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(Pentamethylcyclopentadienyl)nitrosyl(ethylene)iridium Tetrafluoroborate, $[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)][BF_4]$: Synthesis, Characterization, and Some Reactions. X-ray Crystal Structures of the Title Compound and Its Derivatives $(\eta^5\text{-}C_5Me_5)Ir(NO)(CH_2CH_2OEt)$ and $(\eta^5\text{-}C_5Me_5)_2Ir_2X_2(\mu\text{-}X)(\mu\text{-}NO)$ (X = Br, I)

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$[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)][BF_4]$ (1) has been synthesized from the reaction of $(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2$ with $[NO][BF_4]$ in acetone at −10 °C. Compound 1 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 7.454(1)$ Å, $b = 24.381(3)$ Å, $c = 8.536(1)$ Å, $\beta = 93.85(1)°$, $V = 1547.8$ Å^3, and the structure was refined to $R_F = 0.034$ for 1922 data ($I_o \geq 2.0\sigma(I_o)$) and 161 variables. The Ir–NO group is "linear", with N–O = 1.15(1) Å, Ir–N = 1.762(9) Å, and Ir–N–O = 175.8(9)°; the IR spectrum in ethanol exhibits ν(NO) = 1821 cm^{-1}, confirmed by ^{15}N enrichment [$\nu(^{15}NO)$ = 1786 cm^{-1}]. The ethylene ligand is symmetrically bound to iridium with bond lengths Ir–C(1) = 2.19(1) Å, Ir–C(2) = 2.17(1) Å, and C(1)–C(2) = 1.37(2) Å and is oriented with the C(1)–C(2) axis approximately perpendicular to the plane defined by N and the centers of mass of the $\eta^5\text{-}C_5Me_5$ and $\eta^2\text{-}C_2H_4$ ligands, respectively. The barrier to ethylene rotation ($\Delta G^{\ddagger}_{353} = 68.7 \pm 0.2$ kJ mol^{-1}) was determined from variable-temperature ^{1}H NMR data at the coalescence temperature (T_c = 353 K). Products of reaction of 1 with KI, KBr, KCl, NaOEt, and $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ are described. Reaction with KI in ethanol at room temperature gives $(\eta^5\text{-}C_5Me_5)Ir(NO)I$ and at 60 °C gives the binuclear compound $(\eta^5\text{-}C_5Me_5)_2Ir_2I_2(\mu\text{-}I)(\mu\text{-}NO)$ (2). $(\eta^5\text{-}C_5Me_5)Ir(NO)I$ has ν(NO) = 1761 cm^{-1} [$\nu(^{15}NO)$ = 1717 cm^{-1}] in $CDCl_3$ indicating a terminal "linear" nitrosyl group. Compound 2 crystallizes from toluene as 2·toluene in the monoclinic space group $P2_1/c$ with $Z = 4$, $a = 12.7738(11)$ Å, $b = 13.5804(13)$ Å, $c = 18.6110(23)$ Å, $\beta = 100.40(1)°$ and $V = 3175.5$ Å^3. The structure was refined to $R_F = 0.043$ for 3045 data ($I_o \geq 2.5\sigma(I_o)$) and 134 variables. Complex 2 has mutually trans $\eta^5\text{-}C_5Me_5$ groups, trans terminal iodide ligands, and symmetrically bridging nitrosyl and iodide with Ir(1)–N = 2.029(12) Å, Ir(2)–N = 1.974(12) Å, and N–O = 1.24(2) Å. The reaction of 1 with KBr in ethanol at room temperature produces $(\eta^5\text{-}C_5Me_5)Ir(NO)Br$ in solution but this converts on attempted isolation to other products which include $(\eta^5\text{-}C_5Me_5)Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (3). Compound 3 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$, $a = 8.6364(8)$ Å, $b = 9.3766(6)$ Å, $c = 15.501(3)$ Å, $\beta = 101.753(11)°$, $V = 1228.9$ Å^3, and the structure was refined to $R_F = 0.034$ for 1120 data ($I_o \geq 2.5\sigma(I_o)$) and 99 variables. The structure of 3 is essentially similar to that of 2, but is disordered about a crystallographic inversion center. In contrast to these ethylene displacement reactions, NaOEt reacts with 1 to produce the ethoxyethyl derivative $(\eta^5\text{-}C_5Me_5)Ir(NO)(CH_2CH_2OEt)$ (4), which crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 7.291(2)$ Å, $b = 15.274(2)$ Å, $c = 14.362(2)$ Å, $\beta = 96.90(2)°$ and $V = 1587.8$ Å^3. The structure was refined to $R_F = 0.027$ for 1960 data ($I_o \geq 2.5\sigma(I_o)$) and 128 variables. The reaction of 1 with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ in refluxing ethanol yielded $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}CO)(\mu\text{-}NO)][BF_4]$, identified on the basis of analytical and spectroscopic data.

Introduction

The half-sandwich iridium compounds $Cp^*Ir(CO)_2$[1] and $Cp^*Ir(C_2H_4)_2$[2] ($Cp^* = \eta^5\text{-}C_5Me_5$) were first synthesized over 20 years ago. Together with the C_5H_5 counterparts these are fundamental examples of this class of compounds.[3] Therefore, despite the considerable interest in nitrosyl compounds[4] and in particular organometallic nitrosyl compounds,[5] it is perhaps surprising that no nitrosyl derivatives of these compounds had been reported prior to this work.[6] We thus set out to synthesize the cationic complexes $[Cp^*Ir(NO)(CO)]^+$ or [Cp*Ir(NO)-

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[1] Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

[2] Moseley, K.; Kang, J. W.; Maitlis, P. M. J. Chem. Soc. (A) **1970**, 2875.

[3] For leading reviews see: (a) Leigh, G. J.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone F. G. A., Abel, E. W., Eds.; Pergamon Press: Elmsford, NY, 1982; Vol. 5, Chapter 36, pp 603–611. (b) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1. (c) Werner, H. *Angew. Chem. Int. Ed. Engl.* **1983**, 22, 927. (d) Dickson, R. S. *Organometallic Chemistry of Rhodium and Iridium*; Academic Press: New York, 1983.

[4] For recent general reviews of nitrosyl compounds see: (a) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992. (b) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293.

[5] Richter-Addo, G. B.; Legzdins, P. *Chem. Rev.* **1988**, *88*, 991.

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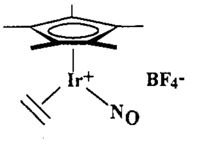
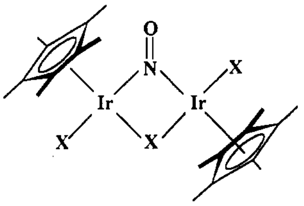
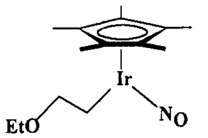
$(C_2H_4)]^+$, in the expectation of using these in order to explore the chemistry of half-sandwich iridium nitrosyl compounds. Here, we describe the synthesis and characterization of the ethylene (nitrosyl) compound $[Cp^*Ir(NO)(C_2H_4)][BF_4]$ (1) and products from some of its reactions.



1



2 (X = I), 3 (X = Br)



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Experimental Section

General Procedures. All solvents were dried and purified by standard methods and were freshly distilled under nitrogen immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double manifold providing vacuum and nitrogen.

Infrared spectra were measured for solutions in CaF_2 cells by using a Bomem Michelson 120 FTIR instrument. Some of the routine ^1H NMR spectra were recorded at 100 MHz by using a Bruker SY-100 Fourier transform spectrometer. Dynamic proton NMR and ^{13}C NMR spectra were obtained by Mrs. M. M. Tracey of the NMR service of Simon Fraser University on a Bruker AMX-400 Fourier transform instrument at operating frequencies of 400.1 and 100.6 MHz for ^1H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm, downfield positive, relative to tetramethylsilane (TMS). The temperatures of the samples used in the dynamic NMR studies were obtained from the temperature controller of the AMX-400 spectrometer, the thermocouple of which had been previously calibrated with an accuracy ±0.2 °C in the temperature range concerned. Free energies of activation at the coalescence temperature T_c were calculated from the Eyring equation (eq 1)[7] where $\Delta\nu$ is the chemical shift difference of the

$$\Delta G^{\ddagger} = -RT_c \ln \frac{\pi \Delta\nu h}{\sqrt{2}kT_c} = aT_c\left[9.972 + \log\left(\frac{T_c}{\Delta\nu}\right)\right] \quad (1)$$

coalescing resonances in the absence of exchange and the reduced parameter $a = 1.914 \times 10^{-2}$ kJ mol^{-1} K^{-1}.

Electron impact (EI) or fast atom bombardment (FAB) mass spectra were obtained by Mr. Greg Owen on a Hewlett-Packard Model 5985 spectrometer equipped with a fast atom bombardment probe (xenon source, Phrasor Scientific, Inc., accessory). Samples for FABMS were dispersed or dissolved in sulfolane or *m*-nitrobenzyl alcohol (NOBA). The observed isotope patterns of the parent and fragment ions were matched with those simulated by computer for the species in question. The masses are quoted for the ^{193}Ir ^{81}Br, and ^{37}Cl isotopes. Microanalyses were performed by Mr. M.-K. Yang of the Microanalytical Laboratory of Simon Fraser University. $(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2$ was prepared by the literature procedure.[2] $NOBF_4$ was purchased from Aldrich and was freshly washed with CH_2Cl_2 before use. $^{15}NOBF_4$ was synthesized from $Na^{15}NO_2$ (95% ^{15}N, MSD Isotopes).[8]

Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)]BF_4$ (1). To a solution of $Cp^*Ir(C_2H_4)_2$ (100 mg; 0.26 mmol) in 10 mL of acetone at −10 °C was slowly added an equimolar amount of $[NO][BF_4]$. The reaction mixture was stirred for 1 h at this temperature and changed from colorless to gray-green in the first 5 min after the addition and remained so until the reaction was finished (as monitored by IR). The solution was evaporated *in vacuo* to *ca.* 5 mL, and then diethyl ether was added slowly to precipitate the gray-green-colored product. The supernatant solvent was removed carefully by pipet and the remaining solid product was washed twice with diethyl ether. Recrystallization of 1 from acetone/diethyl ether afforded the dark-brown crystalline product (110 mg, 0.26 mmol, 88%). IR ν(NO): 1822 cm^{-1} (acetone), 1823 cm^{-1} (EtOH). ^1H NMR (294 K, 400 MHz, $CDCl_3$): δ 2.34 s (15H, C_5Me_5), 3.47 center of broad AA′XX′ multiplet (4H, C_2H_4). $^{13}C\{^1H\}$ NMR (294K, 100 MHz, $CDCl_3$): δ 9.82 (C_5*Me*$_5$), 47.06 (*C*$_2H_4$), 105.16 (*C*$_5Me_5$). FABMS (sulfolane): *m/z* 386 (M^+), 358 ($M^+ - C_2H_4$), 356 (M^+ − NO). Anal. Calcd: C, 30.52; H, 4.05; N, 2.97. Found: C, 30.79; H, 4.03; N, 2.91.

