respect to the construction of both ion-sensing interfaces and electrosynthetic cells.

Experimental Section

Materials. Nickel electrodes consisted of Ni wire of 0.63-mm diameter (Alfa). Nickel plate electrodes used for IR studies were 0.125-mm thick (Alfa) having an area of 1 cm^2. Inco 255 Ni powder was used for UV-vis studies. Reagent grade chemicals were used as derivatizing agents and supporting electrolytes. $Na_3Fe(CN)_5H_2O$ was made by dissolving $Na_3Fe(CN)_5NH_3$ in distilled water at pH 4.[33] $[Fe(CN)_5His]^{2-}$ solution was made by stirring a mixture of 50 mL of 0.2 M $Na_3Fe(CN)_5H_2O$, 50 mL of 6% H_2O_2, and 2.3 g of L-histidine in the dark for 45 min at about 5 °C. A catalytic amount of MnO_2 was added at the end of the reaction to decompose excess H_2O_2.[34]

Electrochemistry. A single-compartment cell with a large Pt-mesh counterelectrode and SCE as reference was used. Measurements were made with a PAR Model 174A potentiostat and a PAR Model 175 programmer. Electrodes were abraded with 150 metalite cloth and washed with distilled water before derivatization. After derivatization, they were wiped with a Kimwipe and washed with distilled water to remove loosely adhering substances. Data were recorded on a Houston Instruments 2000 recorder.

Ideal electrodes were made by potentiostating the Ni-wire electrodes at 1.0 V vs. SCE for 50 s in an electrolyte containing 0.1 M $NaNO_3$ and 0.005 M $[Fe(CN)_6]^{3-}$. By appropriate increase of potentiostating voltage, time, and concentration of $[Fe(CN)_6]^{3-}$, larger coverage electrodes were obtained as desired.

Spectroscopy. Diffuse-reflectance FT IR spectroscopy was carried out on a Digilab FTS.20C spectrometer with a diffuse-reflectance attachment. A derivatized Ni-plate electrode was used as the sample while a nonderivatized abraded Ni plate served as the reference. The model compounds were used as powders and referenced against KBr. UV-vis spectra were recorded on a Hewlett-Packard 8540A UV-vis spectrometer.

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Registry No. $K_3Fe(CN)_6$, 13746-66-2; $Fe(CN)_6^{3-}$, 13408-62-3; $Na_3Fe(CN)_5H_2O$, 14100-31-3; $[Fe(CN)_5His]^{2-}$, 88181-56-0; $Ru(CN)_6^{4-}$, 21029-33-4; $KNiFe(CN)_6$, 53295-14-0; $K_4Fe(CN)_6$, 13943-58-3; $K_2NiFe(CN)_6$, 13601-16-6; $Na_2Fe(CN)_5H_2O$, 14220-67-8; $NiFe(CN)_5H_2O$, 88181-57-1; $Na_2Fe(CN)_5NO$, 14402-89-2; $NiFe(CN)_5NO$, 14709-61-6; $NiFe(CN)_5His$, 88181-58-2; $K_4Ru(CN)_6$, 15002-31-0; $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Fe(CN)_5H_2O]^{3-}$, 18497-51-3; $[Fe(CN)_5NO]^{2-}$, 15078-28-1; $[Fe(CN)_5His]^{3-}$, 60105-82-0; $Ru(CN)_6^{3-}$, 54692-27-2; $[Fe(CN)_5H_2O]^{2-}$, 19413-97-9; $Mn(CN)_6^{3-}$, 14931-63-6; $Mn(CN)_6^{2-}$, 66735-85-1; Ni, 7440-02-0; Cs, 7440-46-2; Rb, 7440-17-7; K, 7440-09-7; NH_4^+, 14798-03-9; Na, 7440-23-5; Ba, 7440-39-3; Li, 7439-93-2; $NaNO_3$, 7631-99-4; TBA^+, 10549-76-5; ferrocene, 102-54-5.

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Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139,
and Colorado State University, Fort Collins, Colorado 80521

Characterization and Photochemistry of Surface-Confined Mononuclear and Trinuclear Phosphine/Carbonyl Complexes of Ruthenium(0)

DAVID K. LIU,[1] MARK S. WRIGHTON,*[1] DALE R. McKAY,[2] and GARY E. MACIEL[2]

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The characterization and photochemistry of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ are reported, where $[SiO_2]-$ represents high surface area (~400 m^2/g) SiO_2. Synthesis of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ is effected by reaction of $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ or $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ with a hydrocarbon suspension of $[SiO_2]-$. Solid-state ^{13}C, ^{29}Si, and ^{31}P CP/MAS NMR, FTIR, UV-vis photoacoustic spectroscopy, and elemental analyses establish the nature of the functionalized $[SiO_2]-$. Typical coverage of $-LRu(CO)_4$ or $-L_3Ru_3(CO)_9$ is $\sim 10^{-10}-10^{-11}$ mol/cm^2. Photoexcitation (near-UV) of $[SiO_2]-LRu(CO)_4$ suspended in hydrocarbon media results in a chemical reaction consistent with the dissociative loss of CO to give a 16-valence-electron, surface-confined species that reacts with 2-electron P-donors. The light-induced extrusion of CO can be effected and detected spectroscopically by chemical trapping in rigid media at low temperature (~90 K). Near-UV irradiation of $[SiO_2]-LRu(CO)_4$ at 298 K exposed to a gas gives chemistry consistent with dissociative loss of CO, also. Complete (>90%) exchange of CO for ^{13}CO can be effected by irradiation under 1 atm of ^{13}CO, as monitored by FTIR/photoacoustic spectroscopy. The photochemistry of $[SiO_2]-L_3Ru_3(CO)_9$ involves metal-metal bond rupture; under 1 atm of CO in a solid/gas reaction or as a suspension in hydrocarbon solvent saturated with CO, $[SiO_2]-L_3Ru_3(CO)_9$ yields $[SiO_2]-(LRu(CO)_4)_3$. The surface-confined mononuclear species formed photochemically from the surface-confined trinuclear species are spectroscopically indistinguishable from the deliberately synthesized $[SiO_2]-LRu(CO)_4$. However, irradiation of $[SiO_2]-(LRu(CO)_4)_3$ leads to reassembly of the surface cluster, $[SiO_2]-L_3Ru_3(CO)_9$, whereas irradiation of $[SiO_2]-LRu(CO)_4$ yields no surface cluster. For small P-donors, L′, irradiation of $[SiO_2]-L_3Ru_3(CO)_9$ yields $[SiO_2]-(LRu(CO)_3L')_3$, whereas $[SiO_2]-LRu(CO)_4$ yields $[SiO_2]-LRu(CO)_3L'$ for large and small L′. Both $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ yield gas-phase CO and CO_2 as products when irradiated while exposed to an O_2-containing atmosphere.

Photochemistry at interfaces is of practical importance in several respects including solar energy conversion and imaging. Potentially, photochemistry at interfaces could have practical value in catalytic synthesis, depending on the nature of the photoreactions that can be effected. Fundamentally, study of light-induced chemistry at interfaces can lead to elucidation of reaction mechanisms and to new photoreactions. One of the exciting prospects associated with photochemistry of surface-confined molecules is that "active sites" on a surface can be prepared rationally and characterized with an arsenal of molecular-specific probes. Additionally, chemistry not possible in homogeneous solution may be possible for molecular entities attached to a surface.

In this paper, we elaborate results previously communicated[3] concerning surface-confined mononuclear and trinuclear ru-

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(2) Colorado State University.

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thenium carbonyl/phosphine complexes. The systems studied are $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$, where $[SiO_2]-$ represents high surface area SiO_2 and L is a phosphine ligand that covalently links the molecular entities to the SiO_2. Reaction of $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ or $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ with SiO_2 yields $[SiO_2]-LRu(CO)_4$ or $[SiO_2]-L_3Ru_3(CO)_9$, respectively. Photoreactions of the solution species $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_9(PPh_3)_3$ and related complexes involve loss of CO and metal-metal bond cleavage, respectively.[4] The Ru-P bond is photoinert, suugesting that the surface link(s) in $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ should survive irradiation. We now report the complete characterization and photochemical behavior of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$.

