

The "Indenyl Effect" on Ethylene Rotation in Iridium(I) Complexes

Lawrence P. Szajek, R. Joe Lawson, and John R. Shapley*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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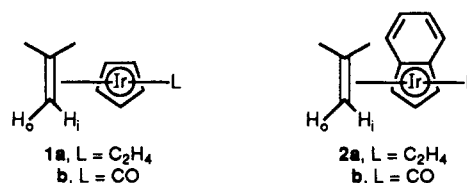
Summary: The new iridium(I) ethylene complexes ($\eta^5\text{-C}_5\text{H}_5\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\text{CO}$ (**1b**) and ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\text{CO}$ (**2b**) have been prepared. For these complexes, as well as for ($\eta^5\text{-C}_5\text{H}_5\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**1a**) and ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**2a**), the barrier to ethylene rotation about the iridium-ethylene bond axis has been determined by line-shape fitting of variable-temperature ^1H NMR spectra. The free energies of activation were found to be 5-6 kcal/mol less for the indenyl complexes than for the corresponding cyclopentadienyl complexes (ca. 14 and 20 kcal/mol, respectively).

Transition-metal indenyl complexes show enhanced reactivity toward substitution¹ and related reactions^{2,3} compared to their cyclopentadienyl analogues. This rate enhancement has generally been attributed to a facile ring slippage of the indenyl ligands from η^5 toward η^3 in an associative transition state.

An intramolecular indenyl effect has been observed for Rh(I) ethylene complexes; i.e., the energy barrier to ethylene rotation decreases dramatically upon substitution of the cyclopentadienyl group by the indenyl group. This effect was first observed by Eshtiagh-Hosseini and Nixon⁴ for ($\eta^5\text{-C}_9\text{H}_7\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$), and it was extended by McGlinchey and co-workers⁵ in studies with ($\eta^5\text{-1-MeC}_9\text{H}_6\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$) and by Marder et al.⁶ with ($\eta^5\text{-Me}_n\text{C}_9\text{H}_{7-n}\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$) ($n = 3, 4, 7$). The study of ($\eta^5\text{-1-MeC}_9\text{H}_6\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$) showed that the rotation barrier was lowered several kilocalories per mole from that measured in the classic work of Cramer⁷ on ($\eta^5\text{-C}_5\text{H}_5\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$). However, this reduced barrier was also very near that measured for indenyl ring rotation, so that any interaction between these two dynamic processes would obscure the actual magnitude of the effect.

There have been qualitative indications that ethylene rotation barriers are higher in Ir(I) complexes compared with those in the analogous Rh(I) complexes.⁸ The current work was begun some years ago with the quantitative

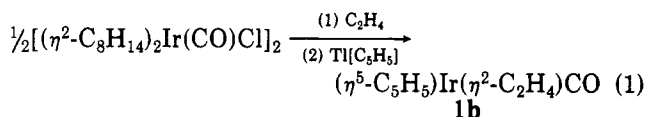
determination by line-shape analysis of the rotation barrier in ($\eta^5\text{-C}_5\text{H}_5\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**1a**)⁹ for comparison with that in ($\eta^5\text{-C}_5\text{H}_5\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$).⁷ More recently we have extended the comparison to include ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**2a**), and we now report these data together with information concerning two analogous complexes, in which one ethylene ligand is replaced by carbon monoxide (**1b**, **2b**).



Results and Discussion

Synthesis of Iridium(I) Ethylene Complexes. ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**1a**) and ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2$ (**2a**) were prepared directly from $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{IrCl}]_2$ ¹⁰ and ethylene together with thallium cyclopentadienide or potassium indenide, respectively. These complexes have also been reported in the literature.^{11,12}

($\eta^5\text{-C}_5\text{H}_5\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\text{CO}$ (**1b**) was readily prepared by the reaction of $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir}(\text{CO})\text{Cl}]_2$,¹³ where C₈H₁₄ is cyclooctene, with ethylene and thallium cyclopentadienide (eq 1). However, ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\text{CO}$ (**2b**) could not be



prepared in this way, and the cyclooctene complex ($\eta^5\text{-C}_9\text{H}_7\text{Ir}(\eta^2\text{-C}_8\text{H}_{14})\text{CO}$ (**3**) was isolated from the reaction mixture instead.¹⁴ Nevertheless, **2b** was successfully prepared by the slow substitution of cyclooctene in **3** by ethylene.

