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Contribution from Department of Chemistry,
Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139

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

Carol L. Reichel and Mark S. Wrighton*

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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 $R_3SiCo(CO)_4$ (eq 1 vs. eq 2). We recently showed[1] that 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 eq 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 eq 1 and 3.

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

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

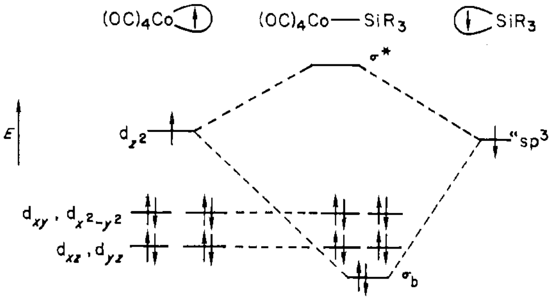
$$2\cdot Co(CO)_4 \rightarrow Co_2(CO)_8 \qquad (3)$$

The relative importance of the two photoreactions represented by eq 1 and 2 is of fundamental interest, since there is considerable ambiguity concerning the importance of primary 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 $\sigma^*(d_{z^2})$ 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 path length amalgam-sealed NaCl cells. Low-temperature spectra were taken by using a Cyrogenics Technology, Inc., Spectrim II cryocooler in conjunction with the spectrophotometer; a 1.1-mm path length 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–near–IR spectrophotometer, in 1.0-cm quartz or 1.1-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 hexane) were carried out on columns of 20% propylene carbonate on Chromosorb P (Johns-Manville, 30 ft × $^1/_8$ in., 20 °C). Hydrosilation products were analyzed (against internal standard decane) on columns of 20% β,β'-oxydipropionitrile on Gaschrom Q (Applied Science Laboratories, 30 ft × $^1/_8$ in., 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 ($^1/_8$ in. × 5 ft, 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.

Scheme I. One-Electron Orbital Diagram for $R_3SiCo(CO)_4$



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 glovebox. 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 Co.) 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 h, filtering off the product, and recrystallizing it 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 glovebox to previously degassed solvent, and the mixture was transferred to o.d. Pyrex tubes with ground glass joint tops which were then sealed with rubber septa. o.d. Pyrex Irradiation samples were generally 1–4 mL in volume, $\sim 10^{-3}$ M in metal carbonyl for catalysis, and 10^{-2}–10^{-4} 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, $I \approx 2 \times 10^{-6}$ einstein/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 or 550 W) filtered with Corning glass filters to isolate the desired emission ($I \approx 10^{-7}$ ein-

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(1) Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6769.

(2) Harrod, J. F.; Chalk, A. J. "Organic Syntheses via Metal Carbonyls"; Pino, P., Wender, I. Eds.; Wiley: New York, 1977; Vol. 2, pp 687–690.

(3) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Severson, R. G.; Wojcicki, A. *J. Organomet. Chem.* **1978**, *157*, 173.

(4) Photoelectron spectroscopy of $H_3SiCo(CO)_4$ shows the $3d_{x^2-y^2}$, d_{xy} and $3d_{xz}$, d_{yz} orbitals to be the highest occupied levels with the σ level more stable: Cradock, S.; Ebsworth, E. A. V.; Robertson, A. *J. Chem. Soc., Dalton Trans.* **1973**, 22.

(5) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640.

(6) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

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

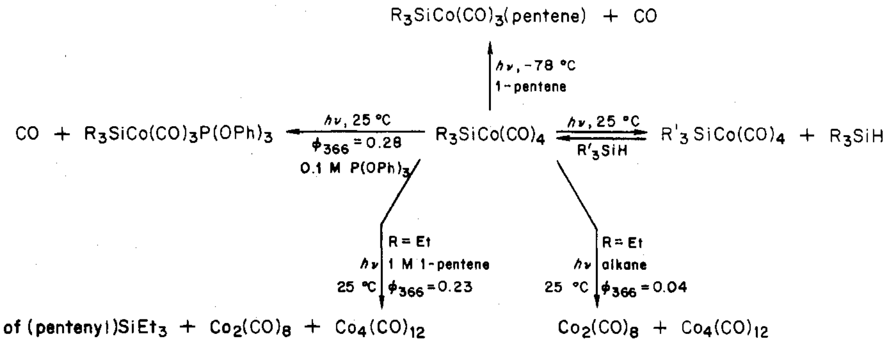


Table I. Photocatalyzed Reaction of 1-Pentene with $HSiEt_3$[a]