Experimental Section

Instruments. UV-vis spectra of solution species were recorded on a Cary 17 spectrophotometer. UV-vis photoacoustic spectra of surface-confined materials were taken with a Princeton Applied Research Model 6001 photoacoustic spectrometer. Solution IR spectra were recorded on a Perkin-Elmer 180 grating or Nicolet 7199 Fourier transform spectrometer. Low-temperature IR spectra were obtained by using a Precision Cell, Inc., Model P/N 21,000 variable-temperature cell with NaCl outer windows and liquid N_2 as coolant. The sample temperature obtained was typically 90-100 K. For surface-confined materials, IR spectra were obtained as Nujol mulls between CaF_2 plates on the FTIR spectrometer. NMR spectra of solution species were obtained on a JEOL FX90Q or Bruker 250-MHz Fourier transform spectrometer. FTIR/PAS spectra were obtained by using a Nicolet 7199 spectrometer, equipped with a photoacoustic detector that allows control of the sample environment.[5] The acoustic coupling gas was either 1 atm of Ar or 1 atm of a 1/4 mixture of O_2/Ar for photolysis experiments. All manipulations of O_2- and H_2O-sensitive materials were carried out in a N_2-filled Vacuum Atmospheres He-43-6 Dri-Lab glovebox with an attached He-493 Dri-Train or under Ar by using conventional Schlenk techniques.

Irradiations. Most photochemical reactions were carried out with use of a Bausch and Lomb SP200 200-W high-pressure Hg lamp with a Pyrex water filter, a Hanovia 450-W medium-pressure Hg lamp with Corning glass filters to isolate the 366- or 436-nm emission, or a GE Blacklite (355 ± 20 nm). In experiments where $[SiO_2]-L_3Ru_3(CO)_9$ was to be photochemically converted to $[SiO_2]-(LRu(CO)_4)_3$, the Hanovia lamp was filtered to pass only visible light to avoid photoexcitation of the mononuclear species.

Materials. Isooctane, hexane, toluene, and CH_2Cl_2 were reagent grade and freshly distilled from CaH_2 under N_2. Methylcyclohexane (99%, Aldrich) was washed twice with H_2SO_4 and then with fuming H_2SO_4, H_2O, dilute $NaHCO_3$, and saturated NaCl, predried over anhydrous $MgSO_4$, and then passed through grade 1 alumina (neutral, Woelm). $Ru_3(CO)_{12}$, PPh_2H, PPh_2Me, $PPh_2CH_2CH_2Si(OEt)_3$, $P(OCH_2)_3CEt$, and $P(t\text{-}C_4H_9)_3$ were obtained from Strem Chemicals and used as received. PPh_3 (Aldrich) was recrystallized three times from absolute EtOH. 1-Pentene (99.9+%, Phillips) was passed through Al_2O_3 prior to use. Trimethoxyvinylsilane was obtained from Petrarch and used without further purification. High surface area SiO_2 (400 m^2/g, Alfa) was pretreated by heating at ~250 °C under vacuum (~10^{-2} torr) for 48 h. ^{13}CO (90% ^{13}C) and $^{18}O_2$ (98% ^{18}O) were obtained from Stohler Isotope Chemicals.

Slight modifications of literature procedures were used to synthesize $Ru_3(CO)_9L_3$ and $Ru(CO)_4L$ ($L = PPh_2CH_2CH_2Si(OEt)_3$).[6] The preparation of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ involves the suspension of ~1 g of pretreated SiO_2 in toluene. Addition of excess $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ or $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ was followed by stirring at 25 °C for 24 h under N_2. The solid was collected by suction filtration and washed repeatedly with toluene, dried under vacuum, and stored under N_2. $Ru(^{13}CO)_n(^{12}CO)_{4-n}(PPh_2CH_2CH_2Si(OEt)_3)$ (n = 1-4) was prepared by near-UV irradiation of a degassed toluene solution containing ~2 × 10^{-3} M $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ under 1 atm of ^{13}CO at 25 °C for 12 h. $[SiO_2]-LRu(^{13}CO)_n(^{12}CO)_{4-n}$ was prepared by the reaction of $Ru(^{13}CO)_n(^{12}CO)_{4-n}(PPh_2CH_2CH_2Si(OEt)_3)$ and high surface area SiO_2 as described above.

$PPh_2CH_2CH_2Si(OMe)_3$ was synthesized by a method analogous to that reported in the literature.[7] A 1/1 mixture of PPh_2H and $CH_2CHSi(OMe)_3$ together with trace amounts of AIBN, 2,2′-azobis(isobutyronitrile), was heated at 110° for 6 h under an Ar atmosphere. Vacuum distillation of the resulting solution gave ~4.0 g (~45% yield) of $PPh_2CH_2CH_2Si(OMe)_3$: bp 145-150 °C (~10^{-2} torr); ^1H NMR ($CDCl_3$) δ 7.18 (m, 10 H, Ph), 3.48 (s, 9 H, Me), 2.10 (t, 2 H, $P-CH_2$), 0.78 (t, 2 H, $Si-CH_2$); IR ν_{C-H}(SiOMe) ~2839 cm^{-1}, ν_{P-Ph} ~1482 cm^{-1}, ν_{P-CH_2} ~1438 cm^{-1}. $Ru_3(CO)_9L_3'$ and $Ru(CO)_4L'$ ($L' = PPh_2CH_2CH_2Si(OMe)_3$) were synthesized according to literature procedures,[6] and $[SiO_2]-L_3'Ru_3(CO)_9$ and $[SiO_2]-L'Ru(CO)_4$ were prepared as discussed above for the analogous $-Si(OEt)_3$ compounds.

CP/MAS NMR. The solid-state NMR measurements were taken on Nicolet spectrometers modified for solid-state work. An NT-150, operating at an observed frequency of 37.7 MHz and a proton irradiation frequency of 150 MHz, was used for the carbon-13 (^{13}C) measurements. The silicon-29 (^{29}Si) measurements were taken on an NT-200 with observed and proton irradiation frequencies of 39.7 and 200 MHz, respectively.

Magic-angle spinning was used to reduce line broadening due to chemical shift anisotropy[8] with spinning rates of about 3 kHz for the ^{29}Si measurements and about 4 kHz for the ^{13}C measurements. In both cases, a spinning system employing "bullet" rotors, similar to that of Bartuska and Maciel,[9] was used. To protect the samples from contamination, gas obtained by boiling liquid N_2 in a pressure vessel was used to drive the rotors.

Cross-polarization and high-power proton decoupling[10] were used in all of the measurements. As discussed in ref 10, cross-polarization enhances sensitivity and allows more rapid signal averaging, while high-power decoupling reduces the observed line width of the NMR signal.

The cross-polarization contact times used were typically 1 ms for ^{13}C and 3 ms for ^{29}Si. The optimum repetition rate for signal averaging appeared to be 500 ms, although 1 s was used in some cases. The proton irradiation field strengths were approximately 10 G in the ^{13}C measurements and 7 G in the ^{29}Si measurements.

Results and Discussion

a. Synthesis of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$. Preparation of the functionalized $[SiO_2]-$ follows well-known chemistry that has been exploited previously in the modification of oxides with organometallic reagents.[11] The key is the use of the phosphine ligand $PPh_2CH_2CH_2Si(OEt)_3$ that has the $-Si(OR)_3$ functionality that can react with surface $-OH$ groups to covalently anchor functional groups to the surface (eq 1).[11] The surface of $[SiO_2]-$ has been rather well

$$\text{surface }-OH + R'Si(OR)_3 \rightarrow \text{surface }-OSi(OR)_2R' + ROH \quad (1)$$

studied, and the approach taken here (detailed in the Experimental Section) to anchor the Ru complexes is unexceptional (eq 2 and 3). However, a variety of important issues

$$[SiO_2]- + Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3) \rightarrow [SiO_2]-LRu(CO)_4 \quad (2)$$

$$[SiO_2]- + Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3 \rightarrow [SiO_2]-L_3Ru_9(CO)_9 \quad (3)$$

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Table I. Solution and Solid-State NMR Data for Relevant Compounds[a]

compd	nucleus		
	^{31}P	^{13}C	^{29}Si
$Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$	46.4 (s)	204.5 (s), 132.0 (m), 58.6 (s), 26.8 (d), 18.0 (s), 3.0 (s)	−54.0
$[SiO_2]$–$LRu(^{13}CO)_4$[c]	41.0	198, 130, 60, 30, 15, 0	−48
$Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$	35.0 (s)	198.2 (s), 131.3 (m), 57.3 (s), 25.5 (d), 17.0 (s), 3.0 (s)	−54.9 (−44)[c]
$[SiO_2]$–$L_3Ru_3(CO)_9$[c]	34.5	. . .,[b] 135, 65, 30, 18, 3	−46, −53

[a] ^{31}P NMR are in δ relative to H_3PO_4 standard; ^{13}C and ^{29}Si NMR are in δ relative to $(CH_3)_4Si$ standard; s ≡ singlet, d ≡ doublet, m ≡ multiplet. [b] Resonance due to metal carbonyl not observed unless ^{13}C enriched. [c] Measured by solid-state CP/MAS NMR technique.