NMR Spectroscopic Data. The ^1H NMR spectra of **1a,b** at ambient temperature and **2a,b** below ambient temperature consist of two inequivalent resonances of "inner" and "outer" ethylene protons. Due to the chemical shift anisotropy of the indenyl and cyclopentadienyl rings the inner protons above the ring are shielded and resonate at approximately 0.5-2 ppm, while the outer protons near the plane of the arenyl ligands are deshielded and resonate at approximately 2.5-3.0 ppm.⁵ The chemical shift difference between inner and outer ethylene protons of **1a** and **2a** is nearly 4 times greater than the chemical shift difference observed for **1b** and **2b**, i.e. ca. 2 ppm compared to 0.5 ppm, respectively. This suggests that the anisotropy of a carbonyl ligand versus that of an ethylene ligand as

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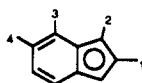
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(14) Further properties of **3** and related complexes, including fluxional behavior and reactivity, will be described separately.

Table I. ¹H NMR Data (ppm) for Iridium(I) Ethylene Complexes^a

complex	C ₅ H ₅	C ₉ H ₇ ^e				C ₂ H ₄		J(HH), Hz
		H ₁	H ₂	H ₃	H ₄	H _{out}	H _{in}	
1a ^b	5.14 s					2.65 m	0.53 m	J _{cis} = 9.2 J _{trans} = 11.8 J _{gem} = -1.2
1b ^b	5.39 s					2.38 m	1.82 m	J _{cis} = 8.3 J _{trans} = 11.0 J _{gem} = -1.5
2a ^c		5.75 d	4.79 d	7.14 m	6.97 m	2.80 m	0.64 m	J _{cis} = 9.2 J _{trans} = 11.8 J _{gem} = -1.2
2b ^d		5.81 t	5.03 t	7.07 m	6.98 m	2.84 m	2.34 m	J _{cis} = 8.9 J _{trans} = 12.3 J _{gem} = -1.4

^aSpectra were recorded at 200, 300, or 360 MHz, and chemical shifts are referenced to residual protiated solvents. ^bIn C₆D₅NO₂ at 273 K. ^cIn C₆D₆/CD₂Cl₂ at 253 K. J(H₁H₂) = 2.5 Hz. ^dIn C₆D₆/CD₂Cl₂ at 233 K. J(H₁H₂) = 2.7 Hz. ^eThe following numbering scheme was used for complexes 2a,b:

Table II. ¹³C NMR Data (ppm) for Iridium(I) Ethylene Complexes^a

complex	C ₅ H ₅	C ₉ H ₇					C ₂ H ₄	CO
		C ₁	C ₂	C _{2a}	C ₃	C ₄		
1a ^b	83.4 (178)						17.9 (156)	
1b ^b	84.9 (177)						11.5 (156)	169.9
2a ^c		84.1 (179)	74.5 (177)	109.2	125.4 (152)	121.3 (157)	24.6 (156)	
2b ^c		89.2 (181)	72.7 (179)	111.5	120.1 (166)	125.2 (161)	19.1 (158)	168.3

^aSpectra were recorded at 125 MHz, and chemical shifts are referenced to residual protiated solvents. Coupling constants (J(CH) in Hz) are given in parentheses. ^bIn C₆D₅NO₂ at 273 K. ^cIn C₆D₆/CD₂Cl₂ at 233 K.

a neighboring ligand is markedly different, probably due to the perpendicular orientation of the π-systems. The ¹H and ¹³C NMR data obtained for 1a,b and 2a,b are summarized in Tables I and II, respectively.

