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PHOTOCHEMISTRY OF COBALT CARBONYL COMPLEXES HAVING A COBALT-SIL--ETC(U)
AUG 80 C L REICHEL, M S WRIGHTON N00014-75-C-0880
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Photochemistry of $R_3SiCo(CO)_4$ (R = Et, Ph) in hydrocarbon solvents shows that the dominant primary excited state process is loss of CO, not cleavage of the Si-Co bond. The 366 nm quantum yield for CO substitution by $P(OPh)_3$ is 0.28 ± 0.05 to give $R_3SiCo(CO)_3P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of 0.1 M $HSiR'_3$ gives $R'_3SiCo(CO)_4$ with a quantum yield nearly the same as that for CO substitution by $P(OPh)_3$; irradiation of $Ph_3SiCo(CO)_4$ in the presence of 0.1 M $HSiEt_3$ and 0.3 M $P(OPh)_3$ yields only $Ph_3SiCo(CO)_3P(OPh)_3$, not

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$Et_3SiCo(CO)_3P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of 1-pentene first gives $R_3SiCo(CO)_3$(alkene), but the dominant Co-containing material is ultimately a mixture $Co_2(CO)_8$ and $Co_4(CO)_{12}$ at 25°C. For R=Et, the dominant Si-containing products have been determined to be isomers of (pentenyl)$SiEt_3$. The quantum yield for reaction of $Et_3SiCo(CO)_4$ with 1-pentene ($\Phi = 0.23$) is significantly higher than the reaction quantum yield for $Et_3SiCo(CO)_4$ in isooctane ($\Phi = 0.04$) solution where mixtures of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are the photoproducts. Irradiation of $R_3SiCo(CO)_4$ in the presence of 1-pentene/$HSiEt_3$ (1/1 mole ratio) yields catalytic alkene isomerization and hydrosilation. Thermal catalysis (25°C) of 1-pentene hydrosilation by $HSiEt_3$ using $Co_2(CO)_8$ yields infrared detectable $Et_3SiCo(CO)_4$. The $Et_3SiCo(CO)_4$ does not catalyze ~~thermal~~ reaction at 25°C at a rate comparable to that initially observed using $Co_2(CO)_8$. Regeneration of catalytic activity in the $Co_2(CO)_8$/1-pentene/$HSiEt_3$ system can be accomplished photochemically by exciting the $Et_3SiCo(CO)_4$ species.

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TECHNICAL REPORT NO. 21

PHOTOCHEMISTRY OF COBALT CARBONYL COMPLEXES HAVING A COBALT-SILICON BOND AND ITS IMPORTANCE IN ACTIVATION OF CATALYSIS

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Photochemistry of Cobalt Carbonyl Complexes Having a Cobalt-Silicon Bond and Its Importance in Activation of Catalysis

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We wish to report results of experiments that establish the relative importance of photochemical cleavage of the Co-Si bond vs. the dissociative loss of CO in $R_3SiCo(CO)_4$, equation (1) vs. (2). We recently showed[1] that