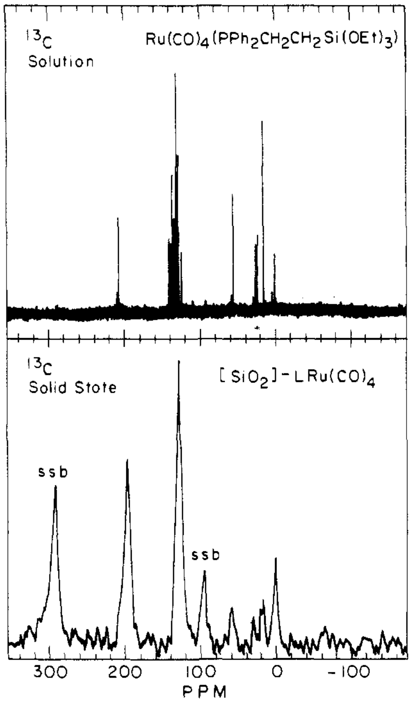

Figure 1. ^{13}C NMR for $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ in CD_2Cl_2 and ^{13}C CP/MAS NMR of $[SiO_2]$–$LRu(CO)_4$. Peaks marked ssb are spinning sidebands. Cf. Table I.

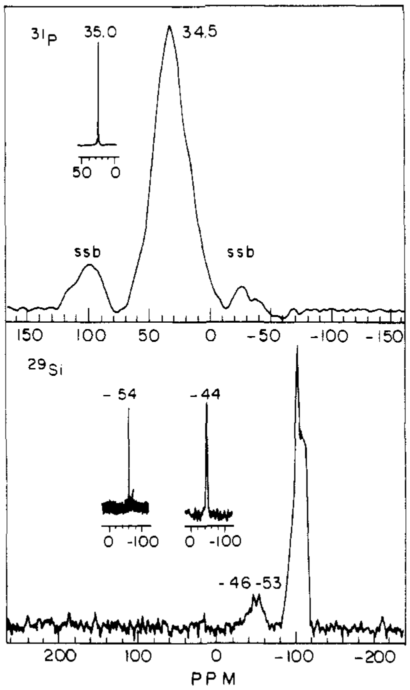

Figure 2. ^{31}P and ^{29}Si CP/MAS NMR of $[SiO_2]$–$L_3Ru_3(CO)_9$. The inset of the top frame is the ^{31}P NMR of $Ru_3(CO)_9$-$(PPh_2CH_2CH_2Si(OEt)_3)_3$ in $CDCl_3$. The left inset in the ^{29}Si spectrum is the ^{29}Si NMR of $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)$ in toluene solution and the right inset is the ^{29}Si CP/MAS NMR of the pure solid. Cf. Table I.

relating to the nature of the attachment of the molecules have generally not been elucidated and are critical to an understanding of the surface and interfacial chemistry of surface-confined molecules. Treatment of $[SiO_2]$– with $Ru(CO)_4$-(PPh_2Me) or with $Ru_3(CO)_9(PPh_2Me)_3$ under the same conditions used to effect reaction according to (2) and (3) results in no detectable color change of the SiO_2 powder. This control experiment establishes that the $-Si(OR)_3$ group is responsible for the attachment of the Ru complexes. In the section below, the characterization of $[SiO_2]$–$LRu(CO)_4$ and $[SiO_2]$–L_3-$Ru_3(CO)_9$ is detailed.

b. Characterization of $[SiO_2]$–$LRu(CO)_4$ and $[SiO_2]$–L_3-$Ru_3(CO)_9$. The white $[SiO_2]$– is colored by reaction according to (2) and (3); $[SiO_2]$–$LRu(CO)_4$ is yellow, and $[SiO_2]$–L_3-$Ru_3(CO)_9$ is red. Elemental analysis of the derivatized powder shows the presence of P and Ru in approximately a 1/1 ratio, and assuming ~400 m^2/g surface area, the coverage of $-LRu(CO)_4$ and $-L_3Ru_3(CO)_9$ is ~10^{-11} mol/cm^2. Taking ~10^{-10} mol/cm^2 to be a monolayer, the average coverage of $-LRu(CO)_4$ and $-L_3Ru(CO)_9$ is well below a monolayer. If the coverage is uniform, the typical mean site–site distance is ~20 Å. This value was determined as previously described.[12] Since it is known that $-Si(OR)_3$ can lead to polymerized (polysiloxane) material in the presence of trace amounts of H_2O,[13] uniformity of coverage is not easily proven. However, the low coverage rules out a uniform coating of polymeric material and is consistent with a uniform, submonolayer coverage. Spectroscopic characterization (vide infra) reveals incomplete hydrolysis of the Si–OR bonds and provides some evidence against the formation of polysiloxane incompletely coating the $[SiO_2]$–.

Cross polarization (CP)[14] and magic-angle spinning (MAS)[15] allow high-resolution NMR spectra to be recorded for surface-confined molecules. Recent examples include ^{13}C, ^{29}Si, and ^{31}P NMR spectra for species confined to $[SiO_2]$–.[16-19] We have applied CP/MAS solid-state NMR to the characterization of $[SiO_2]$–$LRu(CO)_4$ and $[SiO_2]$–$L_3Ru_3(CO)_9$. Table I summarizes NMR data for the derivatized solids and for the pure $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ and Ru-$(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$, and Figures 1 and 2 show some representative spectra. Data for ^{13}C, ^{29}Si, and ^{31}P NMR

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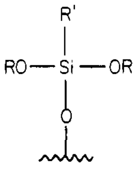
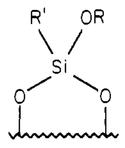
are consistent with the attachment of intact $-LRu(CO)_4$ and $-L_3Ru_3(CO)_9$ entities via the general route represented by (1)-(3). All of the signals for the surface-confined species are significantly broader than for the solution species, but the data are useful. The ^1H NMR spectra were recorded for $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ and $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$, and the integration shows the complexes to be pure; in particular, the species have intact $-Si(OEt)_3$ groups.

The information derived from the ^{13}C NMR spectra of the complexes is the richest of the three nuclei studied. A comparison of the spectra for both the solution and surface species shows six different types of carbons, and the resonances are observed in similar, but not identical, positions for the surface and for the solution species. Comparison with other complexes and free ligands allows the assignment of the resonances. The resonance in the vicinity of 200 ppm, attributable to the CO carbons, is not observable for the surface-confined molecule without enrichment in ^{13}CO. $[SiO_2]-LRu(CO)_4$ was enriched for this measurement. In addition to the expected CO carbon revealed at ~200 ppm, the phenyl carbons at ~130 ppm, the carbon adjacent to the P at ~30 ppm, and the carbon adjacent to the Si at ~3.0 ppm, we find signals at ~15 and ~60 ppm for all of the substances. The resonance at ~15 ppm is attributable to the terminal carbon of the -OEt group, and the ~60 ppm signal is assigned to the carbon adjacent to the O atom in the -OEt group. The observation of the -OEt carbons rules out complete hydrolysis of the Si-OEt bonds during the synthetic procedure, and the relative intensity of the other carbon signals to the -OEt carbons reveals that a large fraction of Si-OEt bonds are intact in the $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ samples. Roughly, the relative signal intensities would suggest that ~50% of the -OEt groups are retained in the present case. This number has been confirmed by IR measurements of surfaces derivatized with complexes of $PPh_2CH_2CH_2Si(OMe)_3$ (vide infra). It is possible that -OEt signals are due to surface -OEt groups from reaction with released EtOH. A control experiment shows that surface -OEt is not FTIR detectable when SiO_2 is treated with 0.1 M EtOH in toluene in the same manner used in derivatization using the Ru complexes. The 0.1 M EtOH represents a ~ 50-fold excess beyond the EtOH that could be available in the hydrolysis of the ~1 mM concentration of Ru complexes used in derivatization. The line widths of the ^{13}C signals for the solids are too great to observe the individual aromatic carbons or to observe splitting of the ^{13}C resonances by the P, but the positions of the signals for the six different kinds of carbons accord well with the assertion that the surface $-LRu(CO)_4$ and $-L_3Ru_3(CO)_9$ are intact analogues of the derivatizing reagents.

