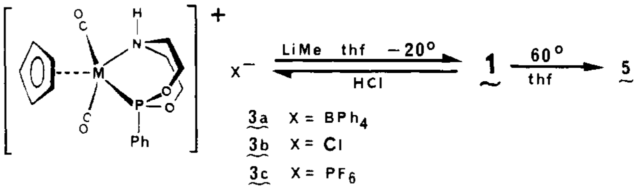
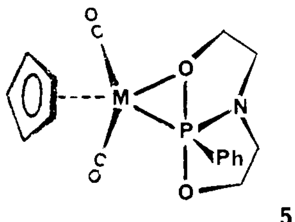
tion-metal phosphoranide adduct was obtained in this laboratory.[6]

Where the coordination of the nitrogen is concerned, there is as far as we know only one report of a transition-metal adduct in which the metal is linked to a P-bound *tri*connected nitrogen atom (exocyclic to a phosphazene ring)[7] and none in which the metal bridges in the P–N bond as in **1**. Only *di*connected nitrogen atoms, such as the skeletal nitrogen atoms of phosphazene rings, are expected and were shown to have a high enough basicity to easily give transition-metal adducts.[7,8]

Reaction 1 can be reversed under the action of an acid: bubbling HCl into a THF solution of **1a** at room temperature converts it quantitatively to **3b**.[1] Upon heating for 4 h in THF at 60 °C, adduct **1a** converts to the deep red compound **5**, which was formerly synthesized by allowing LiMe to react with the hexafluorophosphate salt **3c**.[6]



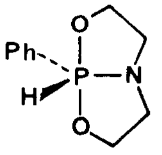
(1)



5

Similar behavior was observed with the tungsten analogue of **3a**, yielding the orange-yellow crystalline compound **1b** (^{31}P NMR δ 26.4, $J_{\text{P-W}} = 232$ Hz) whose spectral and analytical data are consistent with the same formulation.

These results confirm the exceptional versatility of the cyclic P–N ligand **6**, which had already been found to coordinate



6

transition metals through phosphorus alone, both phosphorus and nitrogen in its tautomeric open form,[1,9] or phosphorus and oxygen (after abstraction of a proton) in its closed bicyclic form,[6] and now has been found to do so through phosphorus and nitrogen in its closed form, while under similar experimental conditions the iron analogue of **3** led to a new reaction in which the phenyl group migrates from phosphorus to the metal.[10]

Supplementary Material Available: A table of atomic positions and thermal parameters and a table of bond lengths and angles (2 pages). Ordering information is given on any current masthead page.

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Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry of Surface-Confined Cobalt Tetracarbonyl Monitored by Fourier Transform Infrared Photoacoustic Spectroscopy

John B. Kinney, Ralph H. Staley,* Carol L. Reichel, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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We wish to report the photochemistry of surface-confined –Co(CO)$_4$ fragments exposed to reactive gases. Such photochemistry is of importance in establishing primary events following excitation of the molecular entity attached to the surface and is of relevance to the photoactivation of surface-confined catalysts.[1,2] We apply, for the first time, the technique of Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS)[3] to monitor the photoreactions of a species on the surface including in situ monitoring of reactions involving a gas-phase species. Without any sample manipulation or preparation, this technique has allowed characterization of the photochemistry of surface species with the molecular level specificity generally possible when infrared absorption spectroscopy is used to monitor reactions of metal carbonyls in homogeneous solution. The results herein establish FTIR/PAS as a technique of unequalled capability in monitoring such surface chemistry.[4]

The system studied is [S]$\geqslant$SiCo(CO)$_4$ where [S] represents a high-surface-area silica (~400 m^2/g from Alfa). The synthetic procedure follows from known reaction chemistry and was carried out according to the representation in (1) and (2).[5] The functionalization of metal oxides such as SiO$_2$ using (RO)$_3$SiR′ reagents[6] and reaction of Co$_2$(CO)$_8$ with R$_3$SiH to give

$$\text{surface-OH} \xrightarrow[\text{(EtO)}_3\text{SiH}]{25\ ^\circ\text{C}} \text{surface-O}\geqslant\text{SiH} \qquad (1)$$

$$\text{surface-O}\geqslant\text{SiH} \xrightarrow[\text{Co}_2\text{(CO)}_8]{25\ ^\circ\text{C}} [\text{S}]\geqslant\text{SiCo(CO)}_4 \qquad (2)$$

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(4) There are a number of techniques useful for obtaining vibrational spectra of surface species. See: Bell, A. T.; Hair, M. L. *ACS Symp. Ser.* **1980**, *No. 137*. The FTIR/PAS would appear to offer advantages when monitoring both surface and gas-phase reaction products in situ.