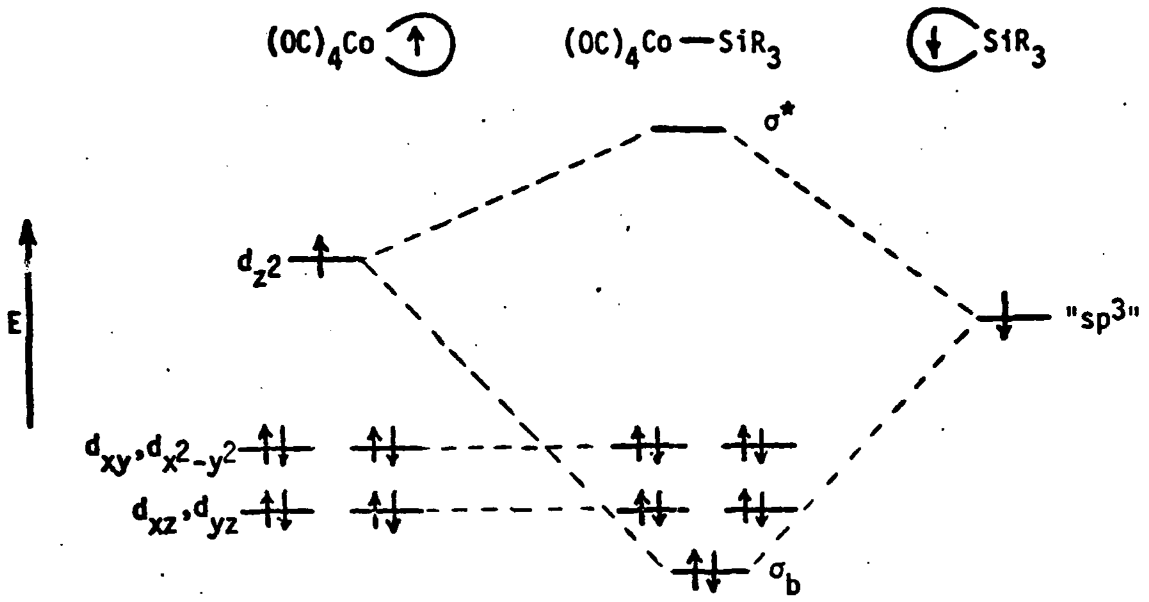
$$R_3SiCo(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} R_3Si\cdot + \cdot Co(CO)_4 \tag{1}$$

$$R_3SiCo(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} R_3SiCo(CO)_3 + CO \tag{2}$$

photogeneration of 17-valence electron, Co-centered radicals can lead to catalysis of alkene isomerization, hydrosilation, and hydrogenation. Reaction of $R_3SiCo(CO)_4$ according to equation (1) is of interest in that the 17-valence electron radical $\cdot Co(CO)_4$ could effect the same alkene/$HSiR_3$ reactions known[2] to be catalyzed by $Co_2(CO)_8$. It is believed that $R_3SiCo(CO)_4$ represents the ultimate fate of Co in the $Co_2(CO)_8$ catalyzed hydrosilation reaction and that it is not an active thermal catalyst at the temperatures that can be used for $Co_2(CO)_8$.[2] We thus wondered whether the $Co_2(CO)_8$ catalyst could be regenerated from irradiation of $R_3SiCo(CO)_4$ according to equations (1) and (3).

$$2\ \cdot Co(CO)_4 \longrightarrow Co_2(CO)_8 \tag{3}$$

The relative importance of the two photoreactions represented by equations (1) and (2) is of fundamental interest, since there is considerable ambiguity concerning the importance of <u>primary</u> photogeneration of 17-valence electron vs. 16-valence electron fragments from coordinatively saturated, 18-valence electron species having both 2- and 1-electron donor ligands.[3] For $R_3SiCo(CO)_4$ the orbital diagram in Scheme I is appropriate,[4] and it is apparent that all lowest excited states involve population of $\sigma^*(d_{z^2})$



Scheme I. One-electron orbital diagram for $R_3SiCo(CO)_4$.

resulting in weakening of the σ-bonding between Co and all of the five ligands.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 180 grating spectrophotometer in matched 1.0 mm or 0.1 mm pathlength amalgam sealed NaCl cells. Low temperature spectra were taken using a Cyrogenics Technology, Inc. Spectrim II cryocooler in conjunction with the spectrophotometer; a 1.1 mm pathlength uncompensated CaF_2 cell was constructed to interface with the cold head. Electronic spectra were taken on a Varian Associates Cary Model 17 uv-vis-nir spectrophotometer, in 1.0 cm quartz or 1.3 cm Pyrex cells. Gas-liquid chromatography was performed on a Varian Associates Model 1440 or 2440 gas chromatograph equipped with flame ionization detectors and interfaced with either a Hewlett-Packard model 3370S electronic recording integrator or a Varian model A25 strip chart recorder. Hydrocarbon analyses (against internal standard n-hexane) were carried out on columns of 20% propylene carbonate on Chromasorb P (Johns-Manville), 30" x 1/8", 20°C, hydrosilation products were analyzed (against internal standard n-decane) on columns of 20% β,β'-oxydepropionitrile on Gaschrom Q (Applied Science Laboratories, 1/8" x 30', 60°C). Organic products of the photolyses of $Ph_3SiCo(CO)_4$ in pentene or isooctane were separated on columns of 1.5% OV-101 on Chromosorb P (1/8" x 5", 120-250°C, programmed at 10-20°C/min.) Nuclear magnetic resonance spectra were obtained with a Hitachi-Perkin Elmer R-24B or Varian T-60 spectrometer (^1H, 60 MHz) or with a Jeolco FX-90Q spectrometer (^1H, 90 MHz). Mass spectra were obtained on a Varian MAT 44 spectrometer, interfaced with a Varian series 1400 gas chromatograph for GC/MS.