Preparation of $(\eta^5\text{-}C_5Me_5)Ir(NO)I$. $[Cp^*Ir(NO)(C_2H_4)][BF_4]$ (1) (32 mg 0.067 mmol) and KI (11 mg; 0.067 mmol) were stirred together in degassed ethanol (7.5 mL) under nitrogen at room temperature for 30 min. The ν(NO) absorption for 1 at 1823 cm^{-1} was replaced by a new ν(NO) absorption band at 1757 cm^{-1}. The solvent was evaporated under vacuum and the residue was extracted with 2 × 2.5 mL portions of benzene to leave a very water-soluble white solid presumed to be KBF_4. The IR spectrum of the bright yellow benzene extract exhibited ν(NO) at 1751 cm^{-1}. Solvent was removed at reduced pressure to yield the orange-brown solid product (28 mg, 0.058 mmol, 86% yield). The analytical sample was synthesized similarly but was extracted into hexane (ν(NO) 1771 cm^{-1}) and recrystallized at −78 °C as fragile orange needles. IR($CDCl_3$): ν(NO) 1761. ^1H NMR ($CDCl_3$): δ 2.29 s (Cp*). EIMS: *m/z* 485 weak (M^+), 455 (complex pattern). Anal. Found: C, 24.99; H, 3.08; N, 3.06. Calcd: C, 24.78; H, 3.10; N, 2.89. A sample synthesized from $[Cp^*Ir(^{15}NO)(C_2H_4)][BF_4]$ [$\nu(^{15}NO)$ 1786 cm^{-1} (acetone)] exhibited $\nu(^{15}NO)$ at 1719 cm^{-1} in ethanol at the conclusion of the synthesis and $\nu(^{15}NO)$ at 1717 cm^{-1} ($CDCl_3$) after isolation.

Preparation of $(\eta^5\text{-}C_5Me_5)_2Ir_2I_2(\mu\text{-}I)(\mu\text{-}NO)$ (2). The synthesis was carried out as above, except that after 30 min the temperature was raised to 60 °C and the solution stirred for a further 2 h. This resulted in disappearance of the ν(NO) absorption at 1757 cm^{-1}. The solvent was evaporated under vacuum and the residue was extracted with toluene.

A sample was recrystallized by slow evaporation of a toluene solution in air. This contained single crystals suitable for X-ray analysis. These were carefully removed and the remainder was dried in vacuo for several hours before analysis. Anal. Found: C, 22.80; H, 2.71; N, 1.27. Calcd: C, 22.53; H, 2.82; N, 1.31. ^1H NMR ($CDCl_3$): δ 1.66 s (Cp*). FABMS: *m/z* 582 $[Cp^*IrI_2]$, 485 $[Cp^*Ir(NO)I]$, 449–455 $[Cp^*IrI$ and overlapping H-loss products].

Preparation of $(\eta^5\text{-}C_5Me_5)_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (3). $[Cp^*Ir(NO)(C_2H_4)][BF_4]$ (1) (30 mg; 0.064 mmol) was stirred together with an excess of KBr in degassed ethanol (10 mL) at room temperature for approximately 2 h. During this time the ν(NO) absorption for 1 at 1823 cm^{-1} was replaced by a ν(NO) absorption band at 1761 cm^{-1} attributed to the formation of $(\eta^5\text{-}C_5Me_5)Ir(NO)Br$. The solvent was pumped off and the product extracted into benzene (ν(NO) 1755 cm^{-1}). Removal of the benzene and dissolving in $CDCl_3$ gave a solution which now exhibited only a weak ν(NO) absorption for $(\eta^5\text{-}C_5Me_5)Ir(NO)Br$ at 1761 cm^{-1}; the ^1H NMR spectrum of this solution exhibited a correspondingly weak resonance at δ 2.22 associated with the Cp* ligand of this monomer, but a strong resonance at δ 1.54. The relative intensities of the δ 2.22 and 1.54 resonances at this stage in repeated syntheses

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(6) Brief mention of compound 1 was included in a preliminary communication, see: Einstein, F. W. B.; Yan, X.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1466.

(7) Thomas, W. A. *Annu. Rev. NMR Spectrosc.* **1968**, *1*, 43.

(8) Connelly, N. G.; Draggett, P. T.; Green, M.; Kuc, T. A. *J. Chem. Soc. Dalton Trans.* 1977, 70.

Table 1. Crystallographic Data for the Structure Determinations of $[Cp^*Ir(C_2H_4)(NO)]BF_4$ (1), $Cp^*_2Ir_2I_2$ (μ-I)(μ-NO)·toluene (2·toluene), $Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (3), and $Cp^*Ir(NO)(CH_2CH_2OEt)$ (4)

	1	**2**·toluene	**3**	**4**
formula	$IrF_4ONC_{12}BH_{19}$	$Ir_2I_3ONC_{27}H_{38}$	$Ir_2Br_3ONC_{20}H_{30}$	$IrO_2NC_{14}H_{24}$
cryst sys	monoclinic	monoclinic	monoclinic	monoclinic
fw	472.31	1157.76	924.61	430.57
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)[a]	7.454(1)	12.7738(11)	8.6364(8)	7.291(2)
b (Å)	24.381(3)	13.5804(13)	9.3766(6)	15.274(2)
c (Å)	8.536(1)	18.6110(23)	15.501(3)	14.362(2)
β (deg)	93.85(1)	100.40(1)	101.753(11)	96.90(2)
V (Å^3)	1547.8	3175.5	1228.9	1587.8
Z	4	4	2	4
ρ_c (g cm^{-3})	2.027	2.422	2.499	1.801
λ (Mo Kα_1) (Å)	0.70930	0.70930	0.70930	0.70930
μ (Mo Kα) (cm^{-1})	86.3	112.5	156.3	83.8
cryst dimens (mm)	0.08 × 0.13 × 0.22	0.30 × 0.35 × 0.40	0.12 × 0.15 × 0.25	0.26 × 0.34 × 0.38
transmission[b]	0.355–0.648	0.032–0.101	0.266–0.344	0.115–0.190
2θ range (deg)	2–50	3–45	4–44	3–48
R_F[c]	0.034	0.043	0.034	0.027
R_{wF}[d]	0.041	0.057	0.036	0.035

[a] Cell dimensions were determined in each case from 25 reflections (28° $\le 2\theta \le$ 40° for **1**; 34° $\le 2\theta \le$ 44° for **2**·toluene and **3**; 39° $\le 2\theta \le$ 46° for **4**). [b] The data were corrected by the Gaussian integration method for the effects of absorption. [c] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, for 1922 (**1**), 3045 (**2**·toluene), 1120 (**3**), and 1960 (**4**) data ($I_o \ge 2.0\sigma(I_o)$ (**1**); $I_o \ge 2.5\sigma(I_o)$ (**2**·toluene, **3**, and **4**)). [d] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$ for observed data (see c, above); $w = [\sigma(F_o)^2 + 0.0003F_o^2]^{-1}$ for **1**; $w = [\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$ for **2**; $w = 1$ for **3**; $w = [\sigma(F_o)^2 + 0.0001F_o^2]^{-1}$ for **4**.

varied widely as did the intensity of the ν(NO) absorption. Recrystallization from 5:1 hexane:dichloromethane by cooling in dry ice produced pale orange needles which gave a ^{1}H NMR spectrum in $CDCl_3$ consisting of essentially only the δ 1.54 resonance. Elemental analysis of this product gave C, 26.71; H, 3.40; N, 1.66; Br, 23.76. $Cp^*_2Br_3Ir_2NO$ requires C, 25.98; H, 3.25; N, 1.51; Br, 25.92. $Cp^*_2Br_2Ir_2NO$ requires C, 28.44; H, 3.55; N, 1.66; Br, 18.92. (A sample obtained similarly from a reaction using LiBr instead of KBr also exhibited the prominent δ 1.54 resonance but gave an elemental analysis with a much lower result for Br. Found: C, 26.3; H, 3.30; N, 1.56; Br, 17.4. See Discussion). The mass spectrum (EI, 70 eV) exhibited correct isotope intensity patterns for $[Cp^*_2Ir_2Br_2NO]^+$ (m/z 848), $[Cp^*_2Ir_2Br_2]^+$ (m/z 818), and $[Cp^*IrBr_2]^+$ (m/z 490), but no parent molecular ion corresponding to $[Cp^*_2Ir_2Br_3NO]^+$ was observed (this approaches the mass limit of the instrument used). Recrystallization of this material from toluene by slow evaporation in air gave a crystalline product characterized by a single methyl resonance at δ 1.65 in $CDCl_3$ in the ^{1}H NMR spectrum. A single crystal from this batch was used for the X-ray structure determination which showed it to be *trans*-$Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (**3**).

Reaction of $[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)][BF_4]$ (1) with Chloride. A solution of **1** (30 mg; 0.064 mmol) and LiCl (2.7 mg; 0.064 mmol) in degassed ethanol (3 mL) was stirred under nitrogen for 30 min. The absorption for **1** at 1823 cm^{-1} was replaced by an absorption at 1759 cm^{-1} which in turn decayed away. The solvent was pumped off and the residue extracted with benzene. Removal of the benzene gave an orange solid which was recrystallized as fine orange needles from CH_2Cl_2–hexane (1:5 v/v) at −78 °C. Yield: 23 mg. ^{1}H NMR ($CDCl_3$): δ 1.49 (s) (Cp*). Anal. Found: C, 30.78; H, 3.85; N, 1.87; Cl, 13.41. $Cp^*_2Ir_2Cl_3NO$ requires C, 30.35; H, 3.82; N, 1.77; Cl, 13.45. $Cp^*_2Ir_2Cl_2NO$ requires C, 31.80; H, 3.97; N, 1.85; Cl, 9.38. EIMS (70 eV): m/z 760 ($Cp^*_2Ir_2Cl_2NO^+$); 730 ($Cp^*_2Ir_2Cl_2^+$) (correct isotope patterns observed).