The slippage of the indenyl ring from planar η⁵ toward allylic η³ bonding is represented in the solid state by the slip distortion parameter Δ,^{15,16} and this slip distortion is thought to persist in solution.^{16,17} Baker and Tulip have shown that changes in the quaternary carbon chemical shifts of the indenyl ligand compared to those of indenylsodium, i.e. Δδ, agree well with the observed solid-state slip distortion parameter Δ for numerous d⁶ and d⁸ metal complexes.¹⁶ The reported crystal structures of (η⁵-C₉H₇)Rh(η²-C₂H₄)₂^{5,18} and (η⁵-C₉H₇)Rh(CO)₂⁶ display slip distortion parameters, Δ, of 0.16 and 0.20 Å, respectively. These complexes also have calculated values of Δδ between -10 and -20 ppm, placing them in the region for slightly distorted η⁵-indenyl systems.¹⁶ The closely related Ir(I) complex (η⁵-C₉H₇)Ir(η⁴-C₈H₁₂) also has a Δδ value between -10 and -20 ppm,¹⁶ and Merola et al.^{3c} have reported that the indenyl ligand is nearly η⁵ by single-crystal X-ray analysis.¹⁹ The observed quaternary carbon chemical shifts of δ 109 and 111 (Δδ values of -20 and -18 ppm, respectively) for 2a and 2b suggest that these iridium

Table III. Activation Parameters for Iridium(I) Ethylene Complexes

complex	T _c , K	ΔG _c [*] , kcal/mol ^a	ΔH [*] , kcal/mol ^b	ΔS [*] , eu ^b
1a	423 ± 1	19.3 ± 0.2	19.4 ± 1.0	-1.4 ± 3.0
1b	417 ± 1	20.0 ± 0.2	19.8 ± 1.0	-1.0 ± 2.0
2a	319 ± 1	14.1 ± 0.2	12.6 ± 0.2	-4.7 ± 0.6
2b	296 ± 1	13.9 ± 0.2	12.4 ± 0.2	-5.0 ± 0.5

^aCalculated from T_c and Δν₀ with the equations K_c = (2π/2^{1/2})-Δν₀ and k_c = (k_bt_c/h) exp[-ΔG_c^{*}/RT_c]. Errors shown are propagated from the estimated errors in T_c. ^bCalculated from the slopes and intercepts of the Eyring plots shown in Figure 2. Error ranges listed correspond to 1 standard deviation.

complexes are also only slightly distorted toward the η³ form in solution.

Energy Barriers to Ethylene Rotation. As a first approach, the free energies of activation for ethylene rotation at coalescence (ΔG_c^{*}) for 1a,b and 2a,b were calculated by using the temperature of coalescence (T_c) of the ethylene resonances and the chemical shift difference of these resonances projected from the slow-exchange limit (Δν₀). The resulting values, listed in Table III, show that the free energy barriers for the indenyl complexes 2a,b are 5-6 kcal/mol lower than for the corresponding cyclopentadienyl complexes 1a,b, i.e., ca. 14 and 20 kcal/mol, respectively. The substitution of CO for one ethylene ligand has very little effect on the free energy of activation for ethylene rotation in both the cyclopentadienyl and indenyl complexes, which indicates that the ancillary ligand and electronic effects of CO versus those of C₂H₄ are rather similar.

Because the coalescence temperatures are quite different for complexes 1a,b compared to those of 2a,b, we have

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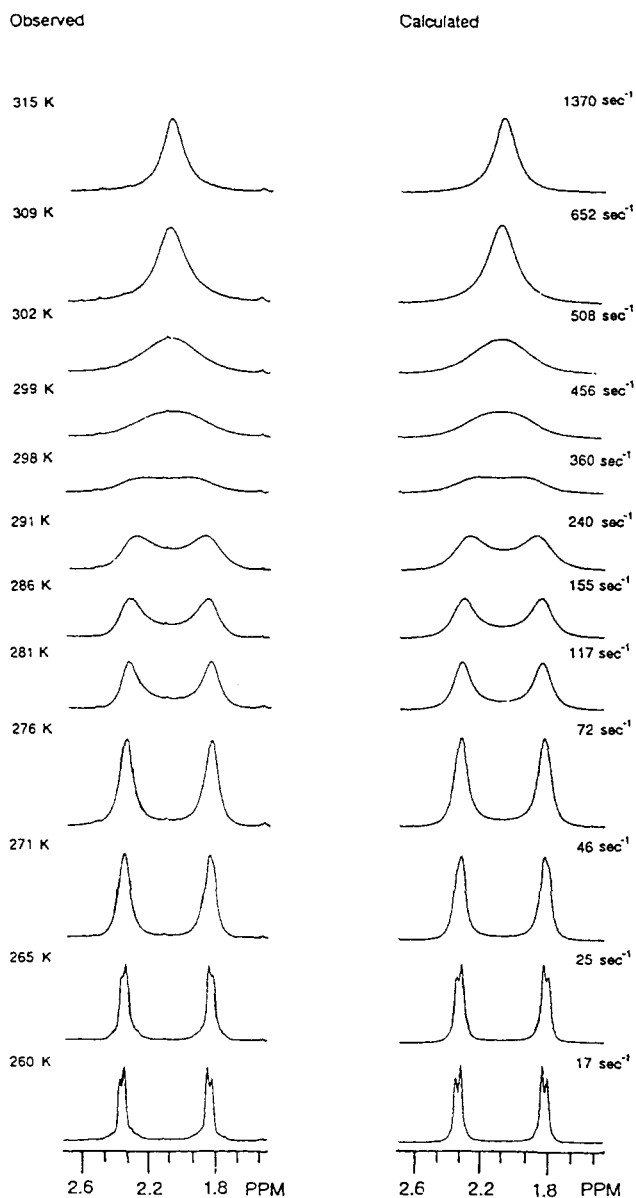