All air-sensitive organometallic compounds were handled under an argon atmosphere by conventional Schlenk techniques, or under an atmosphere of prepurified nitrogen in a Vacuum Atmospheres Dri-Lab glove box. Photosensitive solutions were handled under red safelights or in the dark. $Co_2(CO)_8$ (ROC/RIC, Strem) and $P(OPh)_3$ (Strem) were used as received. PPh_3 (Aldrich) and

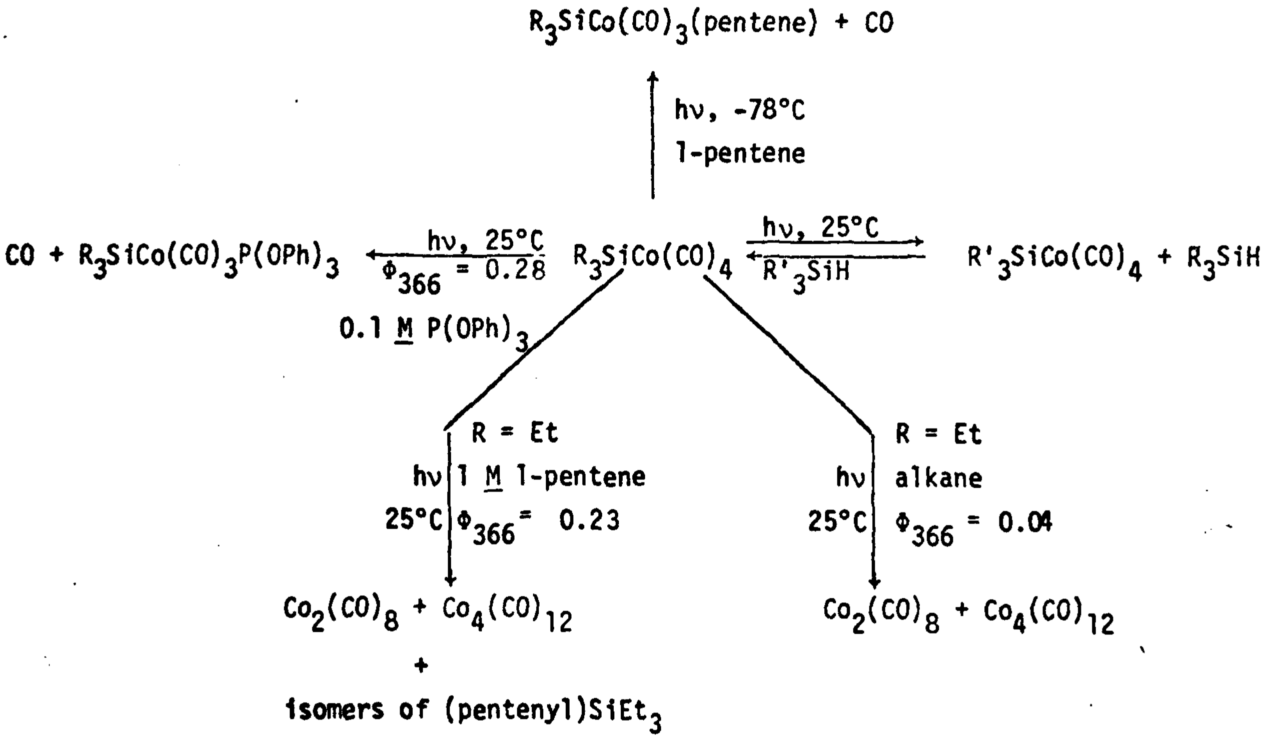
$HSiPh_3$ (Petrarch) were recrystallized from ethanol and pentane, respectively, before use. Alkenes (99%, PCR or Phillips Chemical Company) were passed through activated alumina (MC&B chromatographic grade, 80-325 mesh) prior to use and stored in amber bottles at 4°C. Triethylsilane (Petrarch) was treated similarly. $Co_4(CO)_{12}$ was prepared by heating $Co_2(CO)_8$ under N_2 in isooctane at 80-90°C for 12 hrs, filtering off the product and recrystallizing from benzene/isooctane under N_2. $R_3SiCo(CO)_4$ (R = Et, Ph) were prepared by the literature method of Chalk and Harrod.[5] Solvents were reagent grade or better; isooctane was spectrophotometric grade. For work with air- or water-sensitive species solvents were distilled under argon from appropriate drying agents.