(5) In a typical procedure, ~1 g of high-surface-area SiO$_2$ having some –OH available is suspended in ~25 mL of alkane solvent containing excess (EtO)$_3$SiH at 25 °C under N$_2$. The solution is stirred for 24 h and then filtered to collect a solid. After repeated washing the solid exhibits an infrared signal at ~2250 cm^{-1} associated with Si–H. Infrared transmission experiments indicate that there is ~6.1 mol % of $\geqslant$SiH.[1b] The powder is then reacted with excess Co$_2$(CO)$_8$ in alkane solution under N$_2$ at 25 °C for 24 h. After repeated washing, the solid still exhibits an infrared peak at ~2250 cm^{-1} (~3.4 mol % of SiH) and signals at 2110, 2050, and ~2020 cm^{-1} characteristic of $\geqslant$SiCo(CO)$_4$ (~1.9 mol %).[1b] Reaction of the powder with Co$_2$(CO)$_8$ also leads to some decomposition of the Co$_2$(CO)$_8$ to leave a cobalt oxide/hydroxide on the surface.[1b] Samples were exposed to vacuum for 20 min at 25 °C prior to any experimentation to remove any O$_2$ or H$_2$O from the surface.

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$R_3SiCo(CO)_4$ are both well-known.[7] The reaction to prepare $[S]>SiH$ is established by transmission infrared spectra of $KBr/[S]>SiH$ (10/1 by weight) pellets showing a feature at ~2250 cm^{-1} associated with the Si–H stretch; no feature in this region is observed for the SiO_2 prior to treatment with $(EtO)_3SiH$. Absorption is also observed in the C–H region, reflecting the fact that some residual EtO– groups remain. Reaction of $[S]>SiH$ with $Co_2(CO)_8$ results in additional infrared absorptions in the metal carbonyl region at ~2110 (relative o.d. = 0.3), 2050 (relative o.d. = 0.5), and ~2020 (relative o.d. = 1.0) cm^{-1}. The number of bands and their relative intensities accord well with bands expected for $[S]>SiCo(CO)_4$ based on species such as $(EtO)_3SiCo(CO)_4$.[1,7] From a combination of infrared and elemental analyses the coverage of $>SiCo(CO)_4$ is submonolayer (~10^{-11} mol/cm^2), and there is generally considerable $>SiH$ remaining after reaction with $Co_2(CO)_8$.

Figure 1 includes a typical FTIR/PAS characterization of ~1 mg of $[S]>SiH/>SiCo(CO)_4$. The relative FTIR/PAS signals are proportional to infrared absorbances found for $[S]>SiCo(CO)_4$ in KBr. For both forms of infrared the metal carbonyl signals are broader and less well-resolved than the spectral features for species such as $R_3SiCo(CO)_4$ in alkane solution.[1,7] The FTIR/PAS of the $[S]>SiH/>SiCo(CO)_4$ is just as good in terms of signal to noise as the FTIR/absorption and does not require pelleting or other pretreatment of the sample. Quantities of sample required for FTIR/PAS are as small, or smaller, as those typically used to prepare 1-cm diameter $KBr/[S]>SiH/>SiCo(CO)_4$ pellets.