Figure 1. Observed and calculated ethylene resonances for **2b** from the variable-temperature ^1H NMR study (in $\text{C}_6\text{H}_6/\text{CD}_2\text{Cl}_2$ at 360 MHz).

utilized line-shape analysis as an alternative procedure. Rate constants at different temperatures were calculated by simulation of the exchange-broadened ethylene resonances, with use of the energy density matrix method of DNMR3H. As an example, the observed and calculated resonances for **2b** as a function of temperature are shown in Figure 1. Eyring plots for the kinetic data are shown in Figure 2, and a linear least-squares analysis of these plots provided values of ΔH^\ddagger and ΔS^\ddagger for all the ethylene complexes; these values are also listed in Table III. There is generally good agreement between the two approaches, especially for the cyclopentadienyl complexes **1a,b**, where the values of ΔS^\ddagger are not statistically different from zero. The moderately negative values of ΔS^\ddagger determined for the indenyl complexes **2a,b** appear to be outside the limits of experimental error, although the difficulties involved in determining accurate activation parameters by line-shape analysis are well-known.²⁰ These nonzero values of ΔS^\ddagger

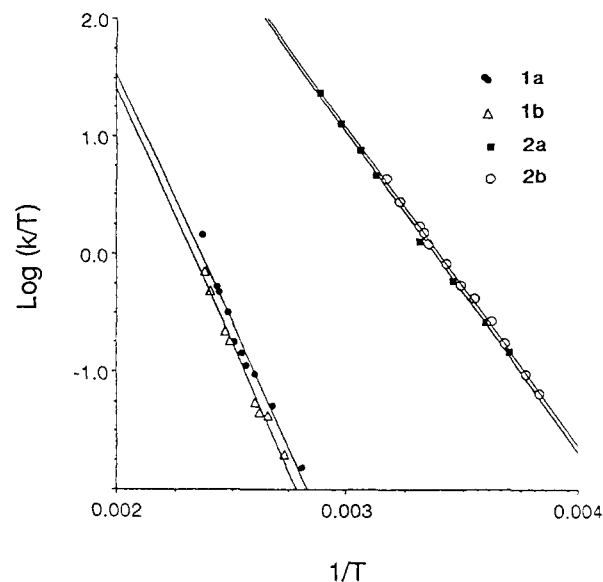


Figure 2. Eyring plots for ethylene rotation in **1a,b** and **2a,b**.

for the indenyl complexes may be related to the extra rearrangement involved in "slippage" (vide infra), or they may be due to selective solvent interactions with the aromatic C_6 ring moiety. Nonselective solvent viscosity effects contributing to dynamical activation have been observed by high-pressure NMR studies of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$.²¹

The existence of a substantial barrier to rotation about the metal-ethylene bond axis has been linked convincingly to a large differential in π bonding ($d_\pi\text{-}\pi^*$) between the ground-state conformer (0° rotation angle) and the transition-state configuration (90° rotation angle).^{5,22} In the particular case of d^8 , 18-electron complexes such as $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$, the large differential derives from one filled $d\pi$ orbital that is raised in energy by repulsion with lower lying cyclopentadienyl π orbitals and therefore becomes energetically more favorable for overlap with the empty π^* ethylene orbital. This favorable interaction is lost upon 90° rotation, since then only a much lower lying $d\pi$ -type orbital is available. In seeking to explain changes in the magnitude of the rotation barrier in such complexes, in particular in comparing cyclopentadienyl with indenyl complexes, one may look for an effect on the energy of the π interaction in the ground state or an effect on the energy of the transition state.