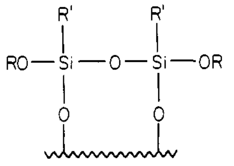
The ^{13}P NMR spectra are consistent with the attachment of the molecular species, but no interesting conclusions can be drawn from the CP/MAS spectra, especially since the line widths are so large. The ^{29}Si spectra do, however, provide some useful information. The -90 to -110 ppm region of $[SiO_2]-$ is affected by the derivatization procedure in a manner consistent with reaction of some of the surface Si-OH groups.[16,17,19] The underivatized $[SiO_2]-$ shows resonances at -91, -100, and -109 ppm corresponding to silicon moieties of the types $(HO)_2Si^*(OSi-)_2$, $(HO)Si^*(OSi-)_3$, and $Si^*(OSi-)_4$, respectively.[16,17,19] The interesting features are in the -44 to -62 ppm range. The derivatized $[SiO_2]-$ shows no signal at -62 ppm attributable to $R'Si^*(OSi-)_3$. Rather, the -46 to -53 ppm signals are attributable to structures where there is at least one -OEt group on the Si, as deduced from the ^{13}C spectra. Indeed, the -48 ppm ^{29}Si signal for $[SiO_2]-LRu(CO)_4$ is most consistent with structure I. The -46 to -53 ppm ^{29}Si signals for $[SiO_2]-L_3Ru_3(CO)_9$ tend to support the presence of an approximately 1/1 mixture of structures I and II. The low resolutions of the ^{29}Si spectra do not allow quantitative answers, but it would seem that the $-LRu(CO)_4$ is present on the surface as a mixture of I and IIa on the basis of the number of -OEt groups, the absence of the -62 ppm ^{29}Si resonance, and the low coverage. The ^{29}Si spectrum of $-L_3Ru_3(CO)_9$ shows that both I and II are important, but a structure like IIb has greater probability than for $-LRu(CO)_4$, since the surface-bound entities have three Si atoms per unit. We conclude that there are no intact $-Si(OEt)_3$ groups on $[SiO_2]-L_3Ru_3(CO)_9$, owing to the absence of a -44 ppm resonance found in the CP/MAS ^{29}Si spectrum of the pure solid $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$. Thus, all three anchoring ligands of the trinuclear Ru species appear to be involved in the covalent attachment. This fact is consistent with photochemical reactions of the surface-bound trinuclear complex (vide infra).



I



IIa



IIb

Fourier transform infrared (FTIR) spectroscopy has also been used to examine the extent of hydrolysis of the Si-OR bonds upon reaction of the derivatizing reagents with $[SiO_2]-$. The spectral features monitored would be those associated with the -OR group compared to those for the remainder of the anchoring ligand. In particular, it would seem sensible to monitor the intensity of C-H stretching bands for the -OR group compared to that for the $P-CH_2$ stretch at ~1430 cm^{-1} that should be unaffected by the attachment of the ligand to the surface. Since the C-H region of the -OEt groups is complex, we have synthesized $PPh_2CH_2CH_2Si(OMe)_3$ (eq 4)

$$PPh_2H + CH_2{=}CHSi(OMe)_3 \xrightarrow[\text{AIBN}]{\Delta} PPh_2CH_2CH_2Si(OMe)_3 \quad (4)$$

to prepare derivatizing reagents because the C-H region of -OMe shows a sharp band at ~2840 cm^{-1}.[20] The complexes $Ru(CO)_4(PPh_2CH_2CH_2Si(OMe)_3)$ and $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OMe)_3)_3$ were prepared and reacted with hydrocarbon suspensions of $[SiO_2]-$ in the usual manner. A comparison of the absorbances of the symmetric C-H stretch of Si-OMe at 2840 cm^{-1} and the $P-CH_2$ stretch at 1430 cm^{-1} in the pure complex with the features at 2853 and 1437 cm^{-1} for the derivatized $[SiO_2]-$ complexes shows that ~50% of the -OMe groups are lost upon reaction of $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OMe)_3)_3$ with the $[SiO_2]-$ and ~65% of the -OMe groups are lost upon reaction of $Ru(CO)_4(PPh_2CH_2CH_2Si(OMe)_3)$ with the $[SiO_2]-$. These results accord well with those for the CP/MAS NMR spectra.

The NMR data are consistent with the retention of the metal-metal bonds in the surface-bound Ru_3 species, but the optical properties provide positive evidence strongly supporting this fact. The color of both $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ and $[SiO_2]-LRu(CO)_4$ is yellow while the color of both $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ and $[SiO_2]-L_3Ru_3(CO)_9$ is red, though the intensity of the color for the derivatized powders is less. Photoacoustic spectra (PAS)[21] in the UV-vis region of the derivatized powders compared to solution absorption properties of mononuclear and trinuclear species reveal that the characteristic visible absorption maximum of Ru_3

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(20) Anderson, D. R. In "Analysis of Silicones"; Smith, A. L., Ed.; Wiley: New York, 1974; p 247.

(21) (a) Rosencwaig, A. *Anal. Chem.* **1975**, *47*, 592A. (b) Rosencwaig, A.; Gersko, A. *J. Appl. Phys.* **1976**, *47*, 64.

Table II. Spectroscopic Data for Relevant Compounds[a]

compd	IR ν_{CO}, cm^{-1} (ϵ or rel OD)	UV-vis λ_{max}, nm (ϵ)
$Ru(CO)_4(PPh_3)$	2060 (2.2), 1984 (1.0), 1951 (3.8)	259 (9400)
$Ru(CO)_4(PPh_2Me)$	2060 (2710), 1984 (1810), 1946 (4860)	254 (9150)
$Ru(CO)_4(P(OCH_2)_3CEt)$	2075 (2.2), 2006 (1.0), 1975 (3.6)	
$Ru(CO)_3(PPh_3)$[b]	2027 (1.0), 1908 (1.3)	425, 342
$Ru(CO)_3(PPh_2Me)$[b]	2024 (1.0), 1889 (1.6)	
$Ru(CO)_3(P(OCH_2)_3CEt)$[b]	2044 (1.0), 1924 (2.1)	
$Ru(CO)_3(PPh_3)_2$[c]	1908	
$[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_4$	2058 (2800), 1982 (1350), 1946 (4840)	257 (9790)
$[(MeO)_3SiCH_2CH_2PPh_2]Ru(CO)_4$	2056 (1.8), 1982 (1.0), 1945 (3.2)	265
$[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(P(t\text{-}C_4H_9)_3)$	1875	
$[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(PPh_3)$	1896 (5040)	
$[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(P(OCH_2)_3CEt)$	1917	
$[SiO_2]\text{-}LRu(CO)_4$[d]	2059 (1.7), 1995 (1.7), 1952 (1.0)	255
$[SiO_2]\text{-}L'Ru(CO)_4$[d]	2064 (1.3), 1996 (1.3), 1961 (1.0)	
$[SiO_2]\text{-}LRu(CO)_3(P(t\text{-}C_4H_9)_3)$[d]	1876	
$[SiO_2]\text{-}LRu(CO)_3(PPh_3)$[d]	1900	
$[SiO_2]\text{-}LRu(CO)_3(P(OCH_2)_3CEt)$[d]	1920	
$Ru_3(CO)_9(PPh_2Me)_3$	2042 (320), 1970 (2800), 1943 (1510)	484 (13 600), 364 (sh)
$[(EtO)_3SiCH_2CH_2PPh_2]_3Ru_3(CO)_9$	2044 (240), 1970 (2790), 1940 (850)	488 (13 200), 366 (sh)
$[(MeO)_3SiCH_2CH_2PPh_2]_3Ru_3(CO)_9$	2038 (1.0), 1960 (19.2), 1940 (5.6)	492, 371 (sh)
$[SiO_2]\text{-}L_3Ru_3(CO)_9$[d]	2056 (1.0), 1988 (1.3), 1950 (sh), 2066 (1.0),[e] 2004 (1.3),[e] 1965 (sh)[e]	490, 370 (sh)
$[SiO_2]\text{-}L'_3Ru_3(CO)_9$[d]	2058 (1.0), 1984 (1.5), 1980 (sh)	

[a] All IR and UV-vis measurements for solution cluster species were made in toluene solution at 298 K. The IR spectra of mononuclear compounds in solution were for toluene solutions unless noted otherwise. The UV-vis spectra for mononuclear species were for hexane solutions at 298 K. For surface-supported species, infrared spectra were recorded as Nujol mulls by FTIR and UV-vis spectra were by the PAS technique. [b] Measured in methylcyclohexane matrix at ~100 K (cf. Figure 5). [c] Measured in methylcyclohexane solution at 298 K. [d] $L = PPh_2CH_2CH_2Si(OEt)_{3-n}$ and $L' = PPh_2CH_2CH_2Si(OMe)_{3-n}$; $n = 1\text{-}3$. [e] Spectrum obtained as a KBr pellet.

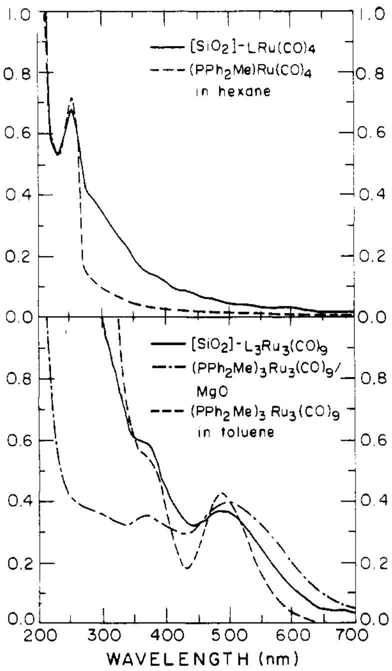

Figure 3. Comparison of optical absorption in solution and UV-vis photoacoustic spectra of powders of mononuclear and trinuclear Ru complexes. Cf. Table II.

