusion that {Si}-O-Rh(allyl)₂ is readily reduced by H₂ at 25 °C to give lower-valent rhodium species, including aggregates of rhodium metal, accompanied by formation of {Si}-OH groups:



This chemistry is consistent with the reported chemistry of the surface-bound allyl complexes of nickel, palladium, and platinum.¹ The supported allyl complexes of the latter two metals were reported to be reduced at 20 °C; higher temperatures were required for nickel.

We regard it as highly unlikely that {Si}-O-Rh(allyl)₂ is reduced by an oxidative addition of H₂ to the Rh(III) center followed by reductive elimination of propene; such a mechanism would require the intermediacy of a high-energy Rh(V) species. We suggest that {Si}-O-Rh(allyl)₂ does not react with molecular H₂ at all. We infer that hydrogen is adsorbed on other rhodium centers, the same ones that adsorb CO (which inhibits the reduction). The hydrogen may then be spilled over onto the silica support to

regenerate surface hydroxyl groups or to react with the $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ groups to eliminate allyls as propene and to generate Rh(III) ions, which are reduced to zerovalent rhodium, which migrates over the surface and aggregates to form metal particles.

A schematic representation of the surface organometallic chemistry is shown in Figure 8. This picture is consistent with (1) the observation that CO inhibited the reaction with H_2 at 25 °C, (2) the observation of D_2 exchange with the hydroxyl groups of the support, (3) production of propene and propane upon reaction with H_2 , (4) electronic considerations regarding the rhodium center, and (5) the observation of rhodium metal formation. The key is that a separate rhodium species acts as the site for H_2 activation, which leads to the ready formation of rhodium metal from $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ groups.

Genesis of Catalytically Active Species. The ease with which $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ is reduced in the presence of H_2 to give rhodium metal led us to suspect that rhodium metal, and not a complex related to $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$, might have been the catalyst in the reported hydrogenations of alkenes and arenes.^{2b,c} If rhodium metal were the actual catalyst, one would expect an induction period followed by a rise in catalytic activity as rhodium metal formed from the diallyl complex. Consistent with this expectation, results of the catalytic hydrogenation experiment carried out in the flow reactor (Figure 9) show that a short induction period

was followed by a rapid rise in the conversion of toluene to methylcyclohexane. Subsequent treatment of the catalyst with helium for 10 h and resumption of flow of toluene and H_2 led to 100% conversion of the toluene. The used catalyst was black. All these results are consistent with the reduction of the $\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2$ to rhodium metal, which we infer to be the catalytically active species. The interpretation is consistent with the results of Ward and Schwartz, who found that the olefin hydrogenation was first order in H_2 and zero order in olefin; these are the dependencies expected for a rhodium metal catalyst.^{26,27}

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Registry No. Rh(allyl)₃, 12082-48-3; CO, 630-08-0; H_2 , 1333-74-0; HCl, 7647-01-0; toluene, 108-88-3.

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(27) Graydon, W. F.; Langan, M. D. *J. Catal.* **1981**, *69*, 180. Rhodium aggregates smaller than 12 Å in diameter apparently have low catalytic activity for benzene hydrogenation, whereas aggregates having diameters between 12 and 20 Å have higher activity.

A Molecular Orbital Calculation of the $[\text{Re}_2\text{Cl}_8]^{2-}$ Ion by the Relativistic SCF- $X\alpha$ -SW Method. Redetermination and Reassignment of the Electronic Absorption Spectrum

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Abstract: The electronic structure and spectrum of the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion have been reinvestigated. A new calculation by the SCF- $X\alpha$ -SW method gives results in essential agreement with the earlier calculation of Mortola et al., but the inclusion of corrections for inner-shell and valence relativistic effects causes appreciable shifts that are important in analyzing the spectrum. The polarized single-crystal spectrum has been remeasured under more defined conditions and better resolution, and the new results reveal several minor and one major flaw in the earlier measurements. The new computational and experimental data lead us to revise the previously proposed assignments of the weak, forbidden bands lying between the $\delta \rightarrow \delta^*$ transition and the strong near-UV absorptions.

The $[\text{Re}_2\text{Cl}_8]^{2-}$ ion occupies a unique place in the development of our understanding of multiple bonds between metal atoms since it was the first well-defined example of such bonding between a discrete pair of metal atoms, as well as the first example of a quadruple bond of any kind, and it remains the prototypal species in this now large field of chemistry. It is thus a matter of more than casual interest to have a thorough understanding of the electronic structure of this particular ion.

Both $[\text{Re}_2\text{Cl}_8]^{2-}$ and the isostructural and isoelectronic $[\text{Mo}_2\text{Cl}_8]^{4-}$ ions have been the subjects of some of the first rigorous MO calculations^{1,2} carried out on quadruply bonded species, in each case by the SCF- $X\alpha$ -SW method. While the published results for $[\text{Mo}_2\text{Cl}_8]^{4-}$ appear to be as reliable as possible within

the scope of the method and have been fully reported, this is not entirely the case for the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion. For one thing, the results of the original calculation¹ have never been presented in full, and because of the tragic death of the senior investigator, A. P. Mortola, probably never can be. Second, for $[\text{Re}_2\text{Cl}_8]^{2-}$, as for all compounds containing atoms of such high atomic number as rhenium, valence corrections for relativistic effects, which can amount to an electron volt, should (and now can) be made in order to justify considering the results as final.

It is our purpose here to present the results in detail for what we believe to be the definitive SCF- $X\alpha$ -SW calculation, including relativistic effects, on the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion and to use these results together with much new spectroscopic data to reexamine the assignments previously proposed by Trogler, Cowman, Gray, and Cotton³ (hereafter cited as TCGC) for the spectral region between the $\delta \rightarrow \delta^*$ transition at about 14 200 cm^{-1} and the first strong

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