Stereodynamics and Reactivity of the Indenyliridium(I) Complex $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})(CO)$. Comparison with the Cyclopentadienyl Analog $(\eta^5\text{-}C_5H_5)Ir(\eta^2\text{-}C_8H_{14})(CO)$

Lawrence P. Szajek and John R. Shapley*

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received August 2, 1993®

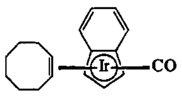
The complexes $(\eta^5\text{-}C_5H_5)Ir(\eta^2\text{-}C_8H_{14})(CO)$ (1) and $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})(CO)$ (2) have been prepared from the reactions of $[(\eta^2\text{-}C_8H_{14})_2Ir(CO)Cl]_2$ with thallium cyclopentadienide and potassium indenide, respectively, and have been characterized by various analytical and spectroscopic methods. Two stereoisomers of 1 and 2, due to restricted rotation about the iridium–olefin bond, have been characterized by 2D-NMR studies. The indenyl complex 2 shows a significantly lower barrier to cyclooctene rotation than the corresponding cyclopentadienyl complex 1 (ca. 15 and 20 kcal/mol, respectively). The labile cyclooctene ligand of 2 is replaced readily by ethylene, carbon monoxide, and triphenylphosphine to give $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_2H_4)(CO)$ (3), $(\eta^5\text{-}C_9H_7)Ir(CO)_2$ (4), and $(\eta^5\text{-}C_9H_7)Ir(PPh_3)(CO)$ (5), respectively. The reaction of phenylacetylene with 2 provides the dinuclear complex $[(\eta^5\text{-}C_9H_7)Ir(CO)]_2(\mu\text{-}C{=}CHPh)$ (6). The oxidative addition reactions of triphenylsilane and allyl bromide with 2 yield $(\eta^5\text{-}C_9H_7)Ir(H)(SiPh_3)(CO)$ (7) and $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (8), respectively. No reactions have been observed for 1 under similiar or more vigorous conditions. Compounds 1 and 2 have been compared also as catalysts for the hydrosilylation of phenylacetylene and ethylene.

Introduction

Transition-metal indenyl complexes frequently show enhanced reactivity toward ligand substitution compared to their cyclopentadienyl analogs,[1,2] in both stoichiometric and catalytic reactions.[3] This rate enhancement has generally been attributed to a facile ring slippage of the indenyl ligands from η^5 toward η^3 and has been named the "indenyl ligand effect" by Basolo.[2d,e] An intramolecular manifestation of this effect has been established by the measurement of energy barriers for ethylene rotation in comparable cyclopentadienyl and indenyl complexes.[4]

As part of our interest in the reactivity of Ir(I) centers, we reported briefly that the cyclooctene ligand in $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})(CO)$ (2) is readily replaced in substitution by ethylene[4a] or in oxidative addition reactions.[5] In this paper we report in detail on the stereodynamics and reactivity of 2 and compare these properties with those of the analogous cyclopentadienyl complex $(\eta^5\text{-}C_5H_5)Ir(\eta^2\text{-}C_8H_{14})(CO)$ (1).

1



2

Experimental Section

General Comments. All manipulations were conducted under an atmosphere of nitrogen using standard Schlenk techniques. The syntheses of $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})(CO)$ (2) and $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_2H_4)(CO)$ (3) have been reported.[4a] $[(\eta^2\text{-}C_8H_{14})_2Ir(CO)Cl]_2$[6] and thallium cyclopentadienide[7] were prepared according to literature methods. Cyclooctene (Aldrich), indene (Aldrich), and phenylacetylene (Aldrich) were distilled before use. $IrCl_3{\cdot}xH_2O$ (Johnson Mathey Co.), triphenylphosphine (Aldrich), triphenylsilane (Aldrich), triisopropylsilane (Aldrich), allyl bromide (Matheson, Coleman & Bell), 1,2-dibromoethane (Aldrich), CO (Air Products), H_2 (Linde), and ethylene (Matheson) were used without further purification. All solvents were dried and distilled before use. Deuterated benzene was distilled from sodium–potassium alloy, and deuterated chloroform was distilled from phosphorus pentoxide; and both solvents were passed through a short column of activated basic alumina immediately before use. Deuterated dichloromethane, cyclohexane, and nitrobenzene were similarly treated immediately before use. Melting points were determined in capillary tubes sealed under vacuum.

^1H NMR spectra were recorded on a Varian XL-200, a General Electric QE-300, or a General Electric GN-500 FT NMR spectrometer. ^{13}C (125 MHz) and correlation NMR spectra were recorded on a General Electric GN-500 NMR FT spectrometer. Temperature calibrations for variable temperature NMR experiments were determined using a capillary of ethylene glycol or methanol as an internal reference.[8] FT-IR spectra were recorded on a Perkin Elmer 1750 spectrometer. Electron-impact (EI), field-desorption (FD), and fast atom bombardment (FAB) mass spectra were recorded by the staff of the School of Chemical

---

® Abstract published in *Advance ACS Abstracts*, March 1, 1994.

[1] (a) Foo, T.; Bergman, R. G. *Organometallics* **1992**, *11*, 1801. (b) Foo, T.; Bergman, R. G. *Organometallics* **1992**, *11*, 1811. (c) Habib, A.; Tanke, R. S.; Holtz, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 1225. (d) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778. (e) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (f) Kakkar, A. K.; Taylor, N. J.; Marder, T. B. *Organometallics* **1989**, *8*, 1765.

[2] (a) Turaki, N. N.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424. (b) Rest, A. J.; Whitwell, L.; Graham, W. A.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624. (c) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (d) Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

[3] (a) Tanke, R. H.; Crabtree, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 7984. (b) Marder, T. B.; Roe, D. C.; Milstein, S. *Organometallics* **1988**, *7*, 1451. (c) Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181. (d) Bönnemann, H. *Angew. Chem.* **1985**, *97*, 264; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248.

[4] (a) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357. (b) Kakkar, A. K.; Taylor, N. J.; Calabrese, J. C.; Nugent, W. A.; Roe, D. C.; Connaway, E. A.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 990. (c) Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Less Common Met.*. **1978**, *61*, 107.

[5] Ma, L.; Szajek, L. P.; Shapley, J. R. *Organometallics* **1991**, *10*, 1662.

[6] Shaw, B. L.; Singleton, F. *J. Chem. Soc. (A)* **1967**, 1683.

[7] Nielson, A. J.; Richard, C. E. F.; Smith, T. M. *Inorg. Synth.* **1978**, *24*, 97.

[8] (a) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (b) Friebohlin, H.; Schilling, G.; Pohl, C. *Org. Magn. Reson.* **1979**, *12*, 569.

0276-7333/94/2313-1395$04.50/0

Sciences Mass Spectrometry Laboratory. Elemental analyses were performed by the staff of the SCS Microanalytical Laboratory.

CpIr(η^2-C_8H_{14})(CO) (1). To a yellow suspension of [(η^2-C_8H_{14})$_2$Ir(CO)Cl]$_2$ (200 mg, 0.21 mmol) in diethyl ether (150 mL) at 0 °C was added 2 equiv of thallium cyclopentadienide (115 mg, 0.24 mmol). The solution immediately turned red; it was stirred for 4 h and allowed to warm to room temperature. Decolorizing carbon was added, and the mixture was filtered via a filter cannula. The dark green filtrate was reduced in volume to ca. 5 mL and eluted down a column (20 × 2 cm) of activated neutral alumina with diethyl ether (100 mL). The pale-red band was collected, and the solvent was removed under reduced pressure to give an off-white residue. The residue was sublimed at 70 °C (10^{-1} Torr), and white crystalline solid 1 was collected on a water-cooled cold-finger. Yield: 117 mg, 0.29 mmol (72%). Mp: 117–118 °C. IR (ν_{co}, C_6H_{12}): 1974 m, 1967 vs cm^{-1}. Anal. Calcd for $IrC_{14}H_{19}O$: C, 42.41; H, 4.83. Found: C, 42.38; H, 4.75.

Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with CO. Carbon monoxide was bubbled slowly through a bright yellow solution of 2 (50 mg, 0.11 mmol) in cyclohexane (15 mL) for 30 min. After 30 min, the solvent was removed under reduced pressure, and the residue was sublimed at 70 °C (10^{-1} Torr). Pale yellow needles of (η^5-C_9H_7)Ir(CO)$_2$ (4) were collected. Yield: 38 mg, 0.11 mmol (98%). Mp: 89–90 °C. IR (ν_{co}, C_6H_{12}): 2040 vs, 1979 vs cm^{-1} (lit.[9] 2042 vs, 1980 vs). Anal. Calcd for $IrC_{11}H_7O_2$: C, 36.36; H, 1.94. Found: C, 36.47; H, 1.91.

Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with PPh_3. To a bright yellow solution of 2 (50 mg, 0.11 mmol) in cyclohexane (2 mL) in a 5-mL culture tube was added PPh_3 (29 mg, 0.11 mmol) with stirring. After 30 min, the yellow precipitate of 5 that formed was isolated by centrifugation and purified by washing with diethyl ether (1 mL) followed by drying in vacuo. Yield: 66 mg, 0.11 mmol (98%). IR (ν_{co}, C_6H_{12}): 1952 vs cm^{-1} (lit.[10] 1934 cm^{-1}, CH_2Cl_2). Anal. Calcd for $IrC_{28}H_{22}OP$: C, 56.18; H, 3.71. Found: C, 55.99; H, 3.89. EI-MS: *m/z* (^{193}Ir) 598 (η^5-C_9H_7)Ir(PPh_3)(CO)$^+$.

Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with PhCCH. A bright yellow solution of 2 (60 mg, 0.13 mmol) and phenylacetylene (0.06 mL, 0.52 mmol) in cyclohexane (15 mL) was heated to reflux for 7 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure, and the remaining orange-red solid was dissolved in diethyl ether (2 mL). Decolorizing carbon was added, and the solution was eluted down a short column (10 × 2 cm) of activated neutral alumina with diethyl ether (50 mL). The dark yellow band was collected, reduced in volume to ca. 1 mL, and left at −20 °C. After 1 week, orange crystals of 6 were isolated by vacuum filtration, washed with diethyl ether (ca. 1 mL), and dried in vacuo. Yield: 36 mg, 0.05 mmol (71%). Mp: 194–195 °C. IR (ν_{co}, C_6H_{12}): 1964 s cm^{-1}. FD-MS: *m/z* (^{193}Ir) 774 (C_9H_7)$_2$Ir$_2$(C=CPhH)(CO)$_2^+$. Anal. Calcd for $Ir_2C_{28}H_{20}O_2$: C, 43.41; H, 2.61. Found: C, 43.09; H, 2.80.

Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with $HSiPh_3$. A bright yellow solution of 2 (65 mg, 0.15 mmol) and triphenylsilane (38 mg, 0.15 mmol) in cyclohexane (25 mL) was heated to reflux for 5 h and allowed to cool to room temperature. The solvent was removed under reduced pressure, and the orange oily residue was dissolved in diethyl ether (2 mL). Decolorizing carbon was added, and the solution was eluted down a short column (10 × 2 cm) of activated neutral alumina with diethyl ether (50 mL). The orange band was collected, reduced in volume to ca. 1 mL, and left at −20 °C. After 1 week, dark yellow crystals of 7 were isolated, washed with diethyl ether (ca. 1 mL), and dried in vacuo. Yield: 69 mg, 0.12 mmol (78%). Mp: 119–120 °C. IR (ν_{CO}, C_6H_{12}): 2011 IR (ν_{CO}, KBr): 1982. In (ν_{IrH}, KBr) 2145. FD-MS: *m/z* (^{193}Ir) 596 (C_9H_7)Ir(H)($SiPh_3$)(CO)$^+$. Anal. Calcd for $C_{28}H_{23}IrOSi$: C, 56.36; H, 3.89. Found: C, 56.63; H, 3.87.

NMR Tube Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with $HSiPh_3$. An NMR tube with a vacuum line adaptor was charged with 2 (30 mg, 0.067 mmol), $HSiPh_3$ (53 mg, 0.20 mmol), and $CDCl_3$ (0.5 mL). The NMR tube was cooled in a liquid nitrogen bath and sealed. After the sample had warmed to room temperature, ^{1}H NMR spectra were recorded at 10-min intervals as the NMR tube was heated to 40 °C in the NMR probe. After 30 min, the resonances for free cyclooctene at δ5.73, 2.25, and 1.65 had grown significantly in intensity, and the resonances for 2 had decreased proportionately. Proton resonances H_1, H_2, and H_2* for two products were as follows: δ 6.13, H_2, 5.32, H_1, and 5.08, H_2*, for the major product, and δ 6.05, H_2, 5.37, H_1, and 5.01, H_2*, for the minor product; ratio of major:minor = 3:1. Only one Ir–H resonance was recorded at δ −15.91. After 24 h at 40 °C, the ^{1}H NMR spectrum showed only the major product.

NMR Tube Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with HSi^iPr_3. An NMR tube with a vacuum line adaptor was charged with 2 (20 mg, 0.045 mmol), HSi^iPr_3 (53 mg, 40 μL, 0.20 mmol), and $CDCl_3$ (0.5 mL). The NMR tube was cooled in a liquid nitrogen bath and sealed. After the sample had warmed to room temperature, ^{1}H NMR spectra were recorded at 10-min intervals as the NMR tube was heated to 40 °C in the NMR probe. After 30 min, the resonances for free cyclooctene at δ 5.73, 2.25, and 1.65 had grown significantly in intensity, and the resonances for 2 had decreased proportionately. Proton resonances at δ 6.17, H_2, 5.91, H_1, and 5.46, H_2*, for only one product were recorded. Only one Ir–H resonance was observed at δ −16.48.

Reaction of (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO) with C_3H_5Br. A bright yellow solution of 2 (50 mg, 0.11 mmol) and allyl bromide (60 μL, 0.60 mmol) in cyclohexane (25 mL) was heated to reflux for 4 h and allowed to cool to room temperature. The solvent was removed under reduced pressure, and the orange oily residue was placed on a column (10 × 2 cm) of activated neutral alumina, eluting with diethyl ether (50 mL). The orange band was collected, reduced in volume to ca. 1 mL, and left at -20 °C. After 1 week, dark orange crystals of 8 were isolated, washed with diethyl ether (ca. 1 mL), and dried in vacuo. Yield: 43 mg, 0.09 mmol (86%). FAB-MS (positive ion): *m/z* (^{193}Ir) 459 [(C_9H_7)Ir(C_3H_5)(CO)]Br$^+$. Anal. Calcd for $C_{13}H_{12}IrBrO$: C, 34.42; H, 2.65. Found: C, 34.08; H, 2.59. IR (C_6H_{12}): ν_{CO} 2054 cm^{-1}.

Kinetics of the Reaction of $HSiPh_3$ with (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO). $HSiPh_3$ (1–75 equiv) was dissolved in cyclohexane (14 mL) in a 3-neck round-bottom flask held in a constant temperature bath; the flask was fitted with a reflux condenser, nitrogen inlet, thermometer, and rubber septum. The temperature inside the flask read 40 + 1 °C. A sample of 2 (20 mg, 0.045 mmol) in cyclohexane (1 mL), preheated in the constant temperature bath, was injected into the flask containing the silane. Samples were withdrawn, and the absorbance of the band at 1976 cm^{-1} in the IR spectrum was recorded. First-order analysis of the data provided the following values of k_{obs}, [$HSiPh_3$]: 1.7(1) × 10^{-4} s^{-1}, 31 mM; 3.5(2) × 10^{-4} s^{-1}, 75 mM; 4.7(1) 10^{-4} s^{-1}, 150 mM; 10.3(2) × 10^{-4} s^{-1}, 224 mM.

Catalytic Addition of HSi^iPr_3 to PhCCH with (η^5-C_9H_7)Ir(η^2-C_8H_{14})(CO). A dry round-bottom flask fitted with a reflux condenser was charged with 2 (15 mg, 0.034 mmol), HSi^iPr_3 (6.9 mL, 5.3 g, 34.0 mmol), PhCCH (5.5 mL, 5.1 g, 50.0 mmol), and dichloromethane (5 mL). The flask was heated in an oil bath at 60 °C for 120 h. After the flask had cooled to room temperature, the solvent was removed under reduced pressure. Styrene, excess silane, and phenylacetylene were removed by vacuum distillation at 90 °C (10^{-1} Torr). The yield of styrene was determined by integration of a ^{1}H NMR spectrum with $BrCH_2CH_2Br$ as the internal standard. Yield(PhCH=CH_2): 0.08 g, 0.034 mmol (22 turnovers, 0.3 turnovers/h). *cis*- and *trans*-PhHC=$CHSi^iPr_3$ were obtained by vacuum distillation at 200 °C (10^{-1} Torr) and weighed. Yield(PhHC=$CHSi^iPr_3$): 2.1 g, 8.1 mmol (240 turnovers, 2.0 turnovers/h). ^{1}H NMR ($CDCl_3$): δ 7.52 (d, 1H, H_α, J_{cis} = 15.6 Hz), 7.45–7.18 (m, 5H, C_6H_5), 6.94 (d, 1H, H_α, J_{trans} = 19.4 Hz), 6.39 (d, 1H, H_β, J_{trans} = 19.4 Hz), 5.74 (d, 1H, H_α, J_{cis} = 15.6 Hz), 1.38–1.05 (m, 21H, SiCH(CH_3)$_2$). FD-MS: *m/z* 260 PhH-

---

[9] (a) Abad, J. A. *Inorg. Chim. Acta* 1986, *121*, 213. (b) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* 1986, *108*, 329.