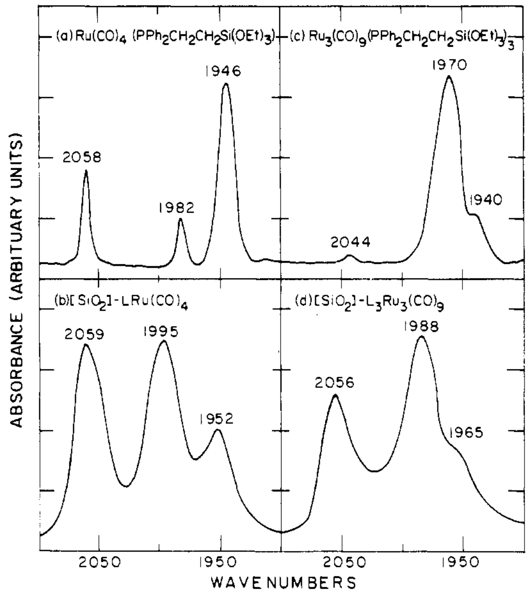

Figure 4. Comparison of FTIR absorption spectra for solution species in hydrocarbon media and for derivatized $[SiO_2]$– as Nujol mulls.

species in solution[4] is present for $[SiO_2]\text{-}L_3Ru_3(CO)_9$ (Figure 3). The yellow $[SiO_2]\text{-}LRu(CO)_4$ and $Ru(CO)_4(PPh_2Me)$ show only tail absorption into the visible region with a well-defined maximum at 255 nm. The 255-nm absorption is likely attributable to intraligand transitions, while the tail absorption is associated with ligand field transitions that terminate in the population of the $4d_{z^2}$ orbital.[4] The low-energy absorptions of the Ru_3 systems are associated with the orbitals of the metal-metal bond framework,[22] and thus the UV-vis/PAS spectra establish retention of the Ru-Ru framework in $[SiO_2]\text{-}L_3Ru_3(CO)_9$.

The FTIR spectra of $[SiO_2]\text{-}LRu(CO)_4$ and $[SiO_2]\text{-}L_3Ru_3(CO)_9$ reveal strong absorptions in the CO stretching region, as would be expected. Table II lists band maxima in the CO stretching region for a variety of complexes and for the derivatized surfaces. The IR spectra of metal carbonyls are very sensitive to the electron density and to the geometry. Figure 4 shows a comparison of the IR spectra in the CO stretching region for $[SiO_2]\text{-}LRu(CO)_4$ and $[SiO_2]\text{-}L_3Ru_3(CO)_9$ and for $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ and $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ in solution. As can be seen, the IR bands are much broader for the derivatized solids in a Nujol mull compared to those for the molecular species in homogeneous hydrocarbon solution. Further, there appear to be significant changes in the relative intensities of the bands

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(22) Tyler, D. R.; Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7888.

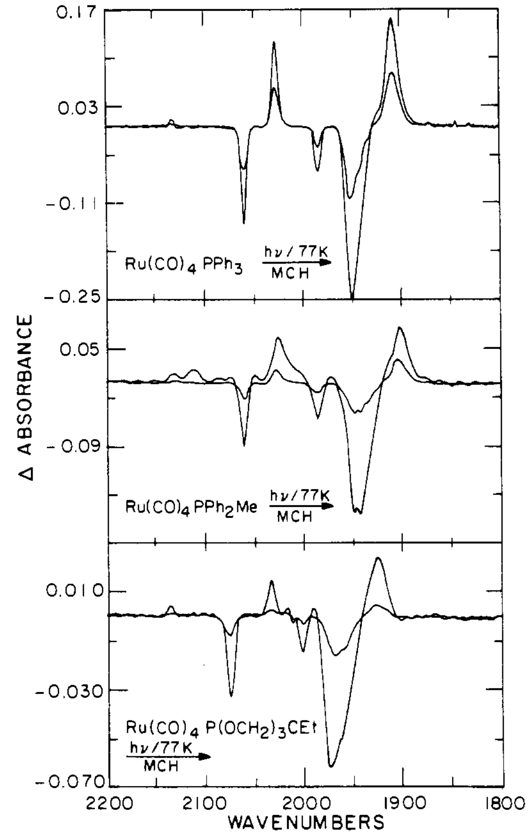

Figure 5. FTIR absorbance changes accompanying UV irradiation of ~5 mM $Ru(CO)_4L$ (L = PPh_3, PPh_2Me, $P(OCH_2)_3CEt$) in a methylcyclohexane matrix at ~100 K. The negative peaks are associated with disappearance of $Ru(CO)_4L$, and the positive peak at 2132 cm^{-1} is attributed to free CO. The other two, strong positive peaks are attributed to the 16-e $Ru(CO)_3L$.

and a general shift to slightly higher energy for the surface-confined systems. These changes in the IR spectra signal subtle changes in geometry and electron density upon attachment of the molecular species onto the surface.

Photochemistry of $[SiO_2]$–$LRu(CO)_4$ Suspended in Hydrocarbon Solvent. The photoexcitation of $Ru(CO)_4$(P-donor) complexes has been shown to yield loss of CO as the only detectable photoreaction.[4] We have shown that $[SiO_2]$–L-$Ru(CO)_4$ also yields loss of CO upon photoexcitation,[3] and here we wish to show that the photoreaction proceeds via dissociative loss of CO with the generation of spectroscopically detectable 16-e $Ru(CO)_3$(P-donor) or $[SiO_2]$–$LRu(CO)_3$. Near-UV irradiation of $[SiO_2]$–$LRu(CO)_4$ suspended in a hydrocarbon solution of a P-donor yields $[SiO_2]$–$LRu(CO)_3$(P-donor), and no $Ru(CO)_4$(P-donor) is detectable in the solution for P-donor = PPh_3 or $P(OCH_2)_3CEt$. The formation of $[SiO_2]$–$LRu(CO)_3$(P-donor) is established by the IR spectral changes accompanying the reaction: the three bands for $[SiO_2]$–$LRu(CO)_4$ in the CO stretching region decline while a single band grows in a region characteristic of *trans*-$Ru(CO)_3$(P-donor)$_2$ complexes. The single CO band for $[SiO_2]$–$LRu(CO)_3(PPh_3)$ is at 1900 cm^{-1} and that for $[SiO_2]$–$LRu(CO)_3(P(OCH_2)_3CEt)$ is at 1920 cm^{-1} in accord with those of the solution analogues (Table II), but with a slight shift to higher energy for the surface species. Thus, the photosubstitution is consistent with dissociative loss of CO from $[SiO_2]$–$LRu(CO)_4$, not loss of $Ru(CO)_4$ from the surface (eq 5). This result parallels the solution photochemistry. We now present spectral evidence for the intermediacy of a 16-e species.

$$[SiO_2]\text{–}LRu(CO)_4 \xrightarrow{h\nu} [SiO_2]\text{–}LRu(CO)_3 + CO \qquad \nrightarrow [SiO_2]\text{–}L + Ru(CO)_4 \tag{5}$$

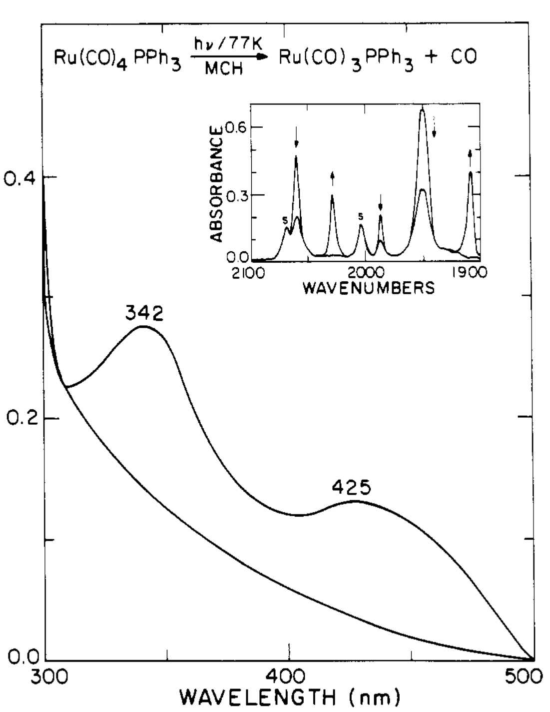

Figure 6. Comparison of UV–vis and IR spectral changes for the methylcyclohexane solution of ~5 mM $Ru(CO)_4PPh_3$ in Figure 5 upon UV irradiation at ~100 K. The 342- and 425-nm features grow in with the 1908- and 2027-cm^{-1} features in the IR spectrum. The peaks marked s in the IR spectrum are due to solvent.