Preparation of $(\eta^5\text{-}C_5Me_5)Ir(NO)(CH_2CH_2OEt)$. A mixture of **1** (20 mg; 0.042 mmol) and NaOEt (10 mg, excess) in ethanol (5 mL) was stirred at room temperature for 2 h. Reaction proceeded with the loss of ν(NO) at 1821 cm^{-1} for **1** and the production of ν(NO) at 1728 cm^{-1} for the product. The solvent was pumped off and the residue extracted with portions of hexane to give a yellow solution. Cooling to −78 °C resulted in yellow-brown crystals. The synthesis was also conducted by replacing NaOEt with Na_2CO_3 and heating the stirred mixture at 50 °C for 1 h. Anal. Found: C, 38.47; H, 5.35; N, 3.76. Calcd: C, 39.05; H, 5.58; N, 3.25. IR (cm^{-1}): ν(NO) 1738 (hexane); 1728 (EtOH); 1713 (KBr) cm^{-1}. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 1.22 (t, 7 Hz, CH_3), 2.06 (s, Cp*), 2.42 (m, $IrCH_2$), 3.41 (m, CH_2CH_2OEt), 3.50 (q, 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$; 100 MHz): δ −5.05 (t, CH_2CH_2OEt), 9.81 (q, C_5Me_5), 15.54 (q, OCH_2CH_3), 65.01 (t, OCH_2), 76.60 (t, OCH_2), 95.16 (s, C_5Me_5). EIMS (70 eV): m/z 431 (M$^+$), 397–401 (M$^+$ − NO and M$^+$ − NO − 2H), 386 (M$^+$ − OEt), 359 ($Cp^*Ir(NO)H^+$), 343 ($Cp^*IrCH_3^+$).

Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}CO)(\mu\text{-}NO)][BF_4]$. $[Cp^*Ir(NO)(C_2H_4)][BF_4]$ (**1**) (20 mg, 0.042 mmol) was dissolved in ethanol (2 mL) to give a light brown solution. To this was added a yellow solution of $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (21 mg, 0.055 mmol) in ethanol (3 mL). There was no observable reaction at room temperature. The mixture was heated at 85 °C, with stirring, for 24 h. The solvent was removed from the dark red-brown solution by pumping and the residue was dissolved in acetone, layered with hexane, and stored at 10 °C. The product precipitated in *ca.* 50% yield and was recrystallized from acetone–hexane at −10 °C to give red crystals in overall yield *ca.* 30%. Repeated recrystallization tended to be accompanied by loss of product through decomposition. Anal. Calcd: C, 31.5; H, 3.79; N, 1.75. Found: C, 31.8; H, 3.75; N, 1.95. IR (KBr): ν(CO) 1811 s, ν(NO) 1501 s, $\nu(BF_4)$ 1053 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.85 (s) (Cp*). FABMS: m/z 712 (M$^+$).

X-ray Structure Determinations for Compounds 1–4. Crystals of **2**·toluene and **3** were sealed in capillary tubes and held in place with a trace of apiezon grease while those of **1** and **4** were mounted on glass fibers using epoxy adhesive. Data were recorded at ambient temperature with an Enraf Nonius CAD4F diffractometer using graphite monochromatized Mo K$_\alpha$ radiation. The data were corrected for absorption by the Gaussian integration method and corrections were carefully checked against measured ψ-scans. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects. The programs used for absorption corrections, data reduction, structure solution, and graphical output were from the NRCVAX Crystal Structure System.[9] Refinement was made using CRYSTALS.[10] Complex scattering factors for neutral atoms[11] were used in the calculation of structure factors. Weighting schemes for which $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $\sin\theta/\lambda$ were used. Computations were carried out on a

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(9) Gabe, E. J.; LePage, Y.; Charland, J-P.; Lee, F. L.; White, P. S. NRCVAX—An Interactive Program System for Structure Analysis. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(10) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS; Chemical Crystallography Laboratory; University of Oxford, Oxford, England, 1984.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, p 99.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for the Non-Hydrogen Atoms of the Complex Cation in [Cp*Ir(C_2H_4)(NO)]BF_4 (1)

atom	x	y	z	U_{iso}
Ir	0.24892(5)	0.39146(1)	0.43954(4)	0.0395[a]
O	0.4601(14)	0.4664(4)	0.6423(10)	0.0856
N	0.3768(13)	0.4383(4)	0.5580(10)	0.0585
C(1)	0.3762(19)	0.3183(5)	0.5467(14)	0.0650
C(2)	0.2374(20)	0.3339(6)	0.6333(14)	0.0746
C(10)	0.0767(14)	0.4353(4)	0.2544(11)	0.0466
C(11)	−0.0313(13)	0.3956(4)	0.3230(11)	0.0471
C(12)	0.0464(15)	0.3442(4)	0.2935(12)	0.0508
C(13)	0.1979(15)	0.3522(4)	0.2033(12)	0.0516
C(14)	0.2204(14)	0.4081(4)	0.1773(12)	0.0480
C(15)	0.0408(19)	0.4960(4)	0.2470(15)	0.0750
C(16)	−0.1992(15)	0.4066(6)	0.4015(17)	0.0756
C(17)	−0.0376(20)	0.2896(5)	0.3355(16)	0.0792
C(18)	0.3033(21)	0.3066(6)	0.1294(16)	0.0862
C(19)	0.3484(18)	0.4351(6)	0.0790(13)	0.0717

[a] The equivalent isotropic temperature factor is the cube root of the product of the principle axes of the thermal ellipsoid.

Table 3. Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for the Non-Hydrogen Atoms of $Cp^*_2Ir_2I_2(\mu\text{-}I)(\mu\text{-}NO)$ (2)

atom	x	y	z	U_{iso}
Ir(1)	6004.0(4)	3037.7(5)	2251.5(3)	382[a]
Ir(2)	8701.7(5)	2617.5(5)	2888.4(3)	396[a]
I(1)	5727(1)	3345(1)	3628.1(6)	635[a]
I(2)	8909(1)	2124(1)	1529.3(6)	696[a]
I(3)	7669.2(8)	4310.2(8)	2409.1(6)	533[a]
O	7021(8)	1256(8)	2784(6)	542(27)
N	7223(9)	2130(9)	2672(6)	453(31)
C(1)	4553(13)	2267(12)	1812(9)	547(19)
C(2)	5287(13)	2142(12)	1332(9)	547(19)
C(3)	5509(13)	3106(12)	1054(9)	547(19)
C(4)	4874(12)	3767(12)	1352(9)	547(19)
C(5)	4287(12)	3294(12)	1793(9)	547(19)
C(6)	9736(13)	1597(13)	3544(9)	571(19)
C(7)	10401(13)	2282(13)	3301(9)	571(19)
C(8)	10135(13)	3210(13)	3599(9)	571(19)
C(9)	9335(13)	3069(13)	3984(9)	571(19)
C(10)	9094(13)	2076(13)	3964(9)	571(19)
C(11)	4055(14)	1433(14)	2138(10)	746(24)
C(12)	5724(14)	1183(14)	1091(10)	746(24)
C(13)	6170(14)	3280(15)	484(10)	746(24)
C(14)	4794(14)	4860(14)	1168(10)	746(24)
C(15)	3449(14)	3711(14)	2171(10)	746(24)
C(16)	9747(15)	449(15)	3397(10)	816(26)
C(17)	11252(15)	2105(16)	2878(10)	816(26)
C(18)	10674(15)	4185(15)	3502(11)	816(26)
C(19)	8904(15)	3821(15)	4428(11)	816(26)
C(20)	8296(14)	1518(15)	4365(10)	816(26)

[a] The equivalent isotropic thermal parameter is the cube root of the product of the principle axes of the thermal ellipsoid.

MicroVAX-II and on 80486-processor-based personal computers. Crystallographic details are summarized in Table 1 and atomic coordinates for 1–4 are listed in Tables 2–5.

The final full matrix least-squares refinement of 1 (161 parameters for 1922 reflections) included anisotropic thermal parameters and coordinates for Ir, O, C, and N atoms; rigid group parameters for each of three regular BF_4^- groups; occupancy parameters for each of these groups, restrained to a total BF_4^- occupancy of one. Also a single parameter for the isotropic thermal motion of each of the following groups of atoms: all fluorine atoms; boron; all the Cp* hydrogen atoms; the ethylene hydrogen atoms. The hydrogen atoms were included in calculated positions (d(C–H) = 0.95) and were made to ride on their respectively bound carbon atoms during refinement. Soft restraints (15) limiting to zero the difference in mean squared atomic displacements along the bond direction for pairs of mutually bonded atoms were retained in the final refinement; however, the release of these restraints and further refinement produced no significant shifts.

Table 4. Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for the Non-Hydrogen Atoms of $Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (3)

atom	x	y	z	U_{iso}
Ir[a]	4055.5(8)	9601.3(6)	837.5(4)	465[b]
Br(1)[a]	3441(3)	12197(2)	946(2)	796[b]
Br(2)	6970(9)	10328(18)	867(4)	794[b]
O	7174(52)	10375(114)	940(23)	847(61)
N	5891(26)	10197(27)	394(14)	547(61)
C(1)	2409(25)	8931(22)	1700(12)	547(24)
C(2)	2286(26)	7966(20)	1038(14)	547(24)
C(3)	3763(24)	7357(21)	1060(14)	547(24)
C(4)	4858(27)	7949(20)	1766(12)	547(24)
C(5)	3984(24)	8956(21)	2173(13)	547(24)
C(11)	1052(33)	9801(25)	1939(19)	961(42)
C(12)	696(31)	7633(29)	411(16)	961(42)
C(13)	4010(40)	6193(22)	397(16)	961(42)
C(14)	6584(27)	7560(30)	2039(20)	961(42)
C(15)	4682(39)	9823(25)	2988(14)	961(42)
C(51)	2788(24)	9028(22)	1883(13)	547(24)
C(52)	2104(27)	8333(19)	1124(14)	547(24)
C(53)	3211(24)	7422(20)	880(14)	547(24)
C(54)	4646(26)	7559(19)	1494(13)	547(24)
C(55)	4372(25)	8591(20)	2123(13)	547(24)
C(61)	1824(37)	10036(22)	2359(18)	961(42)
C(62)	363(28)	8364(29)	649(18)	961(42)
C(63)	2964(40)	6369(23)	99(15)	961(42)
C(64)	6184(30)	6765(26)	1517(21)	961(42)
C(65)	5526(34)	9054(28)	2942(15)	961(42)

[a] Ir and Br(1) have occupancy 1.0 while all other atom sites have occupancy 0.5. [b] The equivalent isotropic thermal parameter is the cube root of the product of the principle axes of the thermal ellipsoid.