[10] Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* 1991, *113*, 9185.

[11] Cawley, S.; Daryluk, S. S. *Can. J. Chem.* 1986, *46*, 2373.

CCHSi^{i}Pr$_3^+$. Anal. Calcd for SiC$_{17}$H$_{28}$: C, 78.40; H, 10.85. Found: C, 78.68; H, 10.70.

Catalytic Addition of HSi^{i}Pr$_3$ to PhCCH with CpIr(η^2-C$_8$H$_{14}$)(CO). A dry round-bottom flask fitted with a reflux condenser was charged with 1 (10 mg, 0.025 mmol), HSi^{i}Pr$_3$ (5.1 mL, 3.9 g, 25.0 mmol), PhCCH (4.1 mL, 3.8 g, 37.5 mmol), and dichloromethane (5 mL). The flask was heated in an oil bath at 60 °C for 96 h. After the flask had cooled to room temperature, the solvent was removed under reduced pressure. Styrene, excess silane, and phenylacetylene (ca. 8 mL) were removed by vacuum distillation (10^{-1} Torr) at 90 °C. The yield of styrene was determined by integration of a ^{1}H NMR spectrum with BrCH$_2$CH$_2$Br as the internal standard. Yield(PhCH=CH$_2$): 0.02 g, 0.009 mmol (4 turnovers, 0.04 turnovers/h). *cis*- and *trans*-PhHC=CHSi^{i}Pr$_3$ were obtained by vacuum distillation at (10^{-1} Torr) at 200 °C and weighed. Yield (PhHC=CHSi^{i}Pr$_3$): 0.55 g, 2.1 mmol (57 turnovers, 0.3 turnovers/h).

Catalytic Isomerization of PhHC=CHSi^{i}Pr$_3$ with 2. A dry round-bottom flask fitted with a reflux condenser was charged with 2 (15 mg, 0.045 mmol), *cis-trans-* (4/1) PhHC=CHSi^{i}Pr$_3$ (1.0 mL), and dichloromethane (10 mL). The flask was heated in an oil bath at 60 °C for 72 h. After the solution had cooled to room temperature, the solvent was removed under reduced pressure. A ^{1}H NMR spectrum of the solution in CDCl$_3$ indicated the presence of only *trans*-PhHC=CHSi^{i}Pr$_3$.

Reaction of HSiPh$_3$ with C$_2$H$_4$ Catalyzed by 2. A dry pressure bottle was charged with 2 (10 mg, 0.022 mmol), HSiPh$_3$ (5.73 g, 22.0 mmol), and cyclohexane (40 mL) and then was pressurized with ethylene (2 atm). The reaction mixture was stirred by a magnetic stirrer at 25 °C for 120 h. The solvent was removed under reduced pressure, and the residue was passed through a short column of silica with cyclohexane. Evaporation of the elutant gave an off-white solid. The yields of the products were determined by integration of the ^{1}H NMR spectrum in CDCl$_3$ with BrCH$_2$CH$_2$Br as the internal standard. Yield(Ph$_3$SiCH$_2$CH$_3$): 3.8 g, 13.2 mmol. Yield(Ph$_3$SiCH=CH$_2$): 1.9 g, 6.8 mmol. ^{1}H NMR (CDCl$_3$): δ 7.58–7.20 (m, 15H, C$_6$*H*$_5$), 6.69 (dd, 1H, C*H*CH$_2$), 6.30 (dd, 2H, CHC*H*$_2$, J_{trans} = 20.1 Hz, J_{cis} = 14.6 Hz, J_{gem} = 3.6 Hz), 5.80 (dd, 1H, CHC*H*$_2$), 1.36 (q, 2H, SiC*H*$_2$CH$_3$), 1.11 (t, 3H, SiCH$_2$C*H*$_3$). See ref 11 for assignments of Ph$_3$SiCH=CH$_2$. FD-MS: *m/z* 286 Ph$_3$SiCHCH$_2^+$, 288 Ph$_3$SiCH$_2$CH$_3^+$. The reaction quickly went to completion when the bottle was heated in an oil bath at 60 °C.

NMR Tube Reaction of HSiPh$_3$ with C$_2$H$_4$ in the Presence of 2. An NMR tube with a vacuum line adaptor was charged with 2 (20 mg, 0.045 mmol), HSiPh$_3$ (35 mg, 0.13 mmol), and CDCl$_3$ (1.0 mL). The solution was deoxygenated five times by first evacuation followed by pressurization with ethylene (1.5 atm). The NMR tube was cooled in a liquid nitrogen bath and sealed. After the sample had warmed to room temperature, a ^{1}H NMR spectrum was recorded. The spectrum consisted of resonances for 7, triphenylethylsilane, triphenylvinylsilane, and a signal at δ 0.86 attributed to ethane.

Results and Discussion

Synthesis of Cyclooctene Complexes. The complexes 1 and 2 are readily prepared from the reaction of [(η^2-C$_8$H$_{14}$)Ir(CO)Cl]$_2$ in diethyl ether solution with thallium cyclopentadienide (eq 1) or potassium indenide (eq 2), respectively.[4a] The yields of the crystalline solids are >70%. Complex 1 is colorless, whereas 2 is pale yellow.

NMR Characterization and Conformational Analysis of 1 and 2. The room temperature ^{1}H and ^{13}C NMR spectra of 1 and the corresponding low-temperature spectra of 2 consist of a complex set of cyclooctene proton resonances due to the presence of two conformational isomers in solution. These isomers result from restricted rotation about the iridium–olefin bond axis; "syn" and "anti" configurations are defined as shown in Scheme 1.

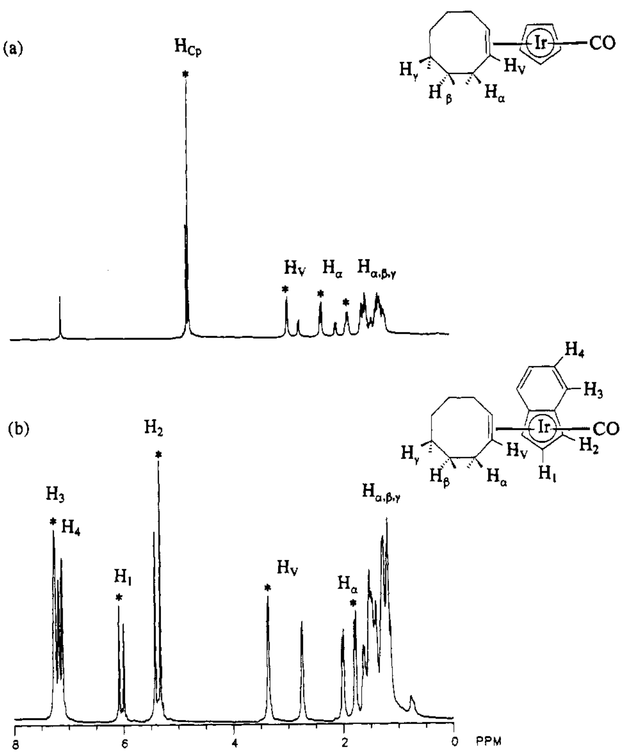
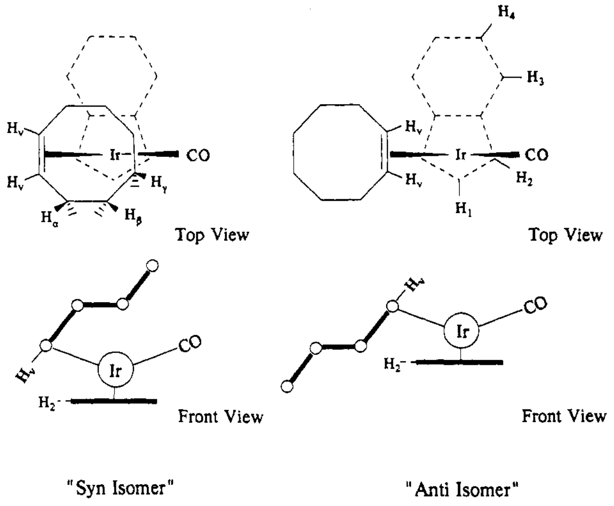


Figure 1. ^{1}H NMR spectra of (a) 1 in C$_6$D$_6$ at 20 °C and (b) 2 in CDCl$_3$ at −20 °C. The configuration depicted for clarity of labeling is the anti configuration as defined in Scheme 1. The asterisks denote resonances assigned to the syn (major) isomer.