Irradiation of $Ru(CO)_4$(P-donor) dissolved in a rigid, low-temperature hydrocarbon matrix results in IR specral changes consistent with loss of CO to form the 16-e $Ru(CO)_3$(P-donor) (Figure 5). Data in Figure 5 (top) are for $Ru(CO)_4(PPh_3)$, but initial spectral changes are quite similar for $Ru(CO)_4(P(OCH_2)_3CEt)$ and $Ru(CO)_4(PPh_2Me)$ when irradiated under the same conditions. Bands for these systems are included in Table II. The peaks associated with the $Ru(CO)_4$(P-donor) disappear while features at 2132 cm^{-1} (free CO) and ~2030 and ~1900 cm^{-1} (assigned to $Ru(CO)_3$(P-donor)) grow. The signal intensity due to free CO is consistent with the loss of one CO per $Ru(CO)_4$(P-donor) consumed on the basis of a comparison with observations in situations where loss of CO is well documented.[23] Warm-up of a low-temperature matrix containing PPh_3 and the irradiated $Ru(CO)_4$(P-donor) results in some formation of *trans*-$Ru(CO)_3$(P-donor)(PPh_3) as reflected in the growth of a single CO absorption in the vicinity of 1900 cm^{-1}, characteristic of such compounds (Table II). Warm-up in the absence of an added ligand results in regeneration of $Ru(CO)_4$(P-donor). The similarity of the spectral changes for $Ru(CO)_4(PPh_3)$, $Ru(CO)_4(PPh_2Me)$, and $Ru(CO)_4(P(OCH_2)_3CEt)$ suggests that ortho metalation of the aromatic rings and/or β-H interactions for PPh_2Me are relatively unimportant in these systems. Finally, the UV–vis spectrum of $Ru(CO)_4(PPh_3)$ in a hydrocarbon matrix at ~100 K changes markedly upon irradiation (Figure 6) in a manner consistent with formation of a coordinatively unsaturated intermediate. For many mononuclear metal carbonyls, loss of a CO leads to a significantly lower first absorption owing to the stabilization of the σ^* LUMO, in this case the $4d_{z^2}$ orbital.[23,24] All of the data, then, are consistent with loss of CO

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(23) We have quantitatively measured light-induced CO loss from $M(CO)_6$ (M = Cr, Mo, W) in alkane matrices to determine the absorptivity for photoejected CO under the conditions used for the Ru carbonyl species. The $M(CO)_6$ complexes are known to lose CO in rigid media at low temperature: Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

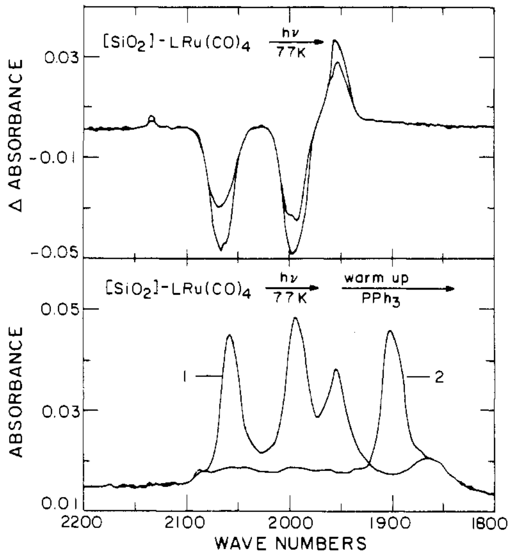

Figure 7. Top: Difference IR spectra upon irradiation of $[SiO_2]$–$LRu(CO)_4$ suspended in a rigid matrix at ~100 K. Bottom: Initial spectrum (1) of $[SiO_2]$–$LRu(CO)_4$ at 298 K suspended in a methylcyclohexane/0.02 M PPh_3 solution and final spectrum (2) after warming the irradiated sample from 77 to 298 K. Spectrum 2 is consistent with complete conversion to $[SiO_2]$–$LRu(CO)_3(PPh_3)$ by capturing photogenerated $[SiO_2]$–$LRu(CO)_3$ with PPh_3 during warm-up.

subsequent to photoexcitation of $Ru(CO)_4$(P-donor) to yield a coordinatively unsaturated $Ru(CO)_3$(P-donor) complex.

$Ru(CO)_4(PPh_2Me)$ differs from the other $Ru(CO)_4$(P-donor) systems investigated in one, potentially significant, way. The primary photoproduct $Ru(CO)_3(PPh_2Me)$ appears to give rapid secondary photochemistry with an absorption at 2112 cm^{-1} and additional free CO. This may be associated with chemistry at the methyl group when a secondary CO is ejected to give $Ru(CO)_2(PPh_2Me)$. This issue is under investigation and will be elaborated elsewhere.

The low-temperature photochemistry of $[SiO_2]$–$LRu(CO)_4$ has also been studied. A suspension of $[SiO_2]$–$LRu(CO)_4$ in a frozen hydrocarbon solvent can be examined by IR spectroscopy. Irradiation results in the loss of CO, as evidenced by the appearance of a feature at 2132 cm^{-1} characteristic of free CO in a hydrocarbon matrix. However, only one band clearly grows in as the $[SiO_2]$–$LRu(CO)_4$ is consumed (Figure 7 (top)). Even the band that does grow in at 1955 cm^{-1} is near that for one of the absorptions of the $[SiO_2]$–$LRu(CO)_4$. Warm-up of an irradiated sample in a matrix containing PPh_3 results in the formation of $[SiO_2]$–$LRu(CO)_3(PPh_3)$ (Figure 7 (bottom)). Accordingly, we conclude that the 1955-cm^{-1} band can be attributed to $[SiO_2]$–$LRu(CO)_3$, a surface-confined, coordinatively unsaturated species. $[SiO_2]$–$LRu(CO)_3$ would be expected to have more than one band in the CO stretching region as we find for solutions of photogenerated $Ru(CO)_3$(P-donor) (Table II). An interesting possibility is that the surface-bound species has a different geometry. $[SiO_2]$–$LRu(CO)_4$ does undergo a color change upon irradiation in a frozen matrix, similar to that for $Ru(CO)_4(PPh_3)$, but the spectrum has not been recorded. The unambiguous result from low-temperature irradiation of $[SiO_2]$–$LRu(CO)_4$ is that CO is ejected, since a feature is observed at 2132 cm^{-1} in the IR spectrum. The remaining surface organometallic species do not appear to have the same structure as do the homogeneous $Ru(CO)_3$(P-donor) species, but the fragments will readily add ligands such as PPh_3 to give $[SiO_2]$–$LRu(CO)_3(PPh_3)$ or the ejected CO to regenerate $[SiO_2]$–$LRu(CO)_4$.

The $[SiO_2]$–$LRu(CO)_4$ system differs from the homogeneous $Ru(CO)_4$(P-donor) systems in one key respect: the surface-confined system does not lead to the formation of trinuclear metal–metal bonded complexes as do the homogeneous species (eq 6). At the site–site separations of the

$$3Ru(CO)_4(\text{P-donor}) \xrightarrow[N_2\ \text{purge}]{h\nu} Ru_3(CO)_9(\text{P-donor})_3 + 3CO\uparrow \quad (6)$$

–$LRu(CO)_4$ entities, the formation of metal–metal bonds is not possible at the coverages used, unless the anchor is labile. The lack of $[SiO_2]$–$L_3Ru_3(CO)_9$ formation does not unambiguously rule out labile anchoring; for now, we can merely state the reaction according to (6) proceeds cleanly in the homogeneous case. Under the same conditions, we observe loss of all metal carbonyl signals on the surface. Presumably, the coordinatively unsaturated species from loss of CO reacts with O_2, or other impurities in the solvent, to lead to decomposition of the metal carbonyl. The reaction represented by eq 7 was attempted in order to establish that the surface species

$$[SiO_2]\text{–}LRu(CO)_4 + 2Ru(CO)_4(PPh_2Me) \xrightarrow[N_2\ \text{purge}]{h\nu} [SiO_2]\text{–}LRu_3(CO)_9(PPh_2Me)_2 + 3CO \quad (7)$$

could form metal–metal bonds. A small yield of surface cluster was detected, but the formation of $Ru_3(CO)_9(PPh_2Me)_3$ dominated the chemistry. Most of the surface carbonyl decomposed. Distinguishing the surface-bound cluster from the solution species is straightforward, since the surface-bound material can be isolated by filtration and independently characterized.