The unique capabilities of the FTIR/PAS are revealed in the photochemistry studies. Typically, a ~1-mg sample of $[S]>SiH/>SiCo(CO)_4$ is placed in the FTIR/PAS cell and irradiated at 25 °C with the 300–400-nm output from a 150-W Xe lamp focused to ~1 cm^2; the input optical power to the sample is ~100 mW/cm^2. The undisturbed sample can then be characterized by FTIR/PAS.[8] The first significant experiment concerns the results from irradiation of $[S]>SiH/>SiCo(CO)_4$ when the cell contains 1 atm of ^{13}CO (90% ^{13}C). Figure 1 includes the FTIR/PAS spectrum that results after an irradiation of 15 min under ^{13}CO, pumping out all gases, and then introducing Ar for acoustic coupling. The spectra before and after irradiation under ^{13}CO establish the photochemistry represented by (3), a result that would

$$[S]>SiCo(CO)_4 + {}^{13}CO \xrightarrow{h\nu} [S]>SiCo(CO)_n({}^{13}CO)_{4-n} \qquad (3)$$

$$[S]>SiCo(CO)_4 \xrightarrow{h\nu} [S]>SiCo(CO)_3 + CO \qquad (4)$$

be expected if (4) represents the primary chemical event following photoexcitation. When irradiation is carried out for short periods of time, spectral changes are consistent with the sequential replacement of bound CO by ^{13}CO. The FTIR/PAS monitoring can be carried out without pumping out the cell, using the reactive gas as the acoustic coupler. When the gases are not pumped out, the ^{13}CO is detected, and ^{12}CO is detected as a gas-phase photoproduct, as expected. Additionally, small amounts of CO_2 and $^{13}CO_2$ are detected as photoproducts (cf. below). Irradiation of $[S]>Si(CO)_n({}^{13}CO)_{4-n}$ for $n \sim 0$ under 1-atm CO results in the regeneration of $[S]>SiCo(CO)_4$ with ~80% recovery of the FTIR/PAS signal for the carbonyl species. Chemically, these results establish CO loss as the principal result of photoexcitation of the $[S]>SiCo(CO)_4$. This finding parallels the conclusion drawn from studies of $R_3SiCo(CO)_4$ in homogeneous solution and $[S]>SiCo(CO)_4$ suspended in solution.[1] In particular, the FTIR/PAS shows little or no importance for photoinduced cleavage of the Si–Co bond that would lead to $Co(CO)_4$ or to the dimer $Co_2(CO)_8$. With the FTIR/PAS technique, the data are much more easily obtained and without sample manipulation, compared to conventional infrared methods.

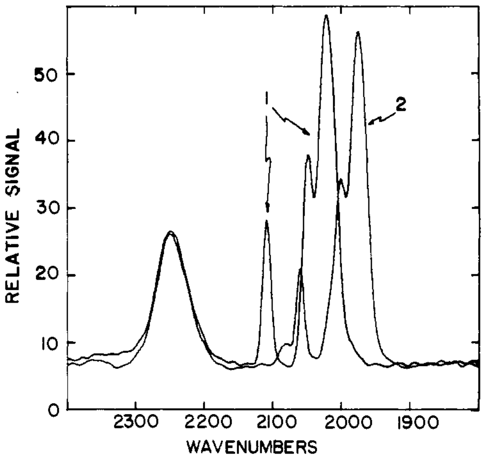

Figure 1. FTIR/PAS spectrum before (curve 1) and after (curve 2) 20 min near-UV irradiation of $[S]>SiCo(CO)_4$ under 1-atm ^{13}CO. In each case the acoustic coupling gas is 1-atm Ar. The spectral changes are consistent with the photochemical generation of $[S]>SiCo({}^{13}CO)_4$. No ^{13}CO exchange occurs in the dark at 25 °C on the time scale of this experimentation.

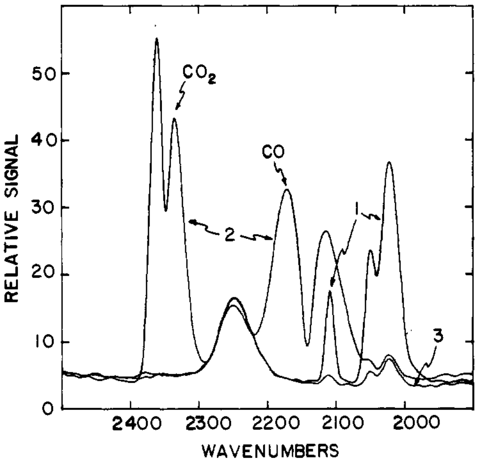

Figure 2. FTIR/PAS spectrum before (curve 1) and after (curve 2) 20 min near-UV irradiation of $[S]>SiCo(CO)_4$ under 1-atm O_2. For spectra 1 and 2 the acoustic coupling gas is the 1-atm O_2. Spectrum 2 shows gaseous CO and CO_2 photoproducts. Spectrum 3 is after evacuating the sample chamber to remove all gases and introducing O_2 at 1 atm as the acoustic coupling gas.