Solutions for irradiation were hermetically sealed into 13 mm o.d. pyrex ampules after at least four freeze-pump-thaw degassing cycles under high vacuum. Alternatively, the organometallic was added, in the glove box to previously degassed solvent, the mixture transferred to 13 mm o.d. pyrex tubes with ground glass joint tops and sealed with rubber septa. Irradiation samples were generally 1-4 ml in volume, $\sim 10^{-3}\underline{M}$ in metal carbonyl for catalysis and 10^{-2}-$10^{-4}\underline{M}$ for spectral studies. Light intensities were determined by ferrioxalate actinometry.[6] Near-ultraviolet irradiation was generated by two General Electric Blacklites ($\lambda_{max} = 355 \pm 20$ nm, $I \sim 2 \times 10^{-6}$ ein/min) or a high-pressure mercury arc lamp (Bausch and Lomb, model SP200, 200 W) with an 18 cm water filter to remove infrared radiation. Monochromatic light was supplied by medium-pressure mercury arc lamps (Hanovia, 450 W or 550 W) filtered with Corning glass filters to isolate the desired emission ($I \sim 10^{-7}$ ein/min with associated merry-go-round). 254 nm irradiation was supplied by a UV-Products low-pressure mercury arc lamp.

The complexes $R_3SiCo(CO)_4$ (R = Et, Ph) were synthesized and purified according to the literature procedures,[5] equation (4). These complexes are

$$Co_2(CO)_8 + 2HSiR_3 \xrightarrow{\Delta} 2R_3SiCo(CO)_4 + H_2 \tag{4}$$
$$R = Et,\ Ph$$

thermally inert at 25°C in deoxygenated hydrocarbon solutions containing 1-pentene, $HSiR_3$, $P(OPh)_3$ or mixtures of these reagents. However, these complexes are photosensitive upon near ultraviolet irradiation. Scheme II summarizes the photochemistry under various conditions. The data support the conclusion that dissociative loss of CO, equation (2), is the main result of photoexcitation of $R_3SiCo(CO)_4$. However, small quantum yields for $Co_2(CO)_8$ and some $Co_4(CO)_{12}$ formation in alkane solution are found and the chemical yield of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are >90% based on $R_3SiCo(CO)_4$ consumed. In the presence of 1.0 M 1-pentene at 25°C the quantum yield for $Co_2(CO)_8$ formation increases markedly, but at -78°C the photoreaction leads to no detectable $Co_2(CO)_8$. At -78°C infrared spectral changes accompanying 355 nm



Scheme II: Photochemistry of $R_3SiCo(CO)_4$.

irradiation in 1.0 M 1-pentene in isooctane are consistent with the formation of $R_3SiCo(CO)_3$(pentene) (R = Et, ν_{CO} = 1966 sh, 1959 cm^{-1}; R = Ph, ν_{CO} = 1977 sh, 1970 cm^{-1}). Addition of $P(OPh)_3$/isooctane in the dark to the irradiated solution at -78°C followed by warmup to 25°C and infrared analysis reveals the presence of $R_3SiCo(CO)_3P(OPh)_3$, evidencing photogeneration of a labile species at -78°C.[7] Warmup of $Et_3SiCo(CO)_3$(pentene) - containing solutions in the absence of added $P(OPh)_3$ gives regeneration of $Et_3SiCo(CO)_4$ and a significant amount of $Co_4(CO)_{12}$. The low temperature irradiations appear to rule out chemistry according to equation (1) as the major pathway to $Co_2(CO)_8$. At 25°C in the presence of 1-pentene, irradiation of $Et_3SiCo(CO)_4$ leads to formation of isomers of (pentenyl)$SiEt_3$ as the dominant Si-containing product,[8] though initial infrared spectral changes are consistent with formation of $Et_3SiCo(CO)_3$(pentene).