Table 5. Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for the Non-Hydrogen Atoms of Cp*Ir(NO)(CH_2CH_2OEt) (4)

atom	x	y	z	U_{iso}
Ir	0.27854(4)	0.13471(2)	0.10210(2)	0.0430[a]
O(1)	0.0212(9)	0.1039(4)	−0.0662(4)	0.076[a]
N	0.1274(9)	0.1111(4)	0.0025(4)	0.054(2)
C(1)	0.352(1)	0.1484(5)	0.2578(5)	0.051(2)
C(2)	0.507(1)	0.1765(5)	0.2111(5)	0.051(2)
C(3)	0.572(1)	0.1025(5)	0.1639(5)	0.052(2)
C(4)	0.456(1)	0.0310(5)	0.1792(5)	0.047(2)
C(5)	0.325(1)	0.0577(5)	0.2377(5)	0.053(2)
C(11)	0.255(1)	0.2006(6)	0.3243(6)	0.079[a]
C(12)	0.601(1)	0.2660(6)	0.2193(6)	0.076[a]
C(13)	0.740(1)	0.0997(8)	0.1138(6)	0.082[a]
C(14)	0.481(1)	−0.0600(5)	0.1471(6)	0.072[a]
C(15)	0.180(1)	0.0022(6)	0.2752(6)	0.067[a]
O(2)[b]	0.209(1)	0.3985(5)	−0.0015(5)	0.074(2)
C(6)[b]	0.182(2)	0.2664(8)	0.0823(9)	0.075(3)
C(7)[b]	0.259(1)	0.3083(5)	0.0062(7)	0.059(3)
C(8)[b]	0.275(2)	0.4387(6)	−0.0804(7)	0.076(3)
C(9)[b]	0.231(2)	0.5313(6)	−0.0901(9)	0.078(4)
O(12)	0.331(3)	0.399(1)	−0.006(1)	0.074(2)
C(16)	0.231(6)	0.272(2)	0.068(3)	0.075(3)
C(17)	0.330(4)	0.305(1)	−0.005(2)	0.059(3)
C(18)	0.190(5)	0.438(2)	−0.071(2)	0.076(3)
C(19)	0.182(5)	0.533(2)	−0.065(3)	0.078(4)

[a] The equivalent isotropic thermal parameter is the cube root of the product of the principle axes of the thermal ellipsoid. [b] O(2) until C(9) have occupancy 0.75(1), while O(12) until C(19) have occupancy 1.0–0.75(1).

In the case of 2·toluene, the final full matrix least-squares refinement of 134 parameters for 3045 observations included coordinates and anisotropic thermal parameters for iridium and iodine atoms; coordinates for all other non-hydrogen atoms of the complex; rigid group parameters for each of two partially occupied orientations for the toluene molecule; a relative occupancy parameter for these two orientations such that the total occupancy is 1 (in the absence of this constraint the total occupancy did not differ significantly from 1); an extinction parameter;[12] a single parameter for the isotropic thermal motion of each of the following groups of atoms: C(1)–C(5), C(6)–C(10), C(11)–C(15), C(16)–C(20), the H atoms of the complex, the toluene molecule. The hydrogen atoms were included in calculated positions 0.95 Å from their respective C atoms and, in the case of the Cp*-methyl groups, were made to ride on them during refinement. The starting values for the isotropic temperature factors of the H atoms were assigned proportionately to the thermal parameters for the respective C-atoms. The methyl C atom of the toluene molecule was arbitrarily assigned a temperature factor 0.03 Å^2 larger than that for the ring C atoms, and the temperature factors for the H atoms of the toluene molecule were made 10% larger than those of their C atoms. Crystal decay, probably because of loss of solvent of crystallization, would appear to have produced some systematic errors in the data set, limiting somewhat the accuracy of the structural determination. The significant features (−1.3–1.5(3) e Å^{-3}) in the final difference map are close to the heavy atoms.

In the case of **3**, the molecule is disordered about a crystallographic inversion center in the space group $P2_1/n$. Extensive systematic measurements at goniometer settings for reflections which either violated the systematic conditions for $P2_1/n$ or corresponded to doubling of one or more crystal axes yielded no significant observations. A full sphere of data $2\theta < 20°$ did not show any pattern of intensities attributable to Friedel inequivalences (R_{merge} = 0.022 for 143 sets of symmetry-equivalent reflections). Nonetheless attempts were made to produce ordered models in space groups $P2_1$ and Pn but these yielded no significant improvement in the structure factor agreement nor more meaningful results than the disordered centrosymmetric solution presented here.

The structure was modeled with two sites of equal (0.5) occupancy for every atom with the exception of Ir and Br(1) which had full occupancy. This model was stabilized by the following soft restraints: the Ir–Br bridging bond distances were restrained toward their mean value, as were the Ir–N bond distances, the Ir–C bond distances, the twenty C(methyl)–C(beta) distances of the disordered Cp* (to maintain symmetric bond angles at the ring carbon atoms), and the Ir–N–O bond angles. The C–C annular bonds were restrained toward 1.39 Å; the C–C bonds to the methyl groups were restrained toward 1.54 Å; the N–O bond distance was restrained toward 1.25 Å; the C_5 rings were restrained to be planar as was each set of five methyl C-atoms; and the mean squared vibrational differences along the Ir–Br bonds were restrained to be near zero.

Final full matrix least-squares refinement of 99 parameters for 1120 observations and 80 restraints for **3** included coordinates and anisotropic thermal parameters for Ir and Br atoms; coordinates for all C, N, and O atoms; a single parameter for the isotropic temperature factors for the N and O atoms (O 0.03 Å^2 greater than N), another for the ring C atoms, another for the methyl C atoms and one for all H atoms; an extinction parameter. The hydrogen atoms were included in calculated positions 0.95 Å from their respective C atoms and were made to ride on them during refinement.

Refinement of an ordered structure solution for **4** produced large anisotropic mean squared atomic displacement parameters and somewhat unreasonable metrical parameters for the ethoxyethyl ligand, indicating disorder of this group. A model with two independent fractionally occupied sites, having a common isotropic temperature factor, for each non-hydrogen atom of this ligand suggested the interpretation of two conformations for the ligand—the major one (75(1)%) having three *anti* torsional relationships for the Ir–C–C–O–C–C segment and the minor (25(1)%) displaying *anti, gauche, anti* relationships. This model produced as good structure factor agreement as the fully ordered model with anisotropic thermal parameters for these atoms and the most reasonable metrical parameters for the ligand of any model tested. All C–O bond lengths were restrained toward their common mean value. The C–C bond lengths of the disordered ligand were restrained, pairwise, toward their respective mean values, as were the four pairs of bond angles (Ir–C–C, H_2C–C–O, C–O–C and O–C–CH_3).

Final full matrix least-squares refinement for **4** of 128 parameters for 1960 observations and 16 restraints included coordinates for all non-hydrogen atoms; anisotropic thermal parameters for Ir, O, and the methyl-C atoms of the Cp* group; isotropic temperature factors for N and the C atoms of the Cp* group; a single isotropic temperature factor for each pair of disordered non-hydrogen atoms of the ethoxyethyl group; a single parameter for the mean isotropic temperature factor for the H atoms of the Cp* group; another for all methylene H atoms; another for the methyl H atoms of the ethoxyethyl ligand; a single relative occupancy parameter for the two conformations of the ethoxyethyl ligand such that the total occupancy remained 1; and an extinction parameter. The hydrogen atoms were included in calculated positions 0.95 Å from their respective C atoms, with site occupancies and isotropic temperature factors dependent upon those of the C atom and were made to ride on these carbon atoms during refinement.

Results

Synthesis and Characterization of $[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)][BF_4]$ (1). Addition of solid $NOBF_4$ to a solution of $Cp^*Ir(C_2H_4)_2$ in acetone at −10 °C gave **1** as a grey-greenish product which recrystallized from acetone–diethyl ether as dark brown crystals suitable for X-ray analysis. A temperature of −10 °C or below is crucial, since at room temperature only an orange-red oil resulted, from which no tractable organometallic compounds were isolable. Compound **1** is soluble in common polar organic solvents including acetone, acetonitrile, ethanol, CH_2Cl_2, or $CHCl_3$ and solutions in the non-halogenated solvents are stable at room temperature over several days. A linear terminal NO ligand is indicated by the ν(NO) absorption in the IR spectrum which occurs strongly near 1820 cm^{-1} in solution and is shifted to 1786 cm^{-1} in the ^{15}N analog. The FABMS of **1** displays peaks corresponding to the parent cation and fragments resulting from the loss of NO and C_2H_4 ligands. The ^1H NMR spectrum is temperature-dependent. The 400-MHz spectrum at 273 K in CD_3CN exhibits a well-resolved AA′XX′ pattern centered at δ 3.47 for the ethylene protons, that is adequately simulated with $\delta_A = 3.18$, $\delta_X = 3.75$, $J_{cis} = 7$ Hz, $J_{trans} = 13$ Hz, and $J_{gem} = 0$ Hz. Ethylene rotation is therefore slow on the NMR timescale at this temperature and the observed AA′XX′ pattern requires the C_2H_4 protons to be related pairwise by a plane of symmetry. The C_2H_4 ligand must be oriented with the C–C axis either perpendicular to, or in, the plane containing Ir, N, O, and the Cp* centroid. The X-ray structure shows that it is the former case in the solid state (see below) i.e., the C–C axis is "parallel" with the Cp* plane. The observation of a single $^{13}C\{H\}$ resonance at δ 47.06 for the two ethylene carbons at 293 K is consistent only with this orientation (or with rapid rotation). The estimated barrier to rotation[13] at the ^1H NMR coalescence temperature (353 K; 400 MHz) is $\Delta G^{\ddagger}_{353} = 68.7 \pm 0.2$ kJ mol^{-1}. The resonances at δ 3.18 and δ 3.75 are assigned to the inner (H_i) and outer (H_o) protons of the C_2H_4 ligand, respectively (see **A**), on the basis of shielding arguments presented in the case of $CpIr(C_2H_4)_2$ and $CpIr(CO)(C_2H_4)$[13a] and related rhodium compounds,[14,15] and the magnitudes of the H–H coupling constants compare with reported values for these compounds. The resonances are

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(12) Larson, A. C. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 293.