Scheme 1



$$[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir(CO)Cl}]_2 + \text{TlCp} \xrightarrow[0\,^\circ\text{C}]{\text{Et}_2\text{O}} \text{CpIr}(\eta^2\text{-C}_8\text{H}_{14})\text{CO}\ (\mathbf{1}) \quad (1)$$

$$[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir(CO)Cl}]_2 + \text{K}[\text{C}_9\text{H}_7] \xrightarrow[0\,^\circ\text{C}]{\text{Et}_2\text{O}} (\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\eta^2\text{-C}_8\text{H}_{14})\text{CO}\ (\mathbf{2}) \quad (2)$$

The ^{1}H NMR spectra of 1 and 2 are compared in Figure 1.

A combination of two-dimensional techniques has been used to assign all of the ^{1}H and ^{13}C NMR resonances for the cyclooctene complexes; the results are summarized in Tables 1 and 2. For example, an attached proton test

Table 1. ^1H NMR Data for Iridium(I) Cyclooctene Complexes[a]

	δ (Multiplicity)								
complex	H_{Cp}	H_1	H_2	H_3	H_4	H_V	H_α	H_β	H_γ
1 (major)	4.81 (s)					3.02	2.40, 1.92	1.64, 1.39	1.6, 1.3
1 (minor)	4.85 (s)					2.81	2.14, 1.37	1.60, 1.42	1.7, 1.4
2 (major)		6.18(t)	5.42(d)	7.32(m)	7.26(m)	3.47	1.87, 1.40	1.54, 1.32	1.5, 1.3
1 (minor)		6.08(t)	5.54(d)	7.35(m)	7.26(m)	2.84	2.15, 1.88	1.64, 1.40	1.6, 1.4
$(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})_2$		5.98(t)	5.12(d)	7.28(m)	7.23(m)	1.22	1.97, 1.65	1.50, 1.28	1.6, 1.2

[a] Recorded at 500 MHz in C_6D_6 at 20 °C for **1**, in $CDCl_3$ at −20 °C for **2**, and in $CDCl_3$ at 20 °C for $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$. The following indenyl ring numbering scheme was used:

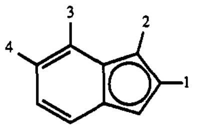


Table 2. ^{13}C NMR Data for Iridium(I) Cyclooctene Complexes[a]

	δ										
complex	C_{Cp}	C_1	C_2	C_{2a}	C_3	C_4	C_V	C_α	C_β	C_γ	C_{CO}
1 (major)	84.5						33.9	32.3	26.7	33.4	171.1
1 (minor)	85.1						39.9	33.6	26.6	33.1	170.0
2 (major)		90.3	72.8	112.4	119.9	124.5	46.3	31.8	26.0	32.2	170.3
2 (minor)		90.6	72.1	112.8	119.4	124.5	41.9	31.1	25.8	32.3	168.6
$(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})_2$		85.7	77.3	109.9	119.9	122.9	51.1	32.4	26.1	32.1	

[a] Recorded at 125 MHz in C_6D_6 at 20 °C for **1**, in $CDCl_3$ at −20 °C for **2**, and in $CDCl_3$ at 20 °C for $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$.

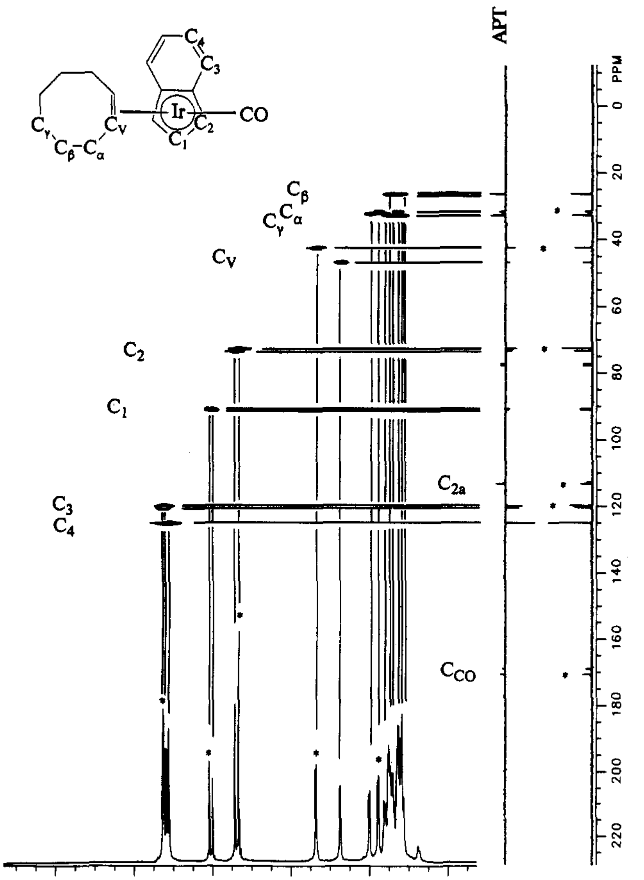


Figure 2. ^1H–^{13}C HETCOR and APT spectra of **2** in $CDCl_3$ at −20 °C. The asterisks denote resonances assigned to the syn isomer.

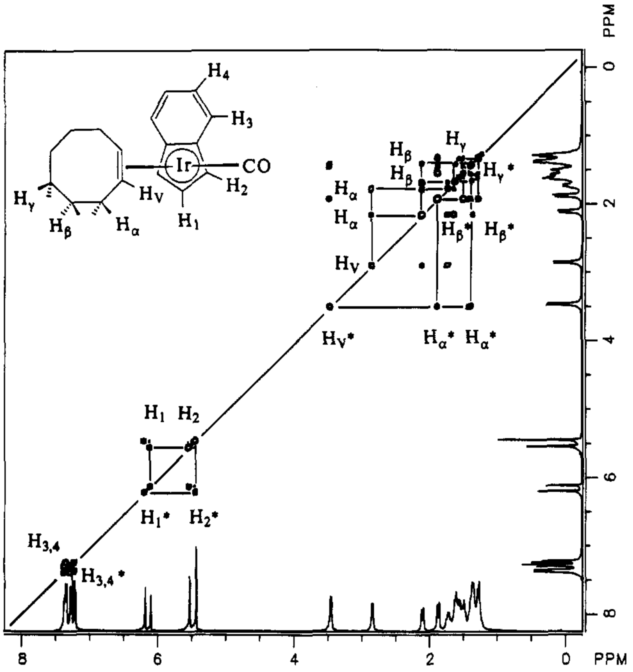


Figure 3. ^1H–^1H COSY spectrum of **2** in $CDCl_3$ at −20 °C. The asterisks denote resonances assigned to the syn isomer.

(APT) spectrum of **2** distinguishes the methylene resonances C_α, C_β, C_γ, C_{2a}, and C_{CO} (positive) from the methyne resonances of C_V and C_1–C_4 (negative), as shown in Figure 2. These resonances can then be correlated to the proton resonances by tracing the cross peaks in the ^1H–^{13}C heteronuclear correlation (HETCOR) spectrum (Figure 2). The cyclooctene carbon resonances for each isomer are connected to two sets each of "exo" and "endo" α-, β-, and γ-methylene protons. Expanded regions of the HETCOR spectrum are given as supplementary material.

In conjunction with the assignment of resonances from the HETCOR spectrum, a ^1H–^1H correlation (COSY) spectrum for both **1** and **2** was obtained. The connectivities between the coupled protons of **2** are displayed in Figure 3; the upper links are for the minor (anti) isomer and the lower links for the major (syn) isomer. The ^1H and ^{13}C NMR assignments for **1** were aided also by analysis of the ^1H–^{13}C HETCOR and ^1H–^1H COSY spectra of **1**, and these spectra are given as supplementary material.