The important conclusions then from the photochemistry of $Ru(CO)_4$(P-donor) and $[SiO_2]$–$LRu(CO)_4$ are that (i) dissociative loss of CO occurs as the exclusive photoreaction, (ii) reactive $Ru(CO)_3$(P-donor) and $[SiO_2]$–$LRu(CO)_3$ can be observed spectroscopically, and (iii) –$LRu(CO)_4$ is inert with respect to metal–metal bond formation, since it is immobilized at site–site separations greater than metal–metal bond distances.

Photochemistry of $[SiO_2]$–$L_3Ru_3(CO)_9$ Suspended in Hydrocarbon Solvent. The $Ru_3(CO)_9$(P-donor)$_3$ complexes generally undergo metal–metal bond cleavage reactions upon photoexcitation.[4] In our earlier communication[3] we reported that $[SiO_2]$–$L_3Ru_3(CO)_9$ undergoes metal–metal bond cleavage reactions to give surface-confined, mononuclear derivatives. The two reactions of note are given in eq 8 and 9.

$$[SiO_2]\text{–}L_3Ru_3(CO)_9 + 3CO \xrightarrow{h\nu} [SiO_2]\text{–}(LRu(CO)_4)_3 \quad (8)$$

$$[SiO_2]\text{–}L_3Ru_3(CO)_9 + 3P(OCH_2)_3CEt \xrightarrow{h\nu} [SiO_2]\text{–}(LRu(CO)_3(P(OCH_2)_3CEt))_3 \quad (9)$$

Interestingly, the photolysis of $[SiO_2]$–$L_3Ru_3(CO)_9$ as a suspension in a hydrocarbon solution containing PPh_3 *does not* result in the formation of $[SiO_2]$–$(LRu(CO)_3(PPh_3))_3$, even though solution $Ru_3(CO)_9$(P-donor)$_3$ species do undergo such reaction. Further, $[SiO_2]$–$(LRu(CO)_4)_3$ does not yield $[SiO_2]$–$(LRu(CO)_3(PPh_3))_3$ upon irradiation under the same conditions. Note that $[SiO_2]$–$LRu(CO)_4$ prepared from $[SiO_2]$– and $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ does undergo clean photosubstitution with PPh_3 (vide supra). –$LRu(CO)_4$ from the cluster as in eq 8 is spectroscopically indistinguishable from the same species formed from the reaction of $[SiO_2]$– with $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$. Moreover, –$LRu(CO)_3(P(OCH_2)_3OEt)$ complexes from either cluster (eq 9) or surface monomer –$LRu(CO)_4$, are spectroscopically the

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(24) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

same. However, the surface-bound mononuclear complexes formed from $[SiO_2]-L_3Ru_3(CO)_9$ are geometrically close to one another and immobilized such that fragments from metal–metal bond cleavage do not move away from each other as would be possible in the case of $Ru_3(CO)_9(P\text{-donor})_3$ complexes in homogeneous solution.

The fact that the fragments from the photolysis of $[SiO_2]-L_3Ru_3(CO)_9$ remain close to one another is established by the fact that the reassembly of the trinuclear cluster can be effected by irradiation of $[SiO_2]-(LRu(CO)_4)_3$ (eq 10).

$$[SiO_2]-(LRu(CO)_4)_3 \xrightarrow[N_2\ purge]{h\nu} [SiO_2]-L_3Ru_3(CO)_9 \qquad (10)$$

The cycle $[SiO_2]-L_3Ru_3(CO)_9 \xrightarrow{+3CO} [SiO_2]-(LRu(CO)_4)_3 \xrightarrow{-3CO} [SiO_2]-L_3Ru_3(CO)_9$ can be effected with less than 10% loss of the $-L_3Ru_3(CO)_9$ system. Moreover, since the irradiation of $[SiO_2]-(LRu(CO)_4)_3$, formed from $[SiO_2]-L_3Ru_3(CO)_9$, in the presence of PPh_3 *does not* yield $[SiO_2]-(LRu(CO)_3(PPh_3))_3$, it would appear that the $-LRu(CO)_4$ complexes generated from $-L_3Ru_3(CO)_9$ are too close together to accommodate a large entering group.

Our conclusion is that the $-LRu(CO)_4$ complexes from $[SiO_2]-L_3Ru_3(CO)_9$ are sterically demanding while the $-LRu(CO)_4$ complexes synthesized from the direct reaction of $[SiO_2]-$ with $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ are not sterically demanding with respect to ligand substitution. Consistent with this, we find that $[SiO_2]-LRu(CO)_4$ undergoes clean photosubstitution with the large P-donor $P(t\text{-}C_4H_9)_3$ (cone angle ≈ 182°)[25] whereas $[SiO_2]-(LRu(CO)_4)_3$ yields only reassembly of the surface-confined cluster. $[SiO_2]-L_3Ru_3(CO)_9$ undergoes no photoreaction with $P(t\text{-}C_4H_9)_3$ under the same conditions. Thus, the large average site–site separation (~20 Å) of the molecular units $-LRu(CO)_4$ or $-L_3Ru_3(CO)_9$ from reacting $[SiO_2]-$ with $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$ or $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$, respectively, accords well with these photoreactivity differences. The photoreaction of $[SiO_2]-L_3Ru_3(CO)_9$ with CO or the small P-donor $P(OCH_2)_3CEt$ (cone angle ≈ 101°),[25] but not with PPh_3 (cone angle ≈ 145°),[25] is consistent with the conclusion that the $-LRu(CO)_4$ formed from the cluster is sterically demanding.

Unlike $[SiO_2]-LRu(CO)_4$, $[SiO_2]-L_3Ru_3(CO)_9$ is not photolabile in rigid hydrocarbon solution at low temperature. At least on the time scale where $[SiO_2]-LRu(CO)_4$ gives a large amount of conversion, we find no reaction for $[SiO_2]-L_3Ru_3(CO)_9$ when monitoring by FTIR spectroscopy. This result merely rules out dissociative loss of CO as a significant photoprocess. The rupture of Ru–Ru bonds would likely be reversible under such conditions.

The ability to interconvert the $[SiO_2]-L_3Ru_3(CO)_9/[SiO_2]-(LRu(CO)_4)_3$ systems without significant loss of the surface-confined molecules is consistent with the results of the CP/MAS NMR, which showed that each anchoring ligand of $[SiO_2]-L_3Ru_3(CO)_9$ is bound to $[SiO_2]-$. The differences in photoreactions of solution vs. anchored $Ru_3(CO)_9(P\text{-donor})_3$ are attributable to the immobilization. The reaction of $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$ with $[SiO_2]-$ provides a route to densely clustered $-LRu(CO)_4$ that is capable of forming Ru–Ru bonds and is more selective with respect to entering groups in photosubstitution reactions.

Solid/Gas Interfacial Photoreactions of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$. We have used an FTIR spectrometer with a photoacoustic detector to monitor aspects of the photochemistry of $[SiO_2]-LRu(CO)_4$ and $[SiO_2]-L_3Ru_3(CO)_9$ when exposed to a gas. The FTIR/PAS technique has been reported previously from this research group.[12,26] The value of the technique is that both gas-phase and surface reactions can be monitored. For example, we find that irradiation of $[SiO_2]-LRu(CO)_4$ or $[SiO_2]-L_3Ru_3(CO)_9$ as powders under an Ar/O_2 atmosphere leads to the decline of all metal carbonyl material and the formation of gas-phase CO and CO_2. The photochemistry of the mononuclear species logically begins with the dissociative loss of CO to form $[SiO_2]-LRu(CO)_3$, which reacts irreversibly with the O_2 to yield oxidative degradation. The irradiation of the $[SiO_2]-LRu(CO)_4$ powder under a ^{13}CO atmosphere yields incorporation of ^{13}CO to eventually form $[SiO_2]-LRu(^{13}CO)_4$, as revealed by the shift in the FTIR/PAS signals in the CO stretching region (Figure 8). Essentially complete exchange can be brought about without significant loss of integrated metal carbonyl signal. Indeed, irradiation of $[SiO_2]-LRu(^{13}CO)_4$ under an atmosphere of natural CO abundance leads to >90% regeneration of the original sample (Figure 8).