(13) (a) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357. (b) Arthurs, M. A.; Nelson, S. M. *J. Coord. Chem.* **1983**, *13*, 29. (c) A comprehensive list of ethylene rotation barriers is given in: Mann, B. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, U. K., 1983; Vol. 3, Chapter 20, p 89.

shifted downfield by comparison with the corresponding resonances for $Cp^*Ir(C_2H_4)_2$ (δ 0.67 and δ 1.53 respectively)[2] and have a much smaller chemical shift separation. This is similar to the effect seen when an ethylene ligand in $CpIr(C_2H_4)_2$ is replaced by CO and presumably is explained in an analogous fashion[13a] in terms of the differing anisotropy of a neighboring nitrosyl ligand compared with a neighboring ethylene ligand resulting from the different orientations of their π-systems with regard to the $CpIr(C_2H_4)$ fragment.

The barrier to ethylene rotation in the parent compound $Cp^*Ir(C_2H_4)_2$ is not known, but must be in excess of 80 kJ mol^{-1}, since only the "frozen" ^{1}H NMR spectrum was observed up to the decomposition temperature (110 °C), though some loss of fine structure was reported above 80 °C.[2,16] The barriers to ethylene rotation in $CpIr(C_2H_4)_2$ and $CpIr(CO)(C_2H_4)$ have been measured[13] and show that substitution of CO for ethylene has very little effect on the energy barriers which are *ca.* 19–20 kcal mol^{-1} (79–84 kJ mol^{-1}). Thus, the replacement of C_2H_4 by NO^+ in the present case of $Cp^*Ir(C_2H_4)_2$ appears to differ by resulting in a substantial decrease in the ethylene rotation barrier, which we attribute to the comparatively greater π-electron withdrawing ability of the nitrosyl ligand in the cation,[17] resulting in a substantially decreased contribution from the dominant[18] metal d_π-ethylene π^* "back-bond" in the ground-state structure.

X-ray Crystal Structure of $[(\eta^5\text{-}C_5Me_5)Ir(NO)(C_2H_4)][BF_4]$ (1). The crystal structure determination for 1 revealed the cation to be crystallographically well-behaved but the BF_4 anion to be disordered. The geometry of the cation (Figure 1) can be described in different ways. It has the typical "half-sandwich" structure or can be described as a "piano-stool" where the "legs" are the NO and C_2H_4 coordination sites (two if the C_2H_4 is considered to occupy a single site, or three if the C_2H_4 is viewed as occupying two sites). In addition it can be classified as a trigonal bipyramidal ML_5 $\{MNO\}^8$ complex[19] with the nitrosyl group equatorial and the C_5Me_5 ligand occupying one axial and two equatorial sites.

The NO and C_2H_4 ligands are situated "below" the Cp^*Ir fragment with the angles subtended at Ir being Cp*–Ir–N = 141.8°, Cp*–Ir–C(1) = 121.3°, and Cp*–Ir–C(2) = 124.2°, where Cp* here denotes the centroid of the C_5Me_5 ring. The Ir atom is approximately located in the plane defined by N and the centers of mass of the Cp* and C_2H_4 ligands. The C_2H_4 ligand is typically η^2-bonded and is oriented close to perpendicular to this plane (as indicated by the torsion angle N–Ir–E–C(1) = −95.1°, where E represents the center of mass of the C_2H_4). In other words, the ethylene ligand's C–C axis is roughly parallel to the C_5Me_5 ring plane. Thus, although there is no actual crystallographic molecular symmetry, the ethylene carbons are approximately symmetrically placed with respect to the Ir–N–O moiety (N–Ir–C(1) = 94.9(4)°, N–Ir–C(2) = 91.6(5)°) as might be expected and are bonded to iridium with equal bond lengths at this precision (Ir–C(1) = 2.19(1) Å, Ir–C(2) = 2.17(1) Å). A list of selected bond lengths and angles for 1 is given in Table 6. The Ir–N–O group is essentially linear (Ir–N–O = 175.8(9)°) and the nitrosyl ligand is rather more angled down from the C_5Me_5 plane by comparison with the ethylene carbons (viz., Cp*–Ir–N = 141.8°, compared with Cp*–Ir–C(1) = 121.3° and Cp*–Ir–C(2) = 124.2). The Ir–N and N–O distances of 1.762(9) and 1.15(1) Å, respectively, are well within the range of these parameters observed in linear metal nitrosyls.[20]

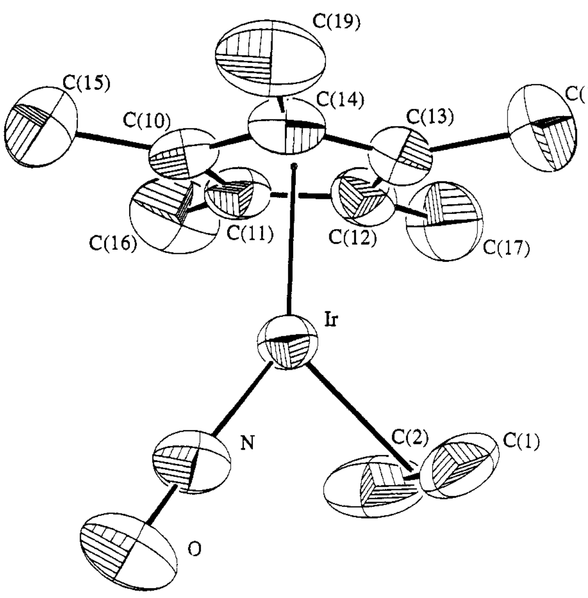

Figure 1. The molecular structure of the complex cation of 1. 50% Probability ellipsoids are shown. Hydrogen atoms have been omitted for clarity.

Table 6. Selected Intramolecular Distances (Å) and Angles (deg) for $[Cp^*Ir(C_2H_4)(NO)]BF_4$ (1)

Ir–N	1.762(9)	Ir–C(1)	2.19(1)
Ir–C(2)	2.17(1)	Ir–Cp[a]	1.89
Ir–C(10)	2.239(9)	Ir–*E*[b]	2.08
Ir–C(12)	2.22(1)	Ir–C(11)	2.255(9)
Ir–C(14)	2.27(1)	Ir–C(13)	2.24(1)
C(1)–C(2)	1.37(2)	O–N	1.15(1)
N–Ir–C(1)	94.9(4)	N–Ir–C(2)	91.6(5)
N–Ir–Cp	141.8	C(1)–Ir–C(2)	36.4(5)
C(1)–Ir–Cp	121.3	C(2)–Ir–Cp	124.2
Ir–N–O	175.8(9)	N–Ir–*E*	93.5
		Cp–Ir–*E*	124.7

[a] Cp denotes the center of mass of the ring C(10)–C(14). [b] *E* denotes the center of mass of C(1) and C(2).

Reactions of $[(\eta^5\text{-}C_5Me_5)Ir(NO)C_2H_4)][BF_4]$ (1) with Halides. (a) Iodide. The reaction of equimolar amounts of 1 (ν(NO) 1823 cm^{-1} in EtOH) and KI in ethanol at room temperature resulted in the appearance of a new ν(NO) absorption at 1757 cm^{-1} [$\nu(^{15}NO)$ 1719 cm^{-1}]. Analytical and spectroscopic data for the product isolated from benzene or hexane extracts allow formulation as the complex $Cp^*Ir(NO)I$. The ^{1}H NMR spectrum exhibits only a Cp* resonance, which occurs at δ 2.29. The IR ν(NO) value supports a terminal linear 3e$^-$-donor NO group

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(14) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodgers, C. A.; Churchill, J. W.; Zeller, J.; Kanz, S.-W.; Albright, T. A. *Organometallics* **1986**, *5*, 1656.

(15) (a) 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. (b) Cramer, R.; Mrowca, J. J. *Inorg. Chim. Acta.* **1971**, *5*, 528. (c) Cramer, R.; Kline, J. R.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2519.

(16) This value is derived from the published 60-MHz ^{1}H NMR data in ref 2 for the "frozen" spectrum $\Delta\delta$ = 0.76 ppm (45.6 Hz), and the assumption that 110 °C (393 K) is the coalescence temperature (whereas in reality coalescence has not yet occurred at this decomposition temperature). The barrier is also expected to be somewhat greater than that of the cyclopentadienyl complex, which had $\Delta G^{\ddagger}_{T_c}$ = 19.3 kcal mol^{-1} (80.7 kJ mol^{-1}) at T_c = 423 K (ref 13a).

(17) For a discussion of the relative π-acceptor abilities of nitrosyl and carbonyl ligands see: (a) Chen, H. W.; Jolly, W. L. *Inorg. Chem.* **1979**, *18*, 2548. (b) Chen, H. W.; Jolly, W. L.; Liang, S.-F.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 1779.

(18) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(19) Feltham, R. D.; Enemark, J. H. In *Topics in Inorganic and Organometallic Stereochemistry*; Wiley: New York, 1981; Vol. 12, p 155.

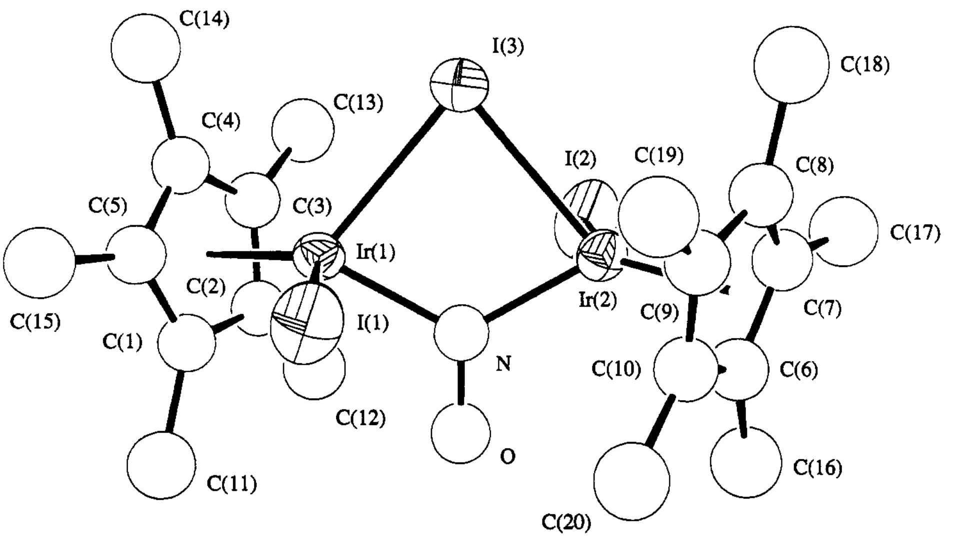
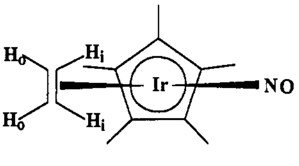
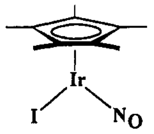


Figure 2. The molecular structure of **2**·toluene. 50% Probability ellipsoids or spheres are shown. Hydrogen atoms have been omitted for clarity.

and the shift compared with ν(NO) of the cation **1** is reasonable if C_2H_4 has been replaced by I^-. A weak mass spectrum pattern at m/z 485 (^{193}Ir) corresponds to M^+, and a complex feature at m/z 455 and below can be assigned to loss of NO and accompanying loss of hydrogens from the C_5Me_5 group (which we frequently observe in the fragmentation of pentamethylcyclopentadienyl compounds).[21] On the basis of these results the compound is formulated as the molecular monomer with structure **B**.