				product anal., %			
catalyst precursor	[1-pentene]/[SiEt$_3$]	irrdn time, h	% consumption of 1-pentene	*n*-pentane	*trans*-2-pentene	*cis*-2-pentene	(*n*-pentyl)-SiEt$_3$
$Ph_3SiCo(CO)_4$ (1.79×10^{-3} M)	1.0 M/1.0 M (in octane)	0 (39-h 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)	3.3 M/3.3 M (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)	3.3 M/3.3 M (neat)	4.7	97	<1	79	14	8
		39	>97	1	32	8	60
$Co_2(CO)_8$ (2×10^{-2} M)	3.3 M/3.3 M (neat)	0 (10-h thermal)[c]	>97				23
		15 after 10-h thermal[d]	>97				35
$Co_2(CO)_8$ (2×10^{-3} M)	3.3 M/3.3 M (neat)	0 (17-h thermal)[c]	>97				15
		10 after 17-h thermal[d,e]	>97				28

[a] Irradiation of 1.0 cm^3 deoxygenated samples in Pyrex ampules using 355 ± 20 nm light at 2×10^{-6} einstein/min and at 25 °C. Solutions were analyzed by GC and quantitated by using internal standards hexane for determination of C_5's and 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.

stein/min with associated merry-go-round). The 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] (eq 4). These complexes are 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 (eq 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 yields of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are >90% on the basis of $R_3SiCo(CO)_4$ 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 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] Warm-up 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 eq 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).

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

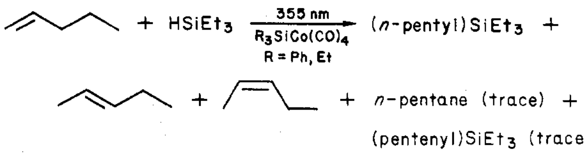
Consistent with dissociative loss of CO as the major primary photoreaction, we find high quantum efficiency ($\Phi = 0.28$) for the substitution of CO by $P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH (Figure 1) results in clean formation of $R'_3SiCo(CO)_4$ with good quantum yield; 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 eq 2 and 5–7 indicating competitive capture of the 16e species by $P(OPh)_3$ or $HSiR'_3$.

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

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

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

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 (eq 8). Only traces of (pente-



(8)

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[7] These $R_3SiCo(CO)_3P(OPh)_3$ complexes have IR spectra in the CO region as follows: R = Et, 1969 sh, 1965 cm^{-1}; R = Ph, 1980 sh, 1973 cm^{-1} in isooctane/1-pentene (1:1 by volume). These spectra are similar to those for the $R_3SiCo(CO)_3$(pentene) detected at -78 °C consistent with a similar arrangement of the CO groups. The spectra accord well with those for $R_3ECo(CO)_3L$ complexes previously reported: Boyd, T. E.; Brown, T. L. *Inorg. Chem.* **1974**, *13*, 422.

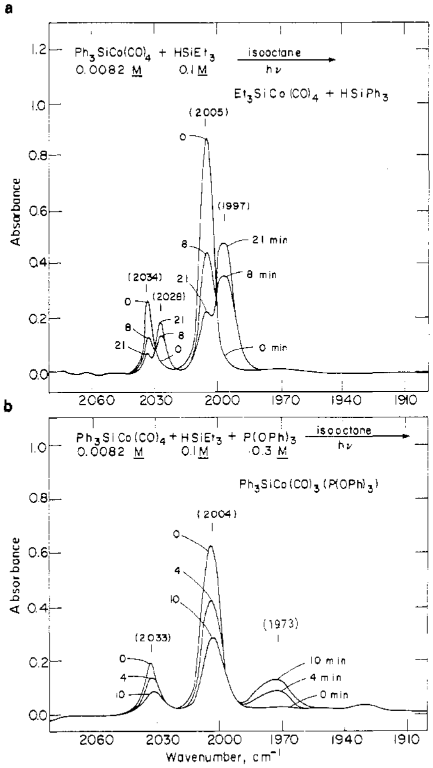

Figure 1. Comparison of the photochemistry of $Ph_3SiCo(CO)_4$ in the presence of $HSiEt_3$ only (a) and $HSiEt_3$ and $P(OPh)_3$ (b). Irradiation of the 25 °C deoxygenated solutions is at 355 nm (±20 nm). Note that the quantum yield for disappearance of $Ph_3SiCo(CO)_4$ is the same in both cases but that silane exchange occurs exclusively in part a, and $P(OPh)_3$ substitution occurs exclusively in part b, consistent with competitive capture of a 16e species by $P(OPh)_3$ or $HSiEt_3$ (eq 5 and 6 in text).