The specific structural assignments for the major and minor isomers shown in Scheme 1 are supported by the results of an NOE experiment with complex **2**. One isomer of **2** has the backbone of the cyclooctene ring above the plane of the indenyl ring in a syn configuration, with the vinyl protons of the cyclooctene ring nearest the plane of the indenyl ring and consequently nearest to proton H_2 of the indenyl ring. The other isomer is held in an anti configuration, with the vinyl protons located well above the plane of the indenyl ring. When the vinyl resonance of the major isomer is irradiated, there is a significant NOE enhancement of the H_2 and H_3 resonances of the indenyl ring, but when the vinyl resonance of the minor isomer is irradiated, there is no observed NOE enhancement. Thus, the major isomer adopts the syn configuration, whereas the minor isomer corresponds to the anti configuration.

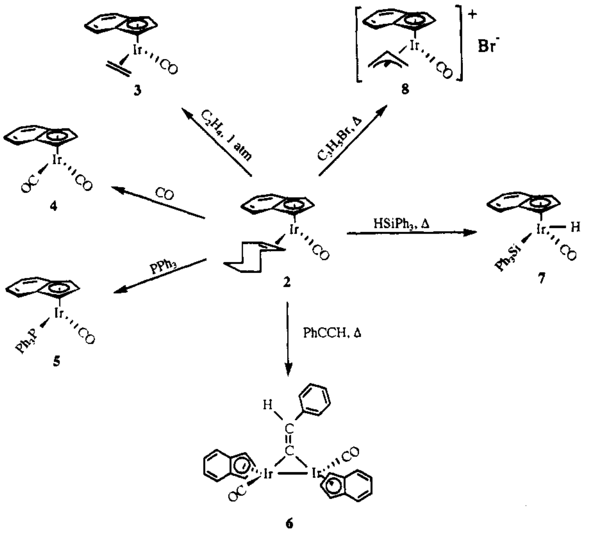
The related complex $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$ was reported by Merola and co-workers.[9b] Our ^1H and ^{13}C NMR data on this compound, which are included in Tables 1 and 2 for specific comparison with those of **1** and **2**, are in generally good agreement with those previously reported,[9b] considering the differences in field strength and solvent. The vinyl protons were previously assigned to a resonance near δ 2.0, but heteronuclear correlation clearly shows that this signal is connected with one of the methylene carbons at δ 32.4 and that the vinyl carbon resonance at δ 51.1 is connected with a proton signal at δ 1.22 (see supplementary material). The upfield shift of the vinyl protons is consistent with their being located in "inner" positions, e.g., as seen with $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_2H_4)_2$ (δ 0.64).[4a] Thus, $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$ apparently adopts an "anti,anti" configuration in solution, expectedly due to steric interactions between the cyclooctene ligands.

Two isomers also have been observed in solution for the hexafluorobenzene complexes $(\eta^5\text{-}C_5R_5)Ir(\eta^2\text{-}C_2H_4)(\eta^2\text{-}C_6F_6)$ (R = H, Me).[12] In this case, the major isomer adopts the configuration that we have defined as "anti" (determined crystallographically for R = H), which is apparently stabilized by significant F···H interactions with the inner protons on the adjacent ethylene ligand.

Energy Barrier to Cyclooctene Rotation of 1 and 2. The free energy of activation for cyclooctene rotation in **1** (in $C_6H_5NO_2$) and **2** (in C_6H_6/CD_2Cl_2) has been estimated by using the equation $k_c = (\pi/\sqrt{2})\Delta\nu_o$ and $k_c = (k_bT_c/h)\exp(-\Delta G_c^{\ddagger}/RT_c)$. Due to the unequal populations of the major and minor isomers, the resultant value is only an approximation;[13] we estimate an uncertainty of ±1 kcal/mol. The coalescence temperatures (T_c) and chemical shift differences ($\Delta\nu_o$) were as follows (at 300 MHz): T_c = 415 K, $\Delta\nu_o$ = 111 Hz for **1** and T_c = 310 K, $\Delta\nu_o$ = 183 Hz for **2**. The calculated $\Delta G^{\ddagger}$ values for cyclooctene rotation are 20.1 kcal/mol for **1** and 14.5 kcal/mol for **2**. Similar values of 20.0(2) and 13.9(2) kcal/mol were determined for the analogous cyclopentadienyl- and indenyliridium ethylene complexes, respectively, by using complete line-shape analysis.[4a]

Reactivity of 2. Under relatively mild conditions, compound **2** was found to undergo a variety of transformations at the metal center, as shown in Scheme 2. The cyclooctene ring is replaced readily at room temperature by ethylene to give $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_2H_4)(CO)$ (**3**),[4a] by carbon monoxide to give $(\eta^5\text{-}C_9H_7)Ir(CO)_2$ (**4**), or by PPh_3 to give $(\eta^5\text{-}C_9H_7)Ir(PPh_3)(CO)$ (**5**). The reaction of **2** with phenylacetylene yields the dinuclear vinylidene complex $[(\eta^5\text{-}C_9H_7)Ir(CO)]_2(\mu\text{-}C{=}CPhH)$ (**6**). Triphenylsilane and allyl bromide also add to **2** to give $(\eta^5\text{-}C_9H_7)Ir(H)(CO)(SiPh_3)$ (**7**) and $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (**8**), respectively.

Scheme 2



Under similar conditions, **1** is inert to both ligand substitution and oxidative addition reactions. No change in the carbonyl region of the infrared IR spectrum was observed when 1 and 2 equiv of PPh_3 were heated to reflux in either cyclohexane or toluene for 48 h. Similar results were obtained for the attempted oxidative addition of excess allyl bromide or triphenylsilane to **1** in either cyclohexane or toluene at reflux over a 3-day period.

The ^1H and ^{13}C NMR data recorded for derivatives **3**-**8**, with the use of two-dimensional spectroscopy when necessary, are given in Tables 3 and 4. Comparable data have been reported previously for **4**,[1d] and ^1H NMR data have been reported for **5**.[10] The characteristics of the indenyl ligands appear closely similar in all of these compounds. The carbon atoms of the complexed five-membered indenyl ring exhibit $^1J_{CH}$ of ca. 180 Hz, whereas the uncomplexed six-membered ring carbons show $^1J_{CH}$ of ca. 165 Hz. The ^{13}C NMR shift of the ring juncture carbon, C_{2a}, has been used as a criterion for the degree of distortion of the indenyl ring from η^5 to η^3.[14] The values of δ 112 and 109 observed for **2** as well as similar values for the derivatives **3**–**8** suggest that the indenyl ligand is at most only slightly distorted toward the η^3 form in these compounds.

The ^1H NMR spectrum of dinuclear complex **6** shows that the protons of each indenyl ring are inequivalent. The ^1H–^1H COSY spectrum of **6** is shown in Figure 4. The ^1H–^{13}C HETCOR and APT spectra for **6** are given as supplementary material. The resonance at δ 6.86, assigned to H_9, is correlated to a carbon resonance at δ 130.8, which is assigned to the β-carbon (C_9) of the vinylidene moiety; the corresponding vinylidene α-carbon (C_{9a}) resonance was not observed.

The proposed structure for **6** is modeled on that established by Green and co-workers[15a] for $[(\eta^5\text{-}C_9H_7)\text{-}$

---

[12] Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911.

[13] Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic: New York, 1982; Chapter 7.

[14] Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

[15] (a) Al-Obaidi, Y.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319. (b) Bruce, M.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

Table 3. ^{1}H NMR Data for Complexes 3–8[a]

	C_9H_7 signals, δ (multiplicity)				
complex	H_1	H_2	H_3	H_4	other signals, δ (multiplicity)
3	5.81(t)	5.03(d)	7.07(m)	6.98(m)	2.34(m), H_{outen}; 1.84(m), H_{inner}
4	6.18(t)	5.80(d)	7.38(m)	7.26(m)	
5	6.29(t)	5.22(br)	7.06(m)	6.86(m)	7.36(m), phenyl H
6[b]	5.64(t), H_1	6.39(d), H_2	7.29(d), H_3	6.97(m), H_4	7.65(d), H_{10}; 7.25(m), H_{11};
		4.97(d), H_2*	6.98(m), H_3*	6.89, H_4*	7.07(m), H_{12}; 6.86(s), H_9
	5.90(t), H_5	6.23(d), H_6	7.34(d), H_7	6.97(m), H_8	
		4.95(d), H_6*	6.98(m), H_7*	6.89(m), H_8*	
7[b]	5.25(t)	6.09(br)	7.46(m)	7.20(m)	7.52(m) 7.32(m), phenyl H;
		4.97(br), H_2*	7.42(m), H_3*	7.20(m), H_4*	−15.91, Ir-H
8	5.65(t)	5.69(d)	7.46(m)	7.34(m)	5.14(m), H_c; 3.92(dd), H_{syn}; 2.37(dd), H_{anti}, (J_{trans} = 9.9 Hz, J_{cis} = 6.3, J_{gem} = 0.6)

[a] Recorded at 500 MHz in $CDCl_3$ at 20 °C, except for **3** at −20 °C in CD_2Cl_2/C_6D_6. [b] Complexes **5** and **6** have no mirror plane perpendicular to the indenyl plane; thus resonances H_2 and H_2*, etc., are inequivalent.