A



B

Repeated crystallization from hexane at −78 °C produced fragile orange needles that unfortunately were unsuitable for X-ray analysis. Attempts to grow crystals by slow evaporation of solutions in benzene or toluene produced a material whose ^{1}H NMR spectrum showed loss of the characteristic δ 2.29 resonance and the presence of new methyl resonances dominated by one at δ 1.66. A sequence of ^{1}H NMR spectra for Cp*Ir(NO)I in $CDCl_3$ confirmed its instability in solution and substantial conversion to the product **2** with δ 1.66 over 48 h at room temperature. This product was also obtained by warming a solution of Cp*Ir(NO)I in ethanol to 60 °C followed by extraction into benzene or toluene. No IR absorption could be assigned to a terminal NO group, but the FABMS exhibited fragments corresponding to $Cp^*IrI_2^+$, $Cp^*Ir(NO)I^+$, and Cp*IrI. Analytical data supported formulation of **2** as $Cp^*_2Ir_2(NO)I_3$, but this molecular mass could not be confirmed by MS with our instrumentation since this exceeded our observable mass range. X-ray quality crystals of **2**·toluene were obtained from toluene solutions, and the crystal structure determination confirmed the formula of **2** and revealed the binuclear structure shown. The fragments $Cp^*Ir(NO)I^+$ and $Cp^*IrI_2^+$ observed in the mass spectrum are readily accounted for by pairwise cleavage of the iodo and nitrosyl bridges. The formal oxidation state of Ir in **2** is III, counting the bridging NO group as NO^-, whereas in Cp*Ir(NO)I it is formally $Ir^{I}(NO^+)$, and the upfield shift in the Cp* methyl resonance for **2** is attributable to this change in formal oxidation state.

The crystal structure shows that in **2**·toluene the iridium atoms are tetrahedrally coordinated (assuming the C_5Me_5 group to occupy a single coordination site) and the overall stereochemistry is trans (Figure 2). The iridium atoms are bridged symmetrically by NO and I.

While **2**·toluene has no crystallographic point symmetry, it closely approximates ideal 2 (or C_2) molecular point symmetry. A slight deviation from this symmetry arises from a tilting of the Ir_2NO unit (which is planar within our errors) about the Ir(1)–Ir(2) vector. The relevant deviations from the Ir(1)–I(3)–Ir(2) plane are 0.040(12) Å for N and 0.077(11) Å for O (toward the I(1) side of the plane). The Cp* groups and, to a lesser degree, the terminal iodine atoms are inclined toward the nitrosyl side of the plane which intersects both iridium atoms and is orthogonal to the Ir(1)–I(3)–Ir(2) plane, as shown by the torsion angles I(1)–Ir(1)–Ir(2)–N = 84.8(3)°, N–Ir(1)–Ir(2)–I(2) = 89.4(3)°, Cp*(1)–Ir(1)–Ir(2)–N = −80.7°, N–Ir(1)–Ir(2)–Cp*(2) = −76.5°, where Cp*(1) and Cp*(2) represent the centers of mass of the C_5-rings C(1)–C(5) and C(6)–C(10), respectively. Observed bond lengths Ir–I (terminal) = 2.681(1), 2.676(1) Å, Ir–I (bridge) = 2.715(1), 2.719(1) Å, Ir–N (bridge) = 1.97(1), 2.03(1) Å, and N–O = 1.24(2) Å are all unexceptional. The Ir(1)···Ir(2) distance

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(20) We are not aware of structural determinations of close analogs of **1** (i.e., CpIr(NO)X) with which to compare. Some pertinent structures of linear iridium NO complexes are reported in: (a) Dobson, A.; Moore, D. S.; Robinson, S. D.; Galas, A. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 611. (b) Dapporto, P.; Denti, G.; Dolcetti, G.; Ghedini, M. *J. Chem. Soc., Dalton Trans.* **1983**, 779. (c) English, R. *Acta Crystallogr.* **1981**, *B37*, 939. (d) Shorthill, W. B.; Buchanan, R. M.; Pierpoint, C. G.; Ghedini, M.; Dolcetti, G. *Inorg. Chem.* **1980**, *19*, 1803. (e) Tiripicchio, A.; Tiripicchio Camellini, M.; Ghedini, M.; Dolcetti, G. *Transition Met. Chem.* (*Weinheim Ger*) **1980**, 5, 102. (f) Einstein, F. W. B.; Sutton, D.; Vogel, P. L. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 671. (g) Bottomley, F. *J. Chem. Soc. Dalton. Trans.* **1975**, 2538. (h) Cheng, P. T.; Nyburg, S. C. *Inorg. Chem.* **1975**, *14*, 327. (i) Clark, G. R.; Waters, J. M.; Whittle, K. R. *Inorg. Chem.* **1974**, *13*, 1628. (j) Angoletta, M.; Gianfranco, C.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1973**, 789. (k) Pratt, C. S.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 2812. (l) Clemens, J.; Green, M.; Kuo, M.-C.; Fritchie, C. J.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc. Chem. Commun.* **1972**, 53. (m) Albano, V. G.; Bellon, P. L.; Sansoni, M. *J. Chem. Soc.* (*A*) **1971**, 2420. (n) Ibers, J. A.; Mingos, D. M. P. *Inorg. Chem.* **1971**, *10*, 1479.

(21) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516.

Table 7. Selected Intramolecular Distances (Å) and Angles (deg) for $Cp^*_2Ir_2I_2(\mu\text{-}I)(\mu\text{-}NO)$·toluene (2·toluene)

Ir(1)–I(1)	2.6814(14)	Ir(2)–I(2)	2.6758(14)
Ir(1)–I(3)	2.7151(13)	Ir(2)–I(3)	2.7193(13)
Ir(1)–N	2.029(12)	Ir(2)–N	1.974(12)
Ir(1)–C(1)	2.16(2)	Ir(2)–C(6)	2.14(2)
Ir(1)–C(2)	2.16(2)	Ir(2)–C(7)	2.22(2)
Ir(1)–C(3)	2.21(2)	Ir(2)–C(8)	2.21(2)
Ir(1)–C(4)	2.23(2)	Ir(2)–C(9)	2.14(2)
Ir(1)–C(5)	2.23(2)	Ir(2)–C(10)	2.11(2)
Ir(1)–Cp1[a]	1.84	Ir(2)–Cp2[b]	1.81
O–N	1.24(2)		
I(3)–Ir(1)–I(1)	91.91(4)	I(3)–Ir(2)–I(2)	91.53(4)
N–Ir(1)–I(1)	87.2(3)	N–Ir(2)–I(2)	88.7(3)
N–Ir(1)–I(3)	79.2(3)	N–Ir(2)–I(3)	80.0(3)
I(1)–Ir(1)–Cp1	123.8	I(2)–Ir(2)–Cp2	123.6
I(3)–Ir(1)–Cp1	128.0	I(3)–Ir(2)–Cp2	128.0
N–Ir(1)–Cp1	132.4	N–Ir(2)–Cp2	131.1
Ir(2)–I(3)–Ir(1)	79.71(4)	Ir(2)–N–Ir(1)	121.0(6)
O–N–Ir(1)	118.6(9)	O–N–Ir(2)	120.5(9)

[a] Cp1 denotes the center of mass of the ring C(1)–C(5). [b] Cp2 denotes the center of mass of the ring C(6)–C(10).

of 3.483(1) Å precludes any direct metal–metal bond. Selected bond distances and angles for **2**·toluene are given in Table 7.

(b) Bromide. When **1** was stirred in ethanol with excess KBr or LiBr, the IR spectrum showed the disappearance of the characteristic ν(NO) absorption for **1** and the concomitant appearance of a new terminal nitrosyl ν(NO) absorption at 1761 cm^{-1}. This is reasonably attributed to the formation of the mononuclear product Cp*Ir(NO)Br by comparison with the ν(NO) absorption at 1757 cm^{-1} established above for the corresponding iodide Cp*Ir(NO)I. Evaporation of the solvent in vacuo and extraction with benzene gave a solution in which the ν(NO) absorption was still visible at 1755 cm^{-1} and an IR spectrum (KBr disk) of the product after evaporation of the benzene also exhibited the terminal nitrosyl absorption (at 1736 cm^{-1}). It was not found possible, however, to isolate and characterize Cp*Ir(NO)Br in the pure state. Solutions in $CDCl_3$ freshly prepared from the isolated solid exhibited weaker than expected absorption at 1761 cm^{-1} for ν(NO), and the ^1H NMR methyl resonance at δ 2.22 attributable to Cp*Ir(NO)Br (by comparison with δ 2.29 for Cp*Ir(NO)I) was accompanied by a much stronger singlet resonance at δ 1.54 for a new product. Similarly, solutions in benzene-d_6 exhibited resonances in 1:1 ratio at δ 1.71 (Cp*Ir(NO)Br) and δ 1.33 (new product). In numerous repetitions of this synthesis the ratio of the δ 2.22 and 1.54 intensities varied considerably, from at best 2:1 in favor of Cp*Ir(NO)Br to instances where this resonance was absent.[22] In all cases the δ 2.22 resonance decayed with time in favor of the δ 1.54 one. The intensity of the latter seemed to remain constant for solutions in $CDCl_3$ at 50 °C for 2 h or overnight at 30 °C. Recrystallization from 5:1 hexane:dichloromethane by cooling in dry ice gave pale orange needles of the δ 1.54 product and the elemental analysis (including Br) obtained for this product supports formulation as $Cp^*_2Ir_2Br_3(NO)$. Further support for this formulation is evident in the mass spectrum. While no parent ion for $[Cp^*_2Ir_2Br_3NO]^+$ could be observed (theoretical *m/z* 929; this is near the limit of our instrumentation) fragments corresponding to $[Cp^*_2Ir_2Br_2NO]^+$, $[Cp^*_2Ir_2Br_2]^+$, and $[Cp^*IrBr_2]^+$ were clearly identified. When this material was recrystallized from toluene by slow evaporation in air the crystals obtained now exhibited a single Cp* methyl resonance at δ 1.65 ($CDCl_3$) in the ^1H NMR spectrum. The X-ray structure obtained using a single crystal from this batch showed it to be *trans*-$Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (**3**) with a structure comparable with the iodide **2** which, it will be recalled, has δ(Cp*) 1.66 in $CDCl_3$.