Additional photochemical results are consistent with the dissociative loss of CO from the surface. First, irradiation of the $[S]>SiCo(CO)_4$ under vacuum leads to disappearance of all metal carbonyl species. This disappearance is dramatically suppressed under CO, as expected. Under 1-atm Ar, irradiation leads to some decomposition, but the rate eventually declines, presumably due to the accumulation of CO in the cell. When decomposition is detected, CO and CO_2 are observed as gas-phase photoproducts. Irradiation of the $[S]>SiCo(CO)_4$ under 1-atm O_2 leads to more rapid decline of the metal carbonyl signals, and a larger signal for gas-phase CO_2 is observed, compared to reaction under Ar (Figure 2). Thus, O_2 is a reactive gas and presumably interacts with the photogenerated, coordinatively unsaturated $>SiCo(CO)_n$ species to lead to the oxidation of CO to CO_2. We estimate the CO/CO_2 product ratio to be ~3/1 when the irradiation is carried out under 1-atm O_2. Irradiation of $[S]>SiCo(CO)_4$ under $^{18}O_2$ leads to the formation of $C^{18}O^{16}O$ and irradiation of ^{13}CO-enriched $[S]>Si(CO)_4$ under $^{18}O_2$ leads to $^{13}C^{18}O^{16}O$. These results establish the source of CO_2 to be CO originally bound to Co and O_2 in the gas phase. The Co product is likely some form of cobalt oxide; PAS in the visible region is consistent with this conclusion.[9]

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[8] FTIR/PAS spectra were obtained by using a Nicolet 7199 FTIR with a gas microphone photoacoustic detector of our own design that allows control of the sample environment. The details are to be published independently by J.B.K. and R.H.S. Data collection for 8-cm^{-1} resolution spectra typically take 4 min. The acoustic coupling gas in all cases was 1-atm Ar (<1-ppm H_2O, O_2) except when monitoring gas-phase products as in photolyses under O_2.

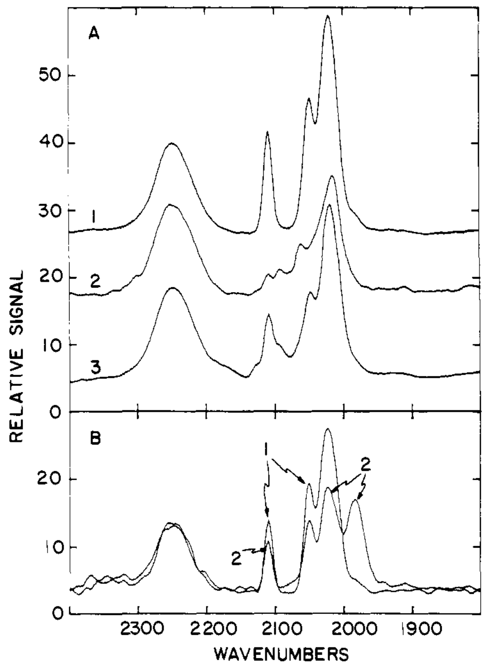

Figure 3. (A) Curve 1 is the initial FTIR/PAS spectrum of a sample of $[S]{>}SiCo(CO)_4$ and curve 2 is the spectrum obtained after near-UV irradiation, of the sample characterized in 1, for 10 min under 1-atm PF_3. The product is $[S]{>}SiCo(CO)_n(PF_3)_{4-n}$. Curve 3 is the spectrum that results when the sample characterized in 2 is irradiated under 1 atm of CO to regenerate $[S]{>}SiCo(CO)_4$. These spectra are recorded using 1-atm Ar as the coupling gas. (B) Spectral changes accompanying the near-UV irradiation of $[S]{>}SiCo(CO)_4$ (curve 1) at low temperature, ~-50 °C, under ~100-torr isobutylene for 10 min to form $[S]{>}SiCo(CO)_3$(isobutylene) (curve 2).