Table 4. ^{13}C NMR Data for Complexes 3–8[a]

	C_9H_7 signals, δ					
complex	C_1	C_2	C_{2a}	C_3	C_4	other signals, δ
3	89.2(181)	72.7(179)	111.5	120.1(166)	125.2(161)	168.3, C_{CO}; 19.1(158), $C_{C_2H_4}$
4	93.2(181)	70.6(185)	114.8	119.4(161)	125.9(171)	170.5, C_{CO}
5	71.0(178)	92.6(175)	116.4	117.5(159)	123.3(159)	175.0(13), C_{CO}; 135.9(57), C_{5a}; 133.6(163) (J_{CP} = 13), C_5; 130.0(160), C_7; 127.8(159) (J_{CP} = 11), C_6
6	91.4, C_1	74.5, C_2	108.3, C_{2a}	121.5, C_3	124.5, C_4	171.9, C_{CO}; 171.0, C_{CO}; 138.2, C_{10a};
		74.6, C_2*	108.4, C_{2a}*	120.7, C_3*	126.3, C_4*	130.8, C_9; 127.8, C_{11}; 126.1, C_{11};
	90.4, C_5	74.8, C_6	114.4, C_{6a}	121.6, C_7	125.0, C_8	124.9, C_{12}
		74.0, C_6*	115.2, C_{6a}*	121.3, C_7*	126.3, C_8*	
7	95.1(180)	69.1(184)	114.4	122.4(163)	126.4(160)	168.1(8), C_{CO}; 141.3, C_{5a};
		76.0(180), C_2*	113.2, C_{2a}*	121.0(164), C_3*	126.2(159), C_4*	135.9(158), C_5; 128.4(159), C_6; 127.3(158), C_7
8	82.5	68.9	107.2	123.0	129.1	168.8, C_{CO}; 69.7, C_{CH}; 42.5, C_{CH_2}

[a] Recorded at 125 MHz in $CDCl_3$ at 20 °C, except for **3** in CD_2Cl_2/C_6D_6 at −20 °C. Values of J_{CH} in hertz are shown in parentheses.

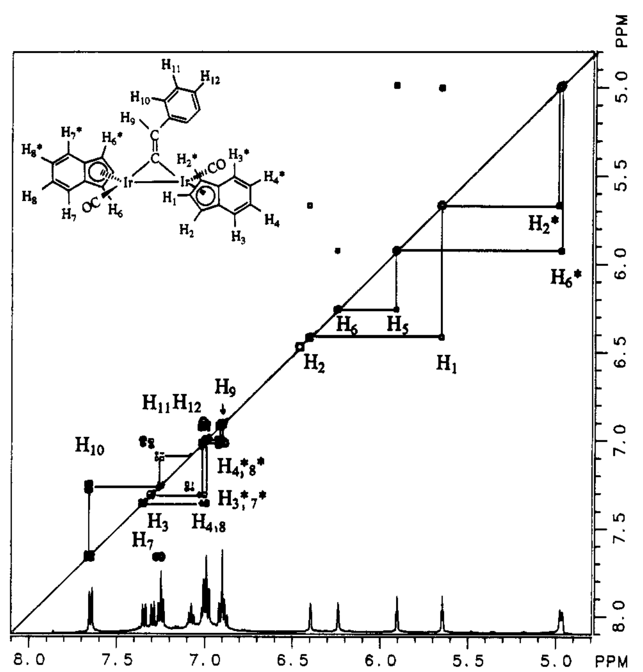


Figure 4. ^{1}H–^{1}H COSY spectrum of **6** in $CDCl_3$ at 20 °C.

$Rh(CO)]_2(\mu\text{-}C{=}CH_2)$. This complex exhibits a similar pattern of inequivalent indenyl ring ^{1}H NMR resonances. The β-carbon of the $\mu\text{-}C{=}CH_2$ ligand has been reported to resonate at δ 111.6.[15b] Werner and co-workers[16] have reported ^{1}H and ^{13}C NMR data for the heterometallic vinylidene complex $[CpRh(^{i}Pr_3P)(\mu\text{-}CO)Fe(CO)_3](\mu\text{-}C{=}CPhH)$. The ^{1}H chemical shift of the vinylidene proton at δ 7.76 (C_6D_6) is similar to what we observe for **6**. In the ^{13}C NMR spectrum the vinylidene β-carbon (C=CHPh) resonates at δ 140.

The chiral character of complex **7** is shown explicitly by the inequivalent indenyl ^{1}H NMR resonances for H_2 (δ 6.39) and H_2* (δ 4.97). The resonance assigned to Ir–H occurs at δ −15.91. Under the experimental conditions (S/N > 200) that should allow observation of any ^{29}Si satellites in the ^{1}H NMR spectrum, no ^{29}Si–H coupling was observed that was larger than the line width at the base of the hydride signal (J_{SiH} < 12 Hz). This fact strongly implies complete oxidative addition of the H–Si bond in **7**.[17] In the ^{13}C NMR spectrum of **7**, when no broad-band decoupling is applied, the carbonyl resonance at δ 168.1 shows coupling of 8.0 Hz to the hydride ligand.

The ^{1}H NMR spectrum of **8** shows the allylic resonances of the proton on the central carbon H_c at δ 5.14, the syn protons at δ 3.97, and the anti protons at δ 2.37. These positions imply the presence of only one allylic conformer, an exo allyl isomer, which has the center allylic proton H_c pointing toward the indenyl ligand. Tanke and co-workers[1c] have also observed only one set of allyl resonances for $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(PPh_3)]SbF_6$: δ 5.07 ($H_c$), 3.67 ($H_{syn}$), and 1.27 ($H_{anti}$). Wakefield and Stryker[18] observed a phosphine-catalyzed conversion of the allylic ligand from exo to endo in $[Cp^*Ir(\eta^2\text{-}C_2H_4)(\eta^3\text{-}C_3H_5)]^+$. The ^{1}H NMR spectrum in $CDCl_3$ of $[Cp^*Ir(\eta^2\text{-}C_2H_4)(\textit{exo-}\eta^3\text{-}C_3H_5)]^+$ exhibits a downfield-shifted H_c resonance at δ 4.11, whereas that for $[Cp^*Ir(\eta^2\text{-}C_2H_4)(\textit{endo-}\eta^3\text{-}C_3H_5)]^+$ exhibits an upfield H_c resonance at δ 2.98 along with an unusual downfield resonance at δ 4.06 for H_{syn}. The crystal structure of the endo complex further confirmed the endo orientation of the allyl ligand.

---

(16) Werner, H.; Alonso, F. J. G.; Otto, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 1565.

(17) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(18) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428.

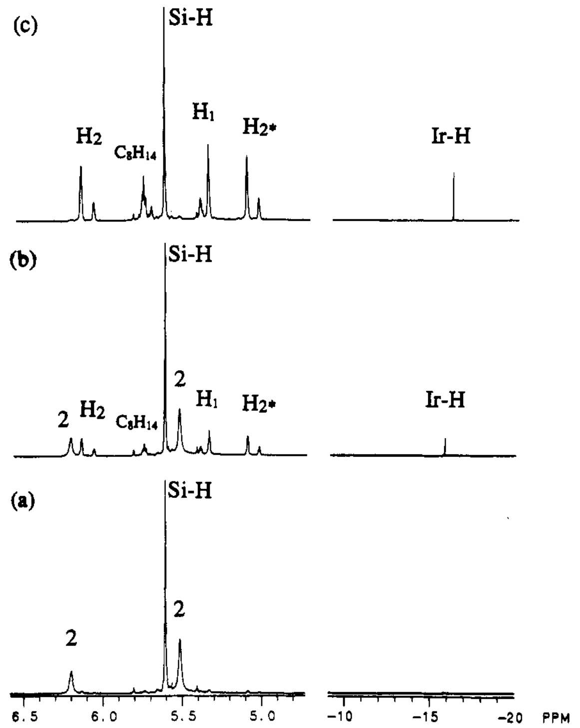


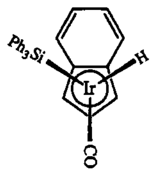
Figure 5. ^1H NMR spectra of **2** with 3 equiv of $HSiPh_3$ showing region of indenyl protons H_1, H_2, and H_2* and hydride region (a) after heating of the sample to 40 °C, (b) 15 min later, and (c) 90 min later.