The difference between analogous rhodium and iridium complexes is clearly attributable to a ground-state effect. The ethylene rotation barriers for $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$ ⁷ and $(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$ ⁴ are reported as 15.7 and 10.5 kcal/mol, respectively, compared with 19.3 and 14.1 kcal/mol for the analogous iridium complexes **1a** and **2a**. Since the atomic radii of rhodium and iridium are very similar,²³ there should be insignificant steric differences in these complexes. However, the reported carbonyl stretching frequencies for $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})_2$ ²⁴ at 2037 and 1957 cm^{-1} are considerably lower than those for $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ ²⁵ at 2051 and 1987 cm^{-1} , indicating stronger $d\pi\text{-}\pi^*$ back-bonding in the iridium complex. A similar comparison can be made between $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)$ -

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CO²⁶ (ν_{CO} at 1988 cm⁻¹) and **1b** (ν_{CO} at 1980 cm⁻¹). Thus, the difference in ethylene rotation barriers in these complexes is due to stronger metal-ethylene π bonding in the iridium complexes, to the extent of about 4 kcal/mol.

In contrast, there is no evidence for a ground-state effect in comparing complexes of the cyclopentadienyl and indenyl ligands. In complexes **1b** and **2b**, the presence of the carbonyl ligand provides a sensitive probe of relative electron density at the metal center, in terms of its effects on either the carbonyl stretching frequency or the ¹³C NMR chemical shift.²⁷ The values of both parameters, however, are very nearly the same for both complexes (**1b**, ν_{CO} 1980 cm⁻¹, δ_{CO} 169.9; **2b**, ν_{CO} 1978 cm⁻¹, δ_{CO} 168.3). Thus, the abilities of the coordinated arenyls to act as electron donors are essentially the same, and the observed different barriers to ethylene rotation cannot be attributed to a difference in metal-ethylene π bonding.

Our results, therefore, are consistent with the analysis of Albright et al.⁵ of a transition-state effect in the indenyl complexes. According to their calculations, slippage of the metal center from η^5 toward η^3 bonding reduces a four-electron repulsion between metal-fragment and ring orbitals and therefore allows stabilization of the transition-state configuration. Slippage is minimal in the ground state, since lowering the energy of the high-energy $d\pi$ orbital would decrease the strength of the metal-ethylene π bond. The magnitude of this intramolecular indenyl effect on ethylene rotation is approximately the same for both rhodium and iridium complexes, namely 5–6 kcal/mol. Note that such an effect depends upon the existence of strongly differential metal-ethylene π bonding in the first place; in several d^6 complexes replacement of cyclopentadienyl by indenyl leads to no significant change in the barrier to ethylene rotation.^{28–30}

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of nitrogen with use of standard Schlenk techniques. $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{IrCl}]_2$,¹⁰ $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir}(\text{CO})\text{Cl}]_2$,¹³ and thallium cyclopentadienide³¹ were prepared by literature methods. Cyclooctene (Aldrich) and indene (Aldrich) were distilled under nitrogen before use. CP grade ethylene was purchased from MG Industries. Solvents for preparative use were dried with use of standard methods and distilled. $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (Engelhard Industries) and potassium hydride (Aldrich) in mineral oil (35% w/w) were used without further purification. Benzene-*d*₆ was distilled from sodium-potassium amalgam, and chloroform-*d* was distilled from phosphorus pentoxide. Each NMR solvent was passed through a short column of activated basic alumina immediately before use.

¹H NMR spectra were recorded on Varian XL-200, General Electric QE-300, or Nicolet NT-360 NMR FT spectrometers. ¹³C NMR spectra were recorded at 125 MHz on a General Electric GN-500 NMR FT spectrometer. Temperature calibrations were performed with a capillary of ethylene glycol or methanol as an internal reference.³² Nicolet's ITRCAL program was used to calculate chemical shifts and coupling constants for ethylene proton resonances at the slow-exchange limit. IR spectra were recorded on a Perkin-Elmer 1750 FT spectrometer. Microanalyses were performed by the staff of the Microanalytical Laboratory

of the School of Chemical Sciences.