We are unable to shed much more light on the composition of the δ 1.54 product at this time. If the analytical data are to be believed, this compound could be the cis isomer of $Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$, but additional work is necessary to establish this unequivocally.

While the formation of the δ 1.54 compound is reasonably reproducible, irrespective of the solvent or metal bromide employed, the analytical data obtained for this compound, and the extent of conversion to the δ 1.65 product on attempted recrystallization, are not wholly reproducible (see Experimental Section). A confusing problem is that similar ^1H NMR resonances cannot necessarily be taken as unambiguous evidence for a particular species in different syntheses. This is illustrated by the recrystallization of a material with δ 1.66 on one occasion from the usual reaction of **1** with KBr in ethanol, which elemental analysis showed to contain only a trace of nitrogen and in fact to be the binuclear bromide complex $Cp^*Ir_2Br_4$ (lit.[23] δ 1.65 $CDCl_3$) rather than **3**.

The X-ray structure of *trans*-$Cp^*_2Ir_2Br_2(\mu\text{-}Br)(\mu\text{-}NO)$ (**3**) (Figure 3) is essentially similar to that of the corresponding iodide **2**. The disorder for **3** precludes determination of precise intramolecular dimensions involving the light atoms, but it seems likely that the iridium atoms are symmetrically bridged by nitrosyl and halide groups as is the case in **2**. The Ir···Ir distance of 3.419(1) Å precludes any direct metal–metal bond. Selected interatomic distances and angles for **3** are given in Table 8.

(c) Chloride. The reaction of **1** with LiCl in ethanol at room temperature showed the loss of the ν(NO) IR absorption for **1** and the growth and subsequent decay of an absorption at 1759 cm^{-1}. This is attributed to the formation of Cp*Ir(NO)Cl as an unstable transient by comparison with the data reported above for the corresponding bromo and iodo compounds. Extraction into benzene gave a good yield of an orange product which no longer exhibited ν(NO) absorption for a terminal nitrosyl and had a characteristic Cp* methyl resonance at δ 1.49 in the ^1H NMR ($CDCl_3$) spectrum. Analytical data favor formulation as $Cp^*_2Ir_2Cl_3(NO)$ and while no parent ion for this formulation was observable in the mass spectrum, the fragments $[Cp^*_2Ir_2Cl_2(NO)]^+$ and $[Cp^*_2Ir_2Cl_2]^+$ could be recognized. This material seems likely to be analogous to the bromide product with δ 1.54, but in this case there was no evidence of any further transformation (*cf.* the conversion of the δ 1.54 product to the δ 1.65 product for the bromide). Therefore, we can only tentatively formulate this product as $Cp^*_2Ir_2Cl_2(\mu\text{-}Cl)(\mu\text{-}NO)$ and cannot specify the stereochemistry. The ^1H NMR spectrum of the monomer Cp*Ir(NO)Cl could be obtained by rapid isolation of the product before decay of the characteristic ν(NO) IR absorption, and this was done following reactions of LiCl and **1** in acetone at −30 °C or PPN^+Cl^- (PPN =

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[22] When **1** was reacted with KBr in acetone at −30 °C, followed by removal of acetone at −30 °C and addition of $CDCl_3$ at the same temperature, the ^1H NMR showed the formation of Cp*Ir(NO)Br (δ 2.22) as the major product, with only a trace of the δ 1.54 product. This slowly converted to the δ 1.54 product over 24 h at room temperature (also weak resonances at δ 1.63 and 1.69 were visible).

[23] Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

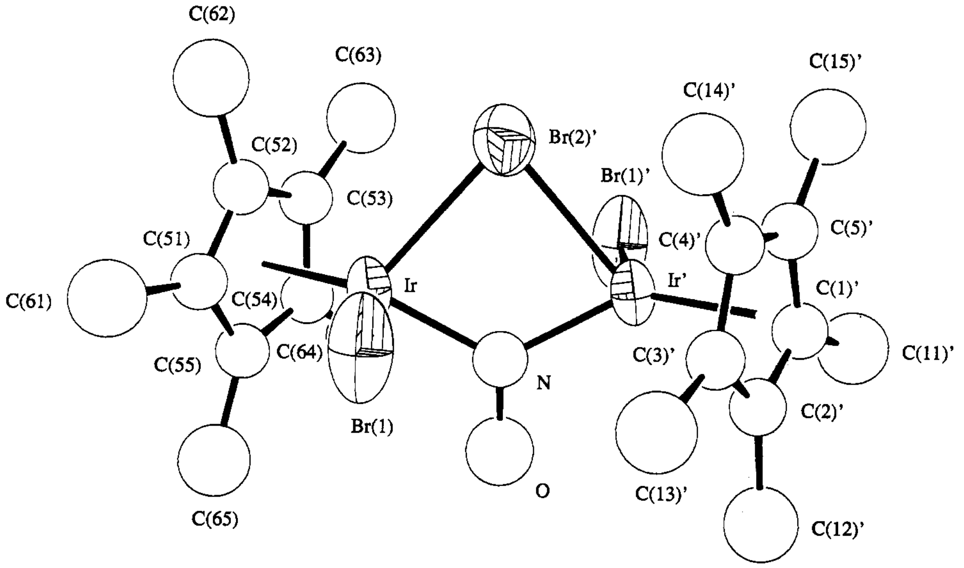


Figure 3. The molecular structure of 3. 50% Probability ellipsoids or spheres are shown. Hydrogen atoms have been omitted for clarity.

Table 8. Selected Intramolecular Distances (Å)[a] and Angles (deg) for Cp*$_2$Ir$_2$Br$_2$(μ-Br)(μ-NO) (3)

Ir–Br(1)	2.504	O–N	1.26
Ir–Br(2)	2.599	Ir–Br(2)′[b]	2.611
Ir–N	1.93	Ir–N′	1.93
Ir–Cp1[c]	1.83	Ir–Cp2[d]	1.83
Ir–C(1)	2.23	Ir–C(51)	2.20
Ir–C(2)	2.23	Ir–C(52)	2.18
Ir–C(3)	2.16	Ir–C(53)	2.18
Ir–C(4)	2.13	Ir–C(54)	2.18
Ir–C(5)	2.17	Ir–C(55)	2.17
Br(2)–Ir–Br(1)	87.8	Br(2)–Ir–Cp1	124.3
Br(2)′–Ir–Br(1)	90.6	Br(2)–Ir–Cp2	125.4
Br(2)–Ir–Br(2)	98.0	Br(2)′–Ir–Cp1	123.2
N–Ir–Br(1)	86.8	Br(2)′–Ir–Cp2	120.6
N′–Ir–Br(1)	91.1	N–Ir–Cp1	140.1
N–Ir–Br(2)′	76.5	N–Ir–Cp2	140.3
N′–Ir–Br(2)	76.9	N′–Ir–Cp1	136.9
Br(1)–Ir–Cp1	123.5	N′–Ir–Cp2	134.3
Br(1)–Ir–Cp2	125.2	Ir–Br(2)–Ir	82.0
Ir–N–Ir	124.5	O–N–Ir′	117.2
O–N–Ir	118.1		

[a] ESDs are not given because of the effects of the disorder and restraints used (see text). [b] The single prime (′) indicates the symmetry-related position $1-x, 2-y, -z$. [c] Cp1 is the center of mass for atoms C(1)–C(5). [d] Cp2 is the center of mass for atoms C(51)–C(55).

[(Ph$_3$P)$_2$N]$^+$) and 1 in ethanol. A Cp* methyl resonance observed at δ 2.29 (CDCl$_3$, −30 °C) under these conditions is reasonably assigned to Cp*Ir(NO)Cl by comparison with the iodo and bromo analogs, and this smoothly became replaced by the δ 1.54 resonance on warming to room temperature. It was not found possible to isolate the pure monomer.

Reaction of [(η^5-C$_5$Me$_5$)Ir(NO)(C$_2$H$_4$)][BF$_4$] (1) with Ethoxide. The reaction of 1 with NaOEt or Na$_2$CO$_3$ in ethanol resulted in the loss of the ν(NO) absorption at 1821 cm^{-1} for 1 and the production of a new terminal ν(NO) absorption at 1728 cm^{-1}. This product is soluble in hexane, benzene, and chloroform and the ^{1}H and ^{13}C NMR spectra unambiguously indicated the presence of an ethoxyethyl ligand rather than an ethoxide ligand. The X-ray crystal structure confirmed the product to be the neutral monomeric complex Cp*Ir(NO)(CH$_2$CH$_2$OEt) (4).