Observations on the Reaction of 2 with $HSiPh_3$. During the reaction of **2** with excess triphenylsilane at 40 °C, two bands in the carbonyl region of the infrared spectrum were observed: an intense band at 2011 cm^{-1} corresponding to the known carbonyl band of **7** and a medium-intensity band at 1998 cm^{-1}. Both bands increased in intensity at the same rate as the bands at 1967 and 1974 cm^{-1} for unreacted **2** decreased. After 3 days, the medium-intensity band at 1998 cm^{-1} was not observed.

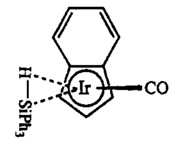
When the reaction was followed by ^1H NMR, a sample containing **2** and a slight excess of $HSiPh_3$ in $CDCl_3$ was heated to 40 °C; selected spectra are shown in Figure 5. The spectrum recorded after 15 min exhibited resonances for **7** and for free cyclooctene at δ 5.73, 2.25, and 1.65. These signals subsequently grew in intensity as those for **2** at δ 6.41 and 5.53 decreased in intensity. Alongside the five-membered ring indenyl resonances at δ 6.13 (H_2), 5.32 (H_1), and 5.08 (H_2*) of **7** was a strikingly similiar set of resonances at δ 6.05, 5.3, and 5.01 for a minor product. Only one Ir–H resonance was observed at δ −15.91, again corresponding to that of **7**. Multiplets were observed also in the aliphatic region of the spectrum at δ 2.59, 2.38, 2.06, and 1.56–1.0. The ratio of the major product (**7**) to minor product was about 3:1. After 24 h, the ^1H NMR spectrum showed resonances due only to product **7**.

We have considered three possible explanations for the set of minor indenyl ^1H NMR resonances and the carbonyl band at 1988 cm^{-1}. These possibilities are (1) the presence of two conformational isomers of **7**, (2) the presence of a species resulting from incomplete oxidative addition of the Si–H bond, i.e., (η^5-C_9H_7)Ir(η^2-$HSiPh_3$)(CO), and (3) the presence of a σ-cyclooctyl insertion product, (η^5-C_9H_7)Ir(CO)($SiPh_3$)(C_8H_{15}).

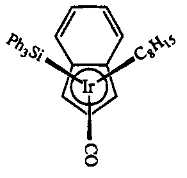
Given that **7** is chiral at the iridium center, there are three inequivalent conformers due to restricted rotation about the iridium-to-η^5-indenyl bond; one of these is shown as **I** below. It is possible that two of these might be significantly more stable than the third, for example, those with the six-membered ring adjacent to the hydride ligand. The observation of broadened indenyl NMR resonances, apparently due to slowed rotation, has been reported for some indenyl iridium phosphine ligand complexes,[1d] but we have not seen any such evidence in our work. In the case of **7**, it is difficult to imagine that the barrier to interconversion of the two conformers would be such that conversion of the initial kinetic mixture to the final thermodynamic product would require 1–3 days. Furthermore, this proposal is inconsistent with the fact that only one hydride NMR signal is seen, and it would be difficult to rationalize the marked difference in ν_{CO} for the two species.



(I)



(II)



(III)

In the second proposal there is a kinetic mixture of **7** and a species arising from incomplete oxidative addition of the Si–H bond. The latter is written as (η^5-C_9H_7)Ir(η^2-$HSiPh_3$)(CO) and is shown as **II**. The dashed lines represent a three-center, two-electron "agostic" bond. Such three-center interactions of a $HSiR_3$ group are well established for a series of $CpMn(CO)_2(\eta^2$-$HSiR_3)$ complexes.[17] The species **II** would be consistent with the low-energy carbonyl stretching frequency at 1998 cm^{-1}.

However, a separate ^1H NMR signal for the bridging hydrogen in species **II** would be expected. For $CpMn(CO)_2(\eta^2$-$HSiR_3)$ complexes, the chemical shifts of Mn–H occur in the range −10 to −11 ppm,[19ab] and for $CpRe(CO)_2(\eta^2$-$HSiR_3)$, the hydride resonance is reported at δ −9.07.[19c] The chemical shift of the hydride ligand in **7** at δ −15.91 is in the region for other cyclopentadienyliridium(III) hydride resonances.[20,21] An analogous Ir(III) silane oxidative addition product (triso)Ir(H)($SiPh_3$)(η^2-C_2H_4), where triso = $C\{Ph_2P{=}O\}_3$, has its Ir—H resonance at δ −24.78.[22] For the related CpRh(III) complexes, the Rh—H resonates at δ −13.4 in $CpRh(Me_2SO)(H)(SiEt_3)$[23a] and at δ −14.8 in $CpRh(\eta^2$-$C_2H_4)(H)(SiEt_3)$.[23b] Nevertheless, careful scrutiny of the spectrum of the reaction mixture revealed no Ir—H or agostic Ir···H···Si resonance other than the signal attributed to **7**.

The third proposal for the minor species is that the double bond of the cyclooctene ligand inserts into the Ir—H bond, yielding a σ-bonded cyclooctyl complex, (η^5-C_9H_7)Ir(C_8H_{15})(CO)($SiPh_3$). The mixture of **7** with this species would require only one hydride resonance in the ^1H NMR spectrum, and the aliphatic proton resonances between δ

---

(19) (a) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4. (b) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368. (c) Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, *59*, 1455.

(20) (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Haddelton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734.

(21) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(22) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415.

(23) (a) Duckett, S. B.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 28. (b) Duckett, S. B.; Haddelton, S. A.; Jackson, R.; Perutz, R. N.; Poliakoff, M.; Upmacis, R. K. *Organometallics* **1988**, *7*, 1526.

1.0–2.59 are in the same region observed for the cyclohexyl complex $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(H)(\sigma\text{-}C_6H_{11})$.[21] Furthermore, the carbonyl absorption should be shifted to lower frequency relative to that of 7, since the cyclooctyl group is a better donor than the hydride ligand.

Strong support for a σ-cyclooctyl species involved in the reaction of $HSiPh_3$ with 2 is afforded by the observation that during the corresponding reaction with dicarbonyl complex 4, only the hydride resonance at δ -15.91 and one set of indenyl resonances corresponding to complex 7 were recorded. Neither of the first two explanations formulated above for the minor species involves the cyclooctene ligand, and if either were feasible, the minor species should have appeared also in the reaction with 4. Since both 7 and the minor species appear to be formed at the same rate initially, the minor species is not a direct intermediate in the formation of 7. However, the minor species clearly converts more slowly into 7. If we accept that the minor species is a σ-cyclooctyl complex with the formula $(\eta^5\text{-}C_9H_7)Ir(\eta^1\text{-}C_8H_{15})(CO)(SiPh_3)$, then its immediate precursor, connected (reversibly) by cyclooctene insertion (deinsertion), must have been a cyclooctene hydride complex with the formula $(\eta^x\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})(CO)(SiPh_3)(H)$, where $x = 3$ or 1. However, this is also the formula of the species expected after an associative reaction of $HSiPh_3$ with 2 (see below), from which 7 would be formed by cyclooctene dissociation. Thus, in being able to form both 7 and the observed cyclooctyl product, this hydridoalkene species either reacts directly in these two ways or exists in two interconvertible forms that separately prefer one reaction over the other. The latter idea is attractive, given the two rotational isomers that are observed for 2. Furthermore, in the reaction of 2 with triisopropylsilane, only one ν_{CO} band and one set of ^1H NMR resonances, consistent with the formation of $(\eta^5\text{-}C_9H_7)Ir(H)(Si^iPr_3)(CO)$, were observed. The lack of an observable minor species in this case, which is qualitatively faster than the reaction with triphenylsilane, clearly shows that the balance between dissociation and insertion is affected by the nature of the silyl reactant and suggests that these processes do not emanate from the identical species.

Kinetics of the Reaction between 2 and Triphenylsilane. The rate of the reaction of triphenylsilane with 2 was studied under pseudo-first-order conditions. After addition of a cyclohexane solution of 2 to excess triphenylsilane in cyclohexane, the carbonyl region of the IR spectrum consisted of four bands. The bands for 2 (at 1976 vs and 1967 s cm^{-1}) decreased in intensity at the same rate as the new bands at 2010 and 1998 cm^{-1} grew in intensity. The observed rates of oxidative addition, k_{obs}, were determined by measuring the decrease in intensity of the carbonyl band in the infrared spectrum of 2 at 1976.7 cm^{-1}. A plot of k_{obs} versus $[HSiPh_3]$ is shown in Figure 6. The mechanism for addition of silane to 2 is thus associative, with $k_2 = (4.4 \pm 0.5) \times 10^{-3}\ M^{-1}\ s^{-1}$.