($\eta^5\text{-C}_5\text{H}_5$)Ir($\eta^2\text{-C}_2\text{H}_4$)₂ (1a**).** A pale orange solution of $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{IrCl}]_2$ (400 mg, 0.45 mmol) in diethyl ether (150 mL) was cooled to 0 °C, and a stream of ethylene was bubbled through for 1 h. The resulting colorless solution was added thallium cyclopentadienide (243 mg, 0.90 mmol), which caused an immediate color change to dark orange. The solution was stirred for an additional 4 h under an ethylene atmosphere. Decolorizing carbon was added, and the solution was filtered via a filter cannula. The dark red filtrate was reduced in volume to ca. 5 mL and eluted down a column (20 by 2 cm) of activated neutral alumina with diethyl ether (100 mL). The pale red band was collected, and the solvent was removed on a rotary evaporator to give a gray solid. This residue sublimed at 65 °C (10⁻¹ Torr) onto a water-cooled cold finger to give a white crystalline solid: yield 190 mg (0.44 mmol, 68%); mp (sealed tube) 93 °C. Anal. Calcd for $\text{IrC}_9\text{H}_{13}$: C, 34.49; H, 4.18. Found: C, 34.68; H, 4.23.

($\eta^5\text{-C}_9\text{H}_7$)Ir($\eta^2\text{-C}_2\text{H}_4$)₂ (2a**).** A pale orange solution of $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{IrCl}]_2$ (400 mg, 0.45 mmol) in diethyl ether (150 mL) was cooled to 0 °C, and a stream of ethylene was bubbled through for 1 h. To the resulting colorless solution was added 2 equiv of a potassium indenide solution (5.3 mL, 0.17 mmol/mL), which had been prepared separately by the addition of 1 equiv of potassium hydride to indene (1.0 gm, 8.6 mmol) in THF (50 mL). The resulting purple solution was stirred for an additional 4 h under an ethylene atmosphere. Decolorizing carbon was added, and the brown solution was filtered via filter cannula. The purple filtrate was reduced in volume to ca. 10 mL and eluted down a column (20 by 2 cm) of activated neutral alumina with diethyl ether (150 mL). The yellow band was collected, and the solvent was reduced to ca. 3 mL under reduced pressure. This dark yellow solution was held at -20 °C overnight, and the pale yellow crystals that formed were isolated by filtration, washed with diethyl ether (ca. 2 mL), and dried in vacuo: yield 210 mg (0.58 mmol, 64%); mp (sealed tube) 138 °C. Anal. Calcd for $\text{IrC}_{13}\text{H}_{15}$: C, 42.96; H, 4.16. Found: C, 43.34; H, 4.33.

($\eta^5\text{-C}_5\text{H}_5$)Ir($\eta^2\text{-C}_2\text{H}_4$)CO (1b**).** A pale yellow solution of $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir}(\text{CO})\text{Cl}]_2$ (200 mg, 0.21 mmol) in diethyl ether (100 mL) was cooled to 0 °C, and a stream of ethylene was bubbled through for 1 h. To the resulting colorless solution was added thallium cyclopentadienide (113 mg, 0.42 mmol), which caused an immediate change in color to dark red. The solution was stirred for an additional 4 h under an ethylene atmosphere. Decolorizing carbon was added, and the solution was filtered via filter cannula. The dark green filtrate was reduced in volume to ca. 5 mL and eluted down a column (20 by 2 cm) of activated neutral alumina with diethyl ether (100 mL). The pale red band was collected, and the solvent was removed on a rotary evaporator to give a gray solid. The residue sublimed at ambient temperature (10⁻¹ Torr) onto a water-cooled cold finger to give a white crystalline solid: yield 97 mg (0.31 mmol, 74%); mp (sealed tube) 35 °C; IR (ν_{CO} , cyclohexane) 1980 cm⁻¹. Anal. Calcd for $\text{IrC}_8\text{H}_9\text{O}$: C, 30.57; H, 2.89. Found: C, 30.81; H, 2.95.