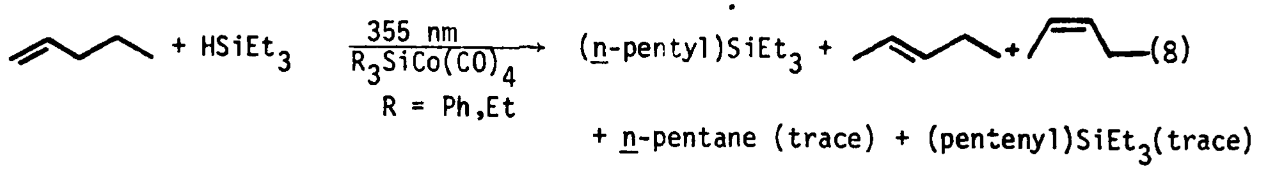
Consistent with dissociative loss of CO as the major primary photoreaction, we find high quantum efficiency ($\Phi \sim 0.28$) for the substitution of CO by $P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH, Figure 1, results in clean formation of $R'_3SiCo(CO)_4$ with good quantum yield; irradiation in the presence of 0.1 M R'_3SiH and 0.3 M $P(OPh)_3$ only yields $R_3SiCo(CO)_3(P(OPh)_3)$. The rationale for these results is given by equations (2) and (5)-(7), indicating competitive capture of the 16$^-$ species by $P(OPh)_3$ or $HSiR_3'$.

$$R_3SiCo(CO)_3 + P(OPh)_3 \longrightarrow R_3SiCo(CO)_3(P(OPh)_3) \qquad (5)$$

$$R_3SiCo(CO)_3 + R'_3SiH \rightleftharpoons R_3SiCo(CO)_3(H)(SiR'_3) \rightleftharpoons R'_3SiCo(CO)_3 + R_3SiH \qquad (6)$$

$$R'_3SiCo(CO)_3 + CO \longrightarrow R'_3SiCo(CO)_4 \qquad (7)$$

With respect to catalysis, we find that irradiation of $R_3SiCo(CO)_4$ in the presence of 1-pentene/$HSiEt_3$ does lead to the isomerization and hydrosilation of the 1-pentene, equation (8). Only traces of (pentenyl)$SiEt_3$



(8)

products are found. Data for the photocatalyzed reactions are given in the Table. The $R_3SiCo(CO)_4$ species lead to extensive pentene isomerization prior to significant extent conversion to (n-pentyl)$SiEt_3$. Of the order of 10^3 molecules of (n-pentyl)$SiEt_3$ have been observed per molecule of $R_3SiCo(CO)_4$ initially added and the turnover rate for formation of this product is of the order of 25 h^{-1} at the light intensity used to generate data given in the Table. Higher light intensities have yielded observed turnover rates for the reaction of ~250 h^{-1}. Thermal activity of $R_3SiCo(CO)_4$ at 25°C for (n-pentyl)$SiEt_3$ formation is low on the scale of light induced activity, but significant isomerization is detectable in thermal controls. The Table also shows data that reveal that when thermal catalytic activity of $Co_2(CO)_8$ is over, catalytic activity can be revived by irradiation. These representative photoactivation data show an additional ~100 turnovers per Co after the catalytic activity for the $Co_2(CO)_8$ is over. While it is tempting to conclude that the same catalyst is generated from irradiation of $Et_3SiCo(CO)_4$ as from $Co_2(CO)_8$ in the dark, we cannot yet unequivocally make this conclusion. We do find that the (n-pentyl)$SiEt_3$ is the dominant detectable Si-containing product in both cases. Thus, it would appear that the $Co_2(CO)_8$ activity can be prolonged by irradiation; infrared analysis of the $Co_2(CO)_8$/pentene/$HSiEt_3$ solution when thermal reaction has stopped shows $Et_3SiCo(CO)_4$ to account for >80% of the Co. The photoreaction of $Et_3SiCo(CO)_4$ in pentene to yield (pentenyl)$SiEt_3$ (*vide supra*) provides a pathway to an active catalyst. The formation of (pentenyl)$SiEt_3$ may occur by first forming $Et_3SiCo(CO)_3$(pentene) followed by insertion to yield (pentenyl$SiEt_3$)$Co(CO)_3$ which then rapidly gives β-hydrogen transfer to yield the substitution labile complex (pentenyl$SiEt_3$)$Co(CO)_3H$. This hydride can then lose the (pentenyl)$SiEt_3$ to leave behind the coordinatively unsaturated $HCo(CO)_3$ that is very likely the active catalyst in the $Co_2(CO)_8$ system.[2,5] In addition to determining its role in forming the active catalyst here, further study of this photoreaction is being undertaken to gain insight into the possible mechanism in $Fe(CO)_5$ photocatalyzed reaction of $HSiR_3$/1-pentene that gives substantial amounts of (pentenyl)SiR_3 as a catalysis product.[8,9]