Graham[24] reported that the kinetics of the reaction of $(\eta^5\text{-}C_9H_7)Ir(CO)_2$ (4) with triphenylsilane was associative, but details have yet to be given. In comparison to 2, we have observed that 4 reacts at a faster rate; reaction is complete upon addition of a slight excess of $HSiPh_3$ to 4 at room temperature. Hart-Davis and Graham[25] also reported asociative oxidative addition reactions of several cyclopentadienyl complexes CpM(CO)L, where M = Co, Rh, or Ir, with alkyl, benzyl, and allyl halides.

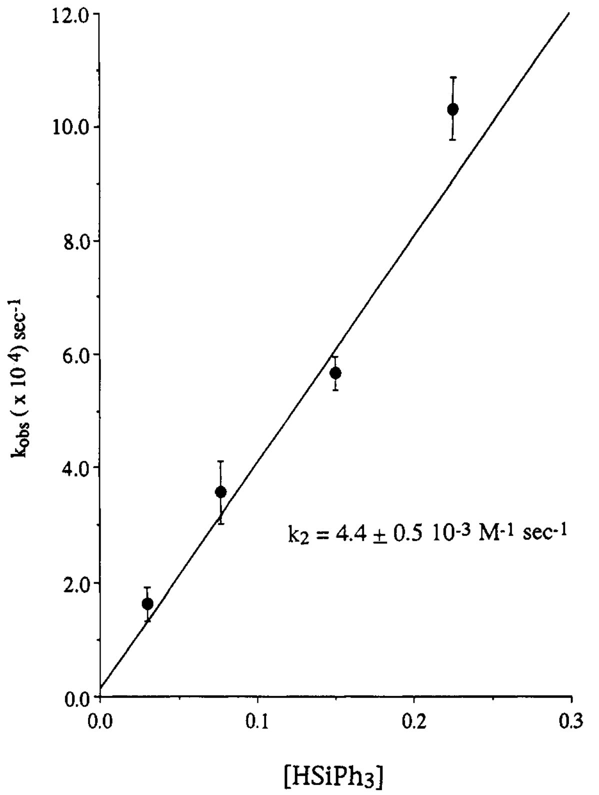
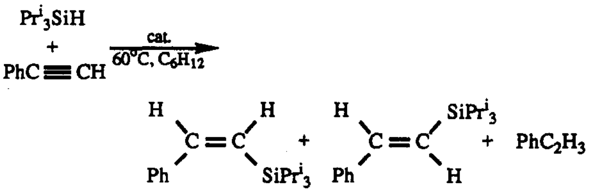
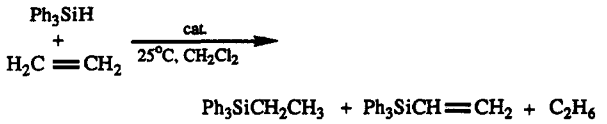


Figure 6. Plot of k_{obs} versus $[HSiPh_3]$ for 2 in cyclohexane at 40 °C.

Catalytic Hydrosilylation. The addition of silanes to alkenes and alkynes is a reaction of considerable industrial importance,[26] and this reaction is catalyzed by many transition-metal ions and complexes.[27-29] Although there are now a variety of rhodium and iridium Cp and Cp* complexes that oxidatively add silanes, the only other reported use of an indenyl complex in a hydrosilylation reaction is that of $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$.[3a] We have found again that 2 is more active than 1 in catalyzing the addition of triisopropylsilane to phenylacetylene (eq 3) and of triphenylsilane to ethylene (eq 4); the specific results of the study are summarized in Table 5.



(3)



(4)

The catalytic addition of triisopropylsilane to phenylacetylene with 2 at 60 °C over a 120-h period gave

---

(24) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81.

(25) (a) Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2658. (b) Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1653.

(26) Noels, A. F.; Hubert, A. J. In *Industrial Applications of Homogeneous Catalysis*; Mortreux, A., Petit, F., Eds.; D. Reidel: Boston, 1988; Chapter 3.1.3.

(27) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1479.

(28) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.

(29) Esteruelas, M. A.; Nürnberg, O.; Oliván, M.; Oro, L. A.; Werner, H. *Organometallics* **1993**, *12*, 3264.

Table 5. Catalytic Hydrosilylation Activity of Complexes 1 and 2

catalyst[a]	[HSi^iPr_3], M	[PhCCH], M	temp, °C	react time, h	product	turnovers (to/h)
2	2.0	2.9	60	120	$PhCH{=}CHSi^iPr_3$	240 (2.0)
					$PhCH{=}CH_2$	22 (0.3)
1	1.8	2.7	60	96	$PhCH{=}CHSi^iPr_3$	57 (0.6)
					$PhCH{=}CH_2$	4 (0.04)

catalyst[b]	[$HSiPh_3$], M	(C_2H_4), atm	temp, °C	react time, h	product	turnovers (to/h)
2	0.6	2	25	120	$Ph_3SiCH{=}CH_2$	311 (2.6)
					$Ph_3SiCH_2CH_3$	600 (5.0)

[a] With 0.04 mol % catalyst precursor, CH_2Cl_2 (5 mL). [b] Approximately 0.1 mol % catalyst precursor, cyclohexane (40 mL). Under these conditions *no* activity was observed with compound **1** as the catalyst charged.

β-(triisopropyl)styrene in a cis:trans ratio of 4:1 as well as a small amount of styrene. The preferential formation of the cis product, resulting from anti addition of the Si–H moiety, has been attributed to insertion of the alkyne into the M–Si bond followed by isomerization to the sterically less congested (*E*)-silylvinyl intermediate.[3a] We observed direct cis-to-trans isomerization of a previously isolated 4:1 cis:trans mixture of β-(triisopropyl)styrene upon heating it at 60 °C for 3 days in the presence of **2**. This suggests that the product mixture observed from the initial hydrosilylation may result from competition between isomerization and elimination steps at the metal center. Although the turnover rate for **2** (2.0 per hour) is not as fast as those for other recently reported iridium catalysts,[3a,29] **2** is a long-lived and robust catalyst; after 5 days at 60 °C, a fresh charge of reactants was consumed with activity comparable to that observed initially. Compound **1** was also found to catalyze the reaction but at a rate significantly slower than for **2**. Finally, dinuclear **6** was found to be unreactive toward HSi^iPr_3 in cyclohexane at 60 °C and completely inactive as a catalyst under these conditions.

Complex **2** was also found to catalyze the silylation and hydrosilylation of ethylene with triphenylsilane at ambient temperature; results are given in Table 5. Complex **1** did not catalyze this reaction to any observable extent, either at 25 °C or at 60 °C. In the presence of **2**, $HSiPh_3$, and ethylene (2 atm) at 25 °C, triphenylethylsilane and triphenylvinylsilane were obtained at turnover rates of 5.0 and 2.6 per hour, respectively. A ^1H NMR experiment showed that 1 equiv of ethane was formed for every equivalent of triphenylvinylsilane and that the dominant iridium species present was complex **7**. Related recent studies of this reaction have suggested insertion of ethylene into a M–Si bond, with subsequent partitioning of the resultant β-silylethyl moiety into either the ethyl- or vinylsilane product.[22,28] It is likely that such a general pathway obtains in the current case as well. Furthermore, our observation of a relatively stable species containing both silyl and cyclooctyl groups in the reaction of **2** with triphenylsilane provides a direct argument against involvement of such a silyliridium ethyl species in the catalytic reaction.

Conclusion

We have shown that the η^5-indenyl compound **2** is a much more reactive compound than the corresponding η^5-cyclopentadienyl analog **1**. Compound **2** readily undergoes ligand substitution and oxidative addition reactions and is a robust catalyst for the hydrosilylation of phenylacetylene and ethylene.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 89-15349. We thank Dr. V. Mainz of the School of Chemical Sciences Molecular Spectroscopy Laboratory for providing assistance with the NMR measurements.

Supplementary Material Available: Figures giving HETCOR and APT spectra of **1** and of $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})_2$, expanded HETCOR and COSY spectra of **1** and **2**, variable-temperature ^1H NMR spectra of **2**, ^1H NMR difference spectra of NOE experiment with **2**, HETCOR, APT, and expanded HETCOR spectra of **6**, and kinetics plots for addition of $HSiPh_3$ to **2** (13 pages). Ordering information is given on any current masthead page.

OM930528V