($\eta^5\text{-C}_9\text{H}_7$)Ir($\eta^2\text{-C}_8\text{H}_{14}$)CO (3**).** To a yellow solution of $[(\eta^2\text{-C}_8\text{H}_{14})_2\text{Ir}(\text{CO})\text{Cl}]_2$ (400 mg, 0.42 mmol) in diethyl ether (150 mL) at 0 °C was added 2 equiv of potassium indenide in THF (5.3 mL, 0.17 mmol/mL), and the resulting purple solution was stirred for 6 h. Decolorizing carbon was added, and the brown solution was filtered via a filter cannula. The green filtrate was reduced in volume to ca. 10 mL and eluted down a column (20 by 2 cm) of activated neutral alumina with diethyl ether (150 mL). The bright yellow band was collected, and the solvent was reduced in volume to ca. 3 mL under reduced pressure. This dark yellow solution was held at -20 °C overnight, and the pale yellow crystals that formed were isolated by filtration, washed with diethyl ether (ca. 2 mL), and dried in vacuo: yield 276 mg (0.62 mmol, 74%); mp (sealed tube) 126 °C; IR (ν_{CO} , C_6H_{12}) 1975 m, 1967 s cm⁻¹. Anal. Calcd for $\text{IrC}_{18}\text{H}_{21}\text{O}$: C, 48.52; H, 4.75. Found: C, 48.63; H, 4.78.

($\eta^5\text{-C}_9\text{H}_7$)Ir($\eta^2\text{-C}_2\text{H}_4$)CO (2b**).** A pale yellow solution of $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\eta^2\text{-C}_8\text{H}_{14})\text{CO}$ (250 mg, 0.56 mmol) in diethyl ether (40 mL) was stirred under 2 atm of ethylene in a pressure bottle at ambient temperature in the dark for 48 h. The solvent was removed under reduced pressure to give a yellow oil. The oil was dissolved in diethyl ether (ca. 10 mL) and the solution eluted down a column (20 by 2 cm) of activated neutral alumina with diethyl ether (100 mL). The yellow band was collected, and the solvent

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was reduced in volume to ca. 4 mL. The solution was held at -20°C overnight, and the pale yellow crystals that formed were isolated by filtration, washed with diethyl ether (ca 2 mL), and dried in vacuo: yield 113 mg (0.31 mmol, 55%); mp (sealed tube) 114°C ; IR (ν_{CO} , cyclohexane) 1978 cm^{-1} . Anal. Calcd for $\text{IrC}_{12}\text{H}_{11}\text{O}$: C, 39.66; H, 3.19. Found: C, 39.65; H, 3.19.

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Supplementary Material Available: ^1H NMR spectra of **1a** and **1b** (Figures 3 and 4), a comparison of observed and calculated ethylene regions of the ^1H NMR spectra of **1b** at the slow-exchange limit (Figure 5), and observed and calculated ethylene resonances for **1a,b** and **2a** from variable-temperature ^1H NMR studies (Figures 6-8) (6 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of a Carbon Suboxide Complex of Nickel, $(\text{PPh}_3)_2\text{Ni}(\text{C},\text{C}':\eta^2\text{-C}_3\text{O}_2)$

Adam K. List, Milton R. Smith III, and Gregory L. Hillhouse*

Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago,
Chicago, Illinois 60637

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Summary: Carbon suboxide reacts with $(\text{PPh}_3)_2\text{Ni}(\text{C}_8\text{H}_{12})$ in cold Et_2O to afford $(\text{PPh}_3)_2\text{Ni}(\text{C},\text{C}':\eta^2\text{-C}_3\text{O}_2)$ (**1**) as a yellow-green precipitate in 85% yield. Although **1** decomposes to nickel carbonyl products on dissolution in hydrocarbon solvents, it has been characterized by solid-state IR ($\nu(\text{CO}) = 1773$, $\nu(\text{CCO}) = 2086\text{ cm}^{-1}$) and multinuclear (^{13}C , ^{31}P) CP-MAS solid-state NMR spectroscopic techniques. The spectroscopic data for **1** and the isotopomers made from $\text{O}=\text{C}=\text{C}=\text{O}$ and $\text{O}=\text{C}=\text{C}=\text{O}$ show that the carbon suboxide ligand is bound to nickel in an η^2 -olefin-like fashion through two carbon atoms.