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Table. Photocatalyzed Reaction of 1-Pentene with $HSiEt_3$.[a]

Catalyst Precursor	1-Pentene/$SiEt_3$	Irrdn Time	% Consumption of 1-Pentene	Product Analysis, %			
				n-pentane	t-2-	c-2-pentene	(n-pentyl) $SiEt_3$
$Ph_3SiCo(CO)_4$ (1.79×10^{-3}M)	1.0 M/1.0M (in n-octane)	0 (39h thermal control)[b]	8	0	91	0	9
		1	26	<1	90	7	4
		4.7	96	<1	64	16	20
		39	97	<1	57	13	30
$Ph_3SiCo(CO)_4$ (1.79×10^{-3}M)	3.3M/3.3M (neat)	1	7.9	1	81	14	6
		4.7	97	<1	79	14	9
		39	>97	<1	38	9	52
$Et_3SiCo(CO)_3$ (1.79×10^{-3}M)	3.3M/3.3M (neat)	4.7	97	<1	79	14	8
		39	>97	1	32	8	60
$Co_2(CO)_8$ (2×10^{-2}M)	3.3M/3.3M (neat)	0 (10h thermal)[c]	>97	----------------------			23
		15 after 10h thermal[d]	>97	----------------------			35
$Co_2(CO)_8$ (2×10^{-3}M)	3.3M/3.3M (neat)	0 (17h thermal)[c]	>97	----------------------			15
		10h after 17h thermal[d,e]	>97	----------------------			28

[a] Irradiation of 1.0 cc deoxygenated samples in Pyrex ampules using 355 ± 20 nm light at 2×10^{-6} ein/min and at 25°C. Solutions were analyzed by GC and quantitated by using internal standards n-hexane for determination of C_5's and n-decane for (pentyl)$SiEt_3$.