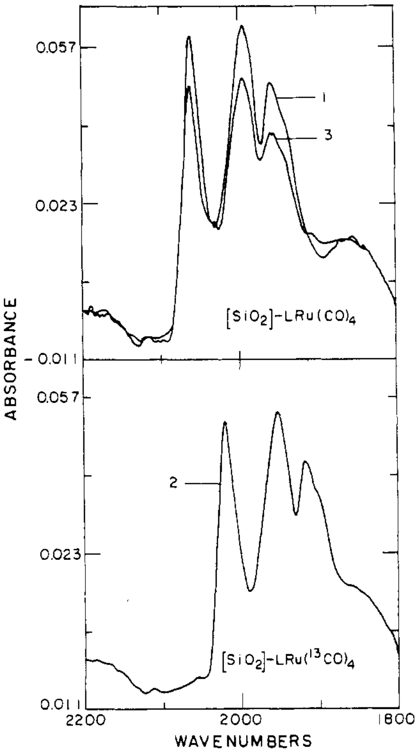

Figure 8. FTIR/PAS spectra of $[SiO_2]-LRu(CO)_4$: (1) initial spectrum; (2) spectrum after complete ^{13}CO enrichment by photolysis under ^{13}CO; (3) spectrum after regeneration of $[SiO_2]-LRu(CO)_4$ by irradiation of $[SiO_2]-LRu(^{13}CO)_4$ under CO (natural adundance).

Irradiation of a sample of $[SiO_2]-LRu(^{13}CO)_4$ under an $Ar/^{18}O_2$ atmosphere yields FTIR/PAS data consistent with the decomposition of the surface complex and the generation of ^{13}CO and $^{13}CO^{18}O$ (Figure 9). This result unambiguously establishes that the CO_2 is formed from added O_2 and complexed CO. $[SiO_2]-LRu(CO)_4$ gives a higher CO/CO_2 ratio than $[SiO_2]-L_3Ru_3(CO)_9$, but the ratio of CO/CO_2 is roughly the same per mole of bound CO. Since $[SiO_2]-L_3Ru_3(CO)_9$ does not undergo dissociative loss of CO, the reaction, with O_2 is presumably with the primary photoproduct that leads to fragmentation. The Ru species on the surface from photoreaction of the surface carbonyls in the presence of O_2 have not been characterized, but presumably the O_2 results in oxidation of the Ru(0).

Irradiation of $[SiO_2]-L_3Ru_3(CO)_9$ under an atmosphere of CO leads to $[SiO_2]-(LRu(CO)_4)_3$ as in hydrocarbon suspension (Figure 10). Likewise, the irradiation of $[SiO_2]-(L-$

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[25] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[26] Kinney, J. B.; Staley, R. H.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 4273.

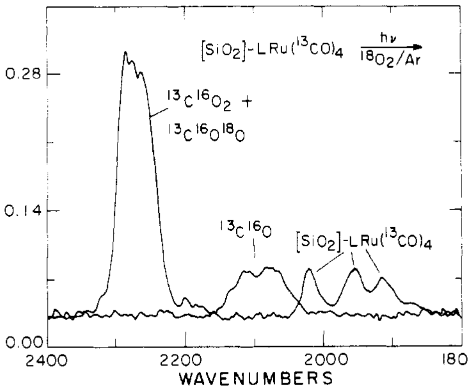

Figure 9. FTIR/PAS spectral changes accompanying irradiation of $[SiO_2]$-$LRu(^{13}CO)_4$ under $^{18}O_2/Ar$ (~1/4 at 1-atm total pressure).

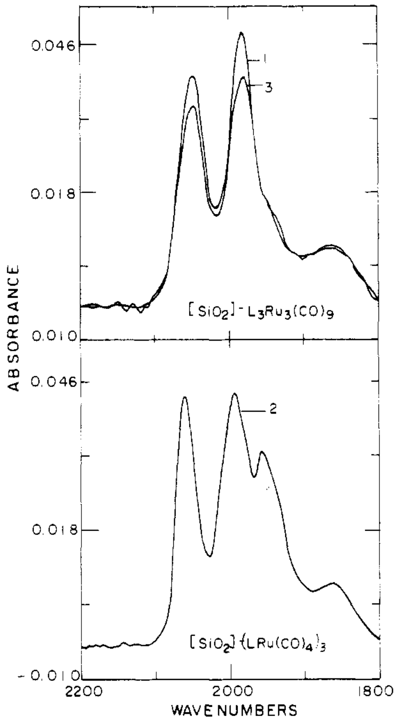

Figure 10. FTIR/PAS spectrum of $[SiO_2]$-$L_3Ru_3(CO)_9$ initially (1). Irradiation under 1 atm of CO yields $[SiO_2]$-$(LRu(CO)_4)_3$ (2) which upon irradiation under Ar nearly quantitatively regenerates $[SiO_2]$-$L_3Ru_3(CO)_9$ (3).

$Ru(CO)_4)_3$ results in the nearly quantitative regeneration of $[SiO_2]$-$L_3Ru_3(CO)_9$. Thus, for both $[SiO_2]$-$LRu(CO)_4$ and $[SiO_2]$-$L_3Ru_3(CO)_9$, we find that the solid/gas reactions parallel the results found when the powders are suspended in hydrocarbon solutions.

Summary

The photochemistry of $[SiO_2]$-$LRu(CO)_4$ involves the dissociative loss of CO as the only detectable chemical result of photoexcitation. Extrusion of $Ru(CO)_4$ via rupture of the Ru-P bond is not a primary photoreaction. Irradiation of $[SiO_2]$-$LRu(CO)_4$ in a rigid, low-temperature matrix provides unambiguous evidence for the dissociative loss of CO and the intermediacy of a 16-e fragment on the surface, $[SiO_2]$-$LRu(CO)_3$. Thus, light can be used to activate a surface species to generate a coordinatively unsaturated site that can be observed spectroscopically. Irradiation of $Ru(CO)_4L$ (L = PPh_3, PPh_2Me, $P(OCH_2)_3CEt$) in rigid, low-temperature matrices parallels the findings for $[SiO_2]$-$LRu(CO)_4$. -$LRu(CO)_4$ on $[SiO_2]$- are effectively isolated from one another (site-site distance of ~20 Å) and do not form trinuclear clusters as do $Ru(CO)_4L$ species in solution. The photochemistry of $[SiO_2]$-$L_3Ru_3(CO)_9$ does not involve dissociative loss of CO. The chemistry is dominated by Ru-Ru bond cleavage to give mononuclear products in the presence of donors, provided the donor is small enough. Under CO, clean formation of $[SiO_2]$-$(LRu(CO)_4)_3$ is effected, consistent with chemistry from $Ru_3(CO)_9L_3$ in solution. The -$LRu(CO)_4$ species formed from clusters on $[SiO_2]$- are spectroscopically indistinguishable from -$LRu(CO)_4$ formed from $[SiO_2]$- derivatized with $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)$. However, -$LRu(CO)_4$ species formed from the cluster are close to each other and tethered in place. This allows efficient cluster reassembly from photoinduced extrusion of CO from $[SiO_2]$-$(LRu(CO)_4)_3$ to form $[SiO_2]$-$L_3Ru_3(CO)_9$. Further, the fact that the -$LRu(CO)_4$ species from the cluster are close geometrically results in different steric demands in photosubstitution using P-donors. This fact may be exploited in catalysis and is presently under study. Both $[SiO_2]$-$LRu(CO)_4$ and $[SiO_2]$-$L_3Ru_3(CO)_9$ undergo very clean chemistry under ^{13}CO or CO to give $[SiO_2]$-$LRu(^{13}CO)_4$ and $[SiO_2]$-$(LRu(CO)_4)_3$, respectively. Also, both undergo photoreaction in the presence of O_2 to give gas-phase CO_2, CO, and oxidized Ru species. Isotope-labeling experiments unambiguously show that a fraction of the bound CO is oxidized by O_2 initially in the gas phase. Presumably, the coordinatively unsaturated intermediates react with O_2 to eventually oxidize the Ru(0) and bound CO.

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Registry No. $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)_3$, 80447-60-5; $Ru(CO)_4(PPh_2CH_2CH_2Si(OEt)_3)_3$, 80441-14-1; $Ru_3(CO)_9(PPh_2CH_2CH_2Si(OMe)_3)_3$, 88000-45-7; $Ru(CO)_4(PPh_2CH_2CH_2Si(OMe)_3)_3$, 88000-46-8; $Ru(CO)_4(PPh_3)$, 21192-23-4; $Ru(CO)_4(PPh_2Me)$, 57894-45-8; $Ru(CO)_4(P(OCH_2)_3CEt)$, 75627-88-2; $Ru_3(CO)_9(PPh_3)_3$, 15663-31-7; $Ru_3(CO)_9(PPh_2Me)_3$, 38686-56-5; $Ru_3(CO)_9(P(OCH_2)_3CEt)_3$, 86276-96-2; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(P(t\text{-}C_4H_9)_3)$, 88000-47-9; $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(PPh_3)$, 80441-15-2; $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(P(OCH_2)_3CEt)$, 80441-16-3; $PPh_2CH_2CH_2Si(OMe)_3$, 88000-44-6; PPh_2H, 829-85-6; $CH_2CHSi(OMe)_3$, 2768-02-7.