During the course of our studies of the organometallic reaction chemistry of carbon suboxide ($\text{O}=\text{C}=\text{C}=\text{O}$), we have reported on the reactivity of C_3O_2 as a source of ligated "C" and "C₂O" fragments^{1,2} and on 1,2-insertion reactions of C_3O_2 with transition-metal hydrides that yield formylketene ligands.³ We also have an interest in exploring the simple coordination chemistry of the C_3O_2 molecule. However, as we and others⁴ have observed, coordinatively unsaturated organometallic complexes normally react with C_3O_2 to extrude carbon monoxide to give the corresponding metal carbonyl derivatives, and this has generally frustrated attempts to prepare stable C_3O_2 complexes. Paiaro and co-workers have reported that $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ reacts with C_3O_2 to yield $(\text{PPh}_3)_2\text{Pt}(\text{C}_3\text{O}_2)$ ^{5,6} and $[(\text{PPh}_3)_2\text{Pt}]_2(\text{C}_3\text{O}_2)$ ⁶ as solid precipitates, the characterizations of which relied primarily on solid-state IR spectroscopy and elemental analyses because of the propensity for these complexes to rapidly decompose in solution via CO extrusion.

We report here that $(\text{PPh}_3)_2\text{Ni}(\text{COD})$ (COD = 1,4-cyclooctadiene), prepared in situ by the addition of 2 equiv of PPh_3 to an Et_2O solution of $\text{Ni}(\text{COD})_2$, reacts at -25°C with a stoichiometric amount of C_3O_2 to afford

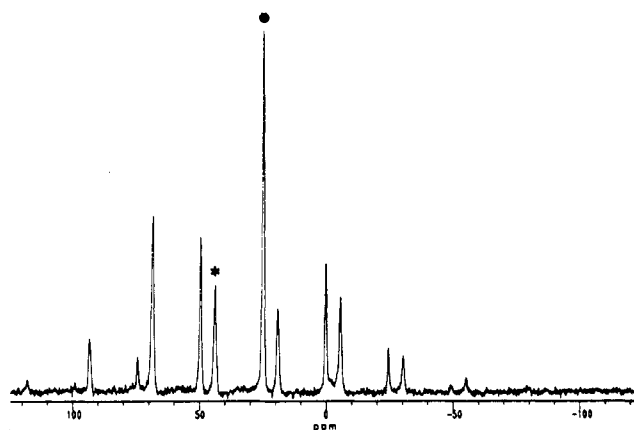


Figure 1. Solid-state CP-MAS $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**. The isotropic chemical shift positions are labeled with asterisks. Integrated intensities include the central resonances and their sidebands.

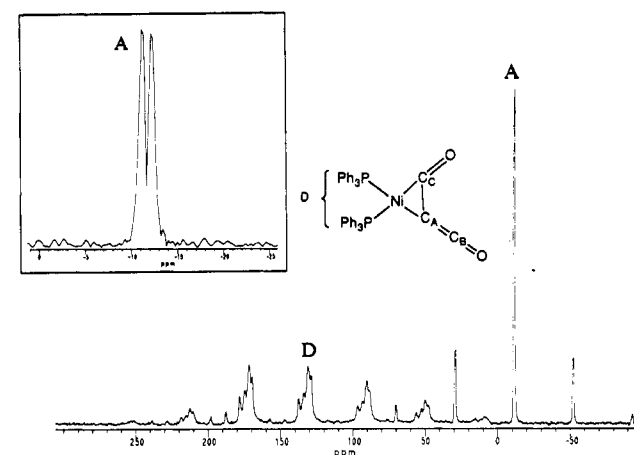


Figure 2. Solid-state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $1\text{-}^{13}\text{C}_1$ (20% isotopically enriched). The isotropic chemical shift positions are labeled with capital letters. The inset shows the resolution-enhanced resonance.

$(\text{PPh}_3)_2\text{Ni}(\text{C},\text{C}':\eta^2\text{-C}_3\text{O}_2)$ (**1**) as an analytically pure, yellow-green precipitate in 85% yield (eq 1). This new coordination complex of carbon suboxide exhibits strong infrared absorptions at 2086 and 1773 cm^{-1} (Fluorolube mull) attributable to $\nu(\text{CCO})$ and $\nu(\text{CO})$, respectively.⁷

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