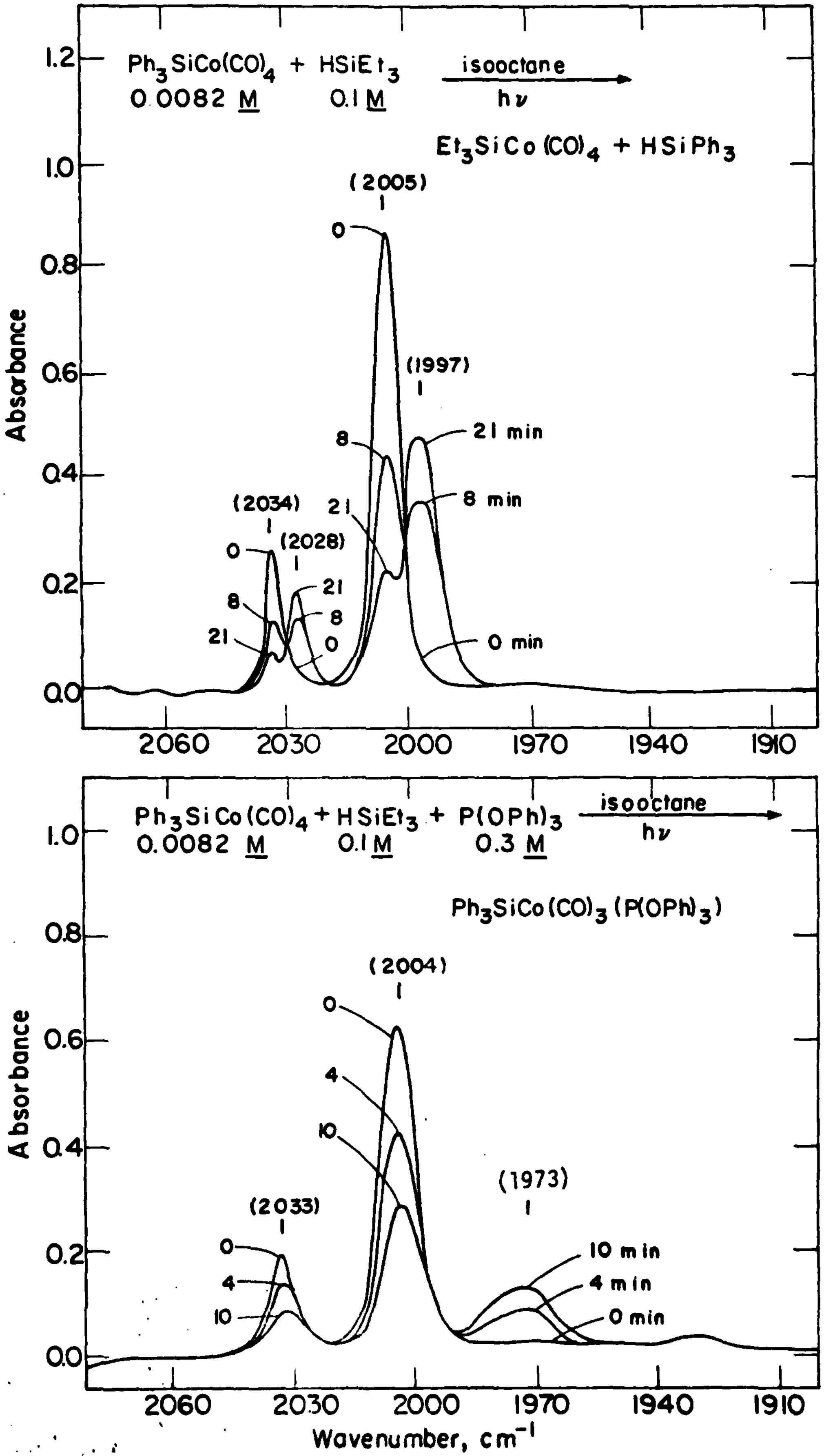
[b] 39 h under same conditions except not irradiated.

[c] This represents a point in the reaction when there is no further detectable activity.

[d] In these experiments the irradiation was not started until thermal activity ceased. The species irradiated is principally $Et_3SiCo(CO)_4$ as detected by infrared.

[e] A higher light intensity was used in this experiment.

Figure Caption. Comparison of photochemistry of $Ph_3SiCo(CO)_4$ in the presence of $HSiEt_3$ only (a) and $HSiEt_3$ and $P(OPh)_3$ (b). Irradiation of the 25°C deoxygenated solutions is at 355 nm ($\pm$ 20 nm). Note that quantum yield for disappearance of $Ph_3SiCo(CO)_4$ is the same in both cases but that silane exchange occurs exclusively in (a) and $P(OPh)_3$ substitution occurs exclusively in (b), consistent with competitive capture of a $16e^-$ species by $P(OPh)_3$ or $HSiEt_3$, equations (5) and (6) in text.



$Ph_3SiCo(CO)_4$ + $HSiEt_3$ $\xrightarrow[h\nu]{isooctane}$
0.0082 M 0.1 M
$Et_3SiCo(CO)_4$ + $HSiPh_3$
(2005)
(1997)
(2034)
(2028)
0
8
21
21 min
8 min
0 min
Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
1.2
2060
2030
2000
1970
1940
1910
$Ph_3SiCo(CO)_4$ + $HSiEt_3$ + $P(OPh)_3$ $\xrightarrow[h\nu]{isooctane}$
0.0082 M 0.1 M 0.3 M
$Ph_3SiCo(CO)_3(P(OPh)_3)$
(2004)
(2033)
(1973)
0
4
10
10 min
4 min
0 min
Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
2060
2030
2000
1970
1940
1910
Wavenumber, cm^{-1}

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