nyl)$SiEt_3$ products are found. Data for the photocatalyzed reactions are given in Table I. The $R_3SiCo(CO)_4$ species lead to extensive pentene isomerization prior to significant extent conversion to (*n*-pentyl)$SiEt_3$. On 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 on the order of 25 h^{-1} at the light intensity used to generate data given in Table I. 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. Table I 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 (pentyl$SiEt_3$)$Co(CO)_3$ 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]

Acknowledgment. We thank the Office of Naval Research for partial support of this research, and M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975–1980. C.L.R. was supported during Spring, 1980, by a fellowship with funds generously provided by Eastman Kodak Co.

Registry No. $Ph_3SiCo(CO)_4$, 14095-19-3; $Et_3SiCo(CO)_4$, 14049-72-0; 1-pentene, 109-67-1; pentane, 109-66-0; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3; (*n*-pentyl)$SiEt_3$, 18044-55-8; $Et_3SiCo(CO)_3P(OPh)_3$, 75030-69-2; $Ph_3SiCo(CO)_3P(OPh)_3$, 75030-70-5; $Et_3SiCo(CO)_3$(pentene), 75030-71-6; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; $HSiEt_3$, 617-86-7.

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(8) The isomers have been characterized by GC and mass spectral analyses compared to authentic samples prepared previously: Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

(9) (a) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189. (b) Nesmeyanov, A. N.; Friedlina, R. K.; Chukovskaya, E. C.; Petrova, R. G.; Belyavsky, A. B. *Tetrahedron* **1962**, *17*, 61. (c) Friedlina, R. K.; Chukovskaya, E. C.; Tsao, J.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 37.

Contribution from Lash Miller Chemistry Laboratory and
Erindale College, University of Toronto,
Toronto, Ontario, M5S 1A1, Canada

Nickel Vapor/Butadiene Matrix Chemistry

Geoffrey A. Ozin* and William J. Power

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It has recently been demonstrated that nickel atom/olefin matrix cocondensation reactions lead to the formation of a wide range of binary nickel π-olefin complexes of the type Ni(olefin)$_n$, where $n = 1$–3.[1] Each complex displayed a single, intense ultraviolet absorption, which monotonically *blue* shifted with increasing olefin stoichiometry. For a particular stoichiometry, the transition energy was essentially *invariant* to olefin substituent. The insensitivity of this "fingerprint" ultraviolet band, with respect to rather dramatic excursions of the olefinic π and π* energy levels, pinpointed the electronic transition in question as one involving nickel-localized d → p excitations with only minimal mixing of the Ni (p)/olefin (π*) orbitals. (This assignment has recently received support from ab initio SCF-HF-LCAO[2] and GVB-CI[3] calculations of $Ni(C_2H_4)_n$.) The optical data established the existence of narrow spectral regions characteristic of olefin stoichiometry, that is, 320–330 nm for Ni(olefin), 280–290 nm for Ni(olefin)$_2$, and 230–250 nm for Ni(olefin)$_3$. Similar correlations were also found for a range of Pd(olefin)$_n$ complexes.[1]

The effect of metal nuclearity on the optical spectra was also investigated in a similar series of experiments under binuclear nickel reaction conditions.[3] In the case of ethylene, $Ni_2(C_2H_4)_{1,2}$ complexes were identified, both displaying bands around 240 and 370–400 nm, quite different from those of $Ni(C_2H_4)_{1,2}$.

With the distinct spectral trends and lack of major substituent effects for numerous mononuclear nickel–olefin complexes, yet considerable sensitivity to metal nuclearity, it is

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(1) G. A Ozin and W. J. Power, *Inorg. Chem.*, **17**, 2836 (1979).

(2) R. M. Pitzer and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **101**, 7176 (1979).

(3) G. A. Ozin, W. J. Power, W. A. Goddard III, and T. Upton, *J. Am. Chem. Soc.*, **100**, 4750 (1978).

0020-1669/80/1319-3860$01.00/0