FTIR/PAS can also be used to monitor photosubstitution of the $[S]{>}SiCo(CO)_4$ by using gas-phase entering groups such as PF_3 and olefins (Figure 3). At 25 °C, the chemistry represented by (5) is detectable. The main infrared feature is at ~2000 cm^{-1}

$$[S]{>}SiCo(CO)_4 + PF_3 \xrightarrow{h\nu} [S]\text{-}SiCo(CO)_n(PF_3)_{4-n} \quad (5)$$

and is associated with $[S]{>}SiCo(CO)_3PF_3$, with the PF_3 occupying an axial position trans to the >Si–, as found for $R_3SiCo(CO)_3P(OPh)_3$ prepared by photosubstitution.[1,10] Irradiation of $[S]\text{-}SiCo(CO)_n(PF_3)_{4-n}$ under 1-atm CO leads to the regeneration of a large fraction of the $[S]{>}SiCo(CO)_4$. Irradiation of $[S]{>}SiCo(CO)_4$ under ethylene or propylene at 25 °C yields loss of all metal carbonyls; $Et_3SiCo(CO)_3$(alkene) was shown previously to decompose at 25 °C.[1] But irradiation of the $[S]{>}SiCo(CO)_4$ at -50 °C under ethylene, propylene, isobutylene, or propyne and monitored by FTIR/PAS at that temperature leads to the generation of new surface metal carbonyl species (Figure 3). The signal at ~1990 cm^{-1} would logically be attributed to $[S]{>}SiCo(CO)_3$(alkene), where the alkene is trans to the >Si–, paralleling solution studies. A signal that grows in at ~2050 cm^{-1} for ethylene, propylene, or propyne, but not isobutylene, is unidentified at this time. Such a signal could be due to another isomer of the $[S]{>}SiCo(CO)_3$(alkene) where the alkene is cis to the >Si–, or the peak could be due to multiple substitution. This point is currently under investigation, but it does appear that the species association with the ~2050 cm^{-1} peak is a primary product, since it appears even at short irradiation times. Interestingly, the ~2050-cm^{-1} peak does not appear in low-temperature irradiations of $Ph_3SiCo(CO)_4$ in solutions containing 1-pentene or ethylene, but the Ph_3Si– group may offer more steric restriction than the [S]>Si–.

To summarize, we have established the primary photoreaction of $[S]{>}SiCo(CO)_4$ to be loss of CO. This can be exploited to study the oxidation of CO by O_2, prepare inert or labile substitution products, and elaborate the mechanism of the reactions of immobilized, photogenerated, coordinatively unsaturated intermediates. The technique of FTIR/PAS is shown to be a molecular specific tool having unique capabilities for the study of photoreactions of the surface species on high-surface-area supports.

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(9) The cobalt oxide product is detected as an absorber in the visible at ~620 nm.[1b] Monitoring a sample by FTIR/PAS and PAS in the visible shows the decline of metal carbonyl to be accompanied by the growth of the ~620-nm feature attributed to cobalt oxide.

(10) Many metal carbonyls undergo photosubstitution under PF_3 (Geoffroy, G. L; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979) including Co carbonyls related to those under study here: Udovich, C. A.; Clark, R. J. *Inorg. Chem.* **1969**, *8*, 938.

Structure of Molecular Complexes of Copper Uroporphyrin with Aromatic Heterocycles[†]

John A. Shelnutt

Surface Physics, Division 5114
Sandia National Laboratories
Albuquerque, New Mexico 87185

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The molecular complexes formed between metalloporphyrins and aromatic ring structures are of interest in a number of areas. These molecular complexes are involved in redox catalysis,[1-3] photosynthesis,[4-10] herbicidal activity,[11] and malaria drug binding to hemoglobin-based pigments.[12] They are also models for the residue–porphyrin interactions in heme proteins that may be involved in control of O_2 affinity in hemoglobin.[13-15]

Recently, I have undertaken a study of these molecular complexes by using Raman difference spectroscopy (RDS). The RDS technique[13,16-18] is sensitive to small frequency differences in the resonance Raman lines of metalloporphyrins, resulting from differences in their protein environment.[13-16] These differences, while small (~1.0 cm^{-1}), indicate large redistributions of the π electrons of the ring, since they represent about 10% of the changes

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