The crystal structure of 4 consists of discrete molecules but displays a disorder of the ethoxyethyl ligand for which the best simple model corresponds to unequal contributions from two conformations of the ligand. The major (75(1)%) conformer (shown in Figure 4) has three *anti* torsional relationships for the Ir–C(6)–C(7)–O(2)–C(8)–C(9) segment while the minor (25%) conformer has *anti–gauche–anti* relationships for the analogous segment, labeled Ir–C(16)–C(17)–O(12)–C(18)–C(19). The respective bond torsion angles are Ir–C(6)–C(7)–O(2) = −174(2)°; C(8)–O(2)–C(7)–C(6) = −176(2)°; C(7)–O(2)–C(8)–C(9) = −179(2)°; Ir–C(16)–C(17)–O(12) = −164(3)°; C(18)–O(12)–C(17)–C(16) = −96(3)°; C(17)–O(12)–C(18)–C(19) = 174(4)°. The dihedral angles between the least squares plane through C(1)–C(5) and the planes defined by Ir, N, and C(6) and Ir, N, and C(16) are, respectively, 95.9(3)° and 90.0(6)°. Selected bond distances and angles are listed in Table 9. There are no intermolecular separations significantly less than the sums of the appropriate pairs of van der Waals radii. It is interesting to compare the Ir–N and N–O distances in 4 with those of the nitrosyl cationic complex 1. These are Ir–N = 1.735(6) Å and N–O = 1.184(7) Å for 4 and Ir–N = 1.762(9) Å and N–O = 1.15(1) Å for 1. The replacement of the C$_2$H$_4$ ligand by

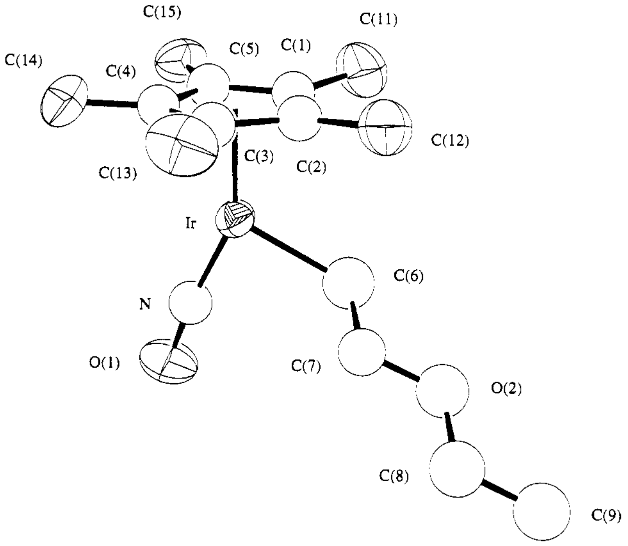


Figure 4. The molecular structure of the major conformational isomer of 4. 50% Probability ellipsoids or spheres are shown. Hydrogen atoms have been omitted for clarity.

Table 9. Selected Intramolecular Distances (Å) and Angles (deg) for $Cp^*Ir(NO)(CH_2CH_2OEt)$ (4)

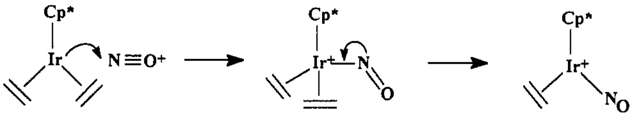
Ir–N	1.735(6)	Ir–C(4)	2.252(7)
Ir–C(1)	2.245(7)	Ir–C(5)	2.266(7)
Ir–C(2)	2.236(7)	Ir–Cp[a]	1.900
Ir–C(3)	2.270(7)	Ir–C(6)	2.139(12)
O(1)–N	1.184(7)	Ir–C(16)	2.17(3)
C(6)–Ir–N	85.4(5)	C(6)–Ir–Cp	120.7
C(16)–Ir–N	87.0(13)	C(16)–Ir–Cp	119.6
N–Ir–Cp	153.3	O(1)–N–Ir	173.3(6)

[a] Cp denotes the center of mass of atoms C(1)–C(5).

the $C_2H_4OEt^-$ ligand is seen to lower ν(NO) and may be expected to shorten the Ir–N and lengthen the N–O bond due to the increased back-bonding to the nitrosyl group. While no statistical difference can be attached to the N–O values, the Ir–N values are certainly in the expected direction and border on statistical significance. The mass spectrum of 4 exhibits a parent peak at m/z 431 (^{193}Ir) and peaks at m/z 401–397 for the loss of the NO group (accompanied by H-loss). There is no fragment corresponding to loss of the ethoxyethyl group as a whole. Instead fragmentation appears to involve loss of OC_2H_5, OC_3H_6, and OC_4H_8 (the latter possibly by β-elimination).

Reaction of 1 with (η^5-C_5Me_5)Ir(CO)$_2$. The cationic nitrosyl complex 1 reacted slowly with (η^5-C_5Me_5)Ir(CO)$_2$ in ethanol at 85 °C. Monitoring the reaction by IR was not very informative; while the ν(NO) absorption for 1 almost completely disappeared, absorptions for the dicarbonyl were still evident and the only new absorption appeared to be a weak unidentified one at 1981 cm^{-1}. A red crystalline product obtained by extraction into acetone and layering with hexane is formulated as the binuclear compound $[Cp^*_2Ir_2(\mu\text{-}CO)(\mu\text{-}NO)][BF_4]$ on the basis of analytical and spectroscopic data. Repeated attempts to grow X-ray quality crystals were unsuccessful and generally led to deterioration of the product and yellow coloration of the hexane layer due to formation of an unidentified neutral compound. The IR spectrum in KBr showed strong absorptions at 1811 and 1501 cm^{-1}. These are assigned to bridging CO and NO groups, respectively, and may be compared with corresponding strong absorptions at 1867 and 1545 cm^{-1} (CH_2Cl_2 solutions) for $[Cp^*_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)][BF_4]$,[24] 1846 and 1524 cm^{-1} for $[Cp^*_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)][PF_6]$,[25-27] and 1897 and 1582 cm^{-1} for $[Cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)][PF_6]$.[25] The ^{1}H NMR ($CDCl_3$) spectrum exhibits only a single resonance for the two equivalent C_5Me_5 groups at δ 1.85 which may be compared with δ 1.74 for the corresponding rhodium compound.[24,25] The fast atom bombardment mass spectrum provided the most definitive evidence for the proposed binuclear structure. The isotopic mass pattern for the quite intense parent ion is characteristic and agreed with the computed isotope intensity pattern involving two iridium atoms (isotopes ^{193}Ir (62.7%) and ^{191}Ir (37.3%)). A weak complex pattern around M$^+$ − 28 and M$^+$ − 30 can be attributed to fragmentation by the loss of the CO and NO groups, respectively.

Scheme 1



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Discussion

Of the compounds of the cobalt group of general formula $Cp'ML_2$ (where Cp′ = Cp or Cp*; M = Co, Rh, Ir; and L = CO or C_2H_4) the bis-ethylene compound $Cp^*Ir(C_2H_4)_2$ appears to be the most inert toward ligand substitution. Few examples of thermal substitution of ethylene in this compound have been reported in the literature.[3c,28] The complex $Cp^*Ir(PMe_3)(C_2H_4)$ is known but was synthesized by a different route.[29] Attempts in our laboratory to effect substitution by saturating solutions of $Cp^*Ir(C_2H_4)_2$ with CO or by refluxing it with PPh_3 in ethanol for days were unsuccessful. The electron-rich iridium complex presumably resists nucleophilic attack by an incoming ligand; therefore the facile substitution of ethylene by NO$^+$ to give 1 requires explanation. It seems likely that the substitution occurs by either an electron transfer mechanism or by *electrophilic* attack by the nitrosonium cation. Scheme 1 illustrates a possible pathway for the latter, involving the formation of an intermediate 18e complex with a bent 1e NO group, which converts to the final product 1 with a linear 3e NO group by expulsion of one ethylene ligand. An EHMO frontier orbital analysis indicates that the principal interaction in the formation of the intermediate is between the filled HOMO of $Cp^*Ir(C_2H_4)_2$ (which is largely d_{yz} in character, and lies in the plane which equates the two ethylene ligands) and the π^*_{yz} LUMO of the incoming NO$^+$ group, the approach being in this plane between the two ethylenes. This interaction removes electron density from the HOMO of $Cp^*Ir(C_2H_4)_2$ thereby reducing the back-bonding to the ethylene and facilitating its dissociation from the intermediate.

Cobalt or rhodium analogs of 1 with C_5H_5 or C_5Me_5 coligands do not appear to have been characterized. To our knowledge, the only one believed to have been observed is $[CpRh(NO)(C_2H_4)]^+$, which was reported[25,26] to be formed in equilibrium with the reagents in solution in the reaction of ethylene with $[Cp_2Rh_2(CO)_2(NO)]^+$ and has ν(NO) = 1859 cm^{-1}. However, the corresponding η^2-cyclooctene and η^2-cyclohexadiene complexes were fully characterized,[25] and an unstable cobalt complex with η^2-cyclooctadiene, $[CpCo(C_8H_{14})(NO)]^+$, is also known.[30]

The presence of the NO ligand, together with the cationic nature of the complex 1, facilitates ethylene substitution by halide ions. In each case, the initial result appears to be the formation of the neutral, mononuclear, half-sandwich complex (η^5-C_5Me_5)Ir(NO)X, but the stability decreases markedly as X$^-$ is changed from I$^-$ to Br$^-$ and Cl$^-$. The only other comparable nitrosyl halides of the

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(24) Dimas, P. A.; Shapley, J. R. *J. Organomet. Chem.* **1982**, *228*, C12.

(25) Clamp, S.; Connelly, N. G.; Howard, J. A. K.; Manners, I.; Payne, J. D.; Geiger, W.E. *J. Chem. Soc., Dalton Trans.* **1984**, 1659.

(26) Clamp, S.; Connelly, N. G.; Payne, J. D. *J. Chem. Soc., Chem. Commun.* **1981**, 897.

(27) These IR absorptions appear to be incorrectly assigned to the C_5H_5 analog in the preliminary communication (ref 26) by comparison with the full paper (ref 25).

(28) (a) Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437. (b) Ruiz, J.; Bentz, P. O.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, *11*, 2709. (c) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 737. (d) For photochemical substitution, see: Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911.

(29) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(30) Connelly, N. G.; Payne, J. D.; Geiger, W. E. *J. Chem. Soc. Dalton Trans.* **1983**, 295.

Table 10. IR and ^{1}H NMR Data for Cobalt Group Binuclear Complexes [(η^5-C_5R_5)$_2$$M_2$($\mu$-CO)($\mu$-NO)]$^+$

complex	ν(CO)	ν(NO)	δ(Cp*/Cp)	ref
[$Cp^*_2Rh_2$(CO)(NO)]BF_4	1867^a	1545^a	1.74^b	24
[$Cp^*_2Rh_2$(CO)(NO)]PF_6	1846^c	1524^c	1.75^b	25
[Cp_2Rh_2(CO)(NO)]PF_6	1897^c	1582^c	5.85^d	25
[$Cp^*_2Co_2$(CO)(NO)]PF_6	1857^a		1.52^e	26, 30
	1843^c	1552^c		
[Cp_2Co_2(CO)(NO)]PF_6	f	f	f	25, 26
[$Cp^*_2Ir_2$(CO)(NO)]BF_4	1811^g	1501^g	1.85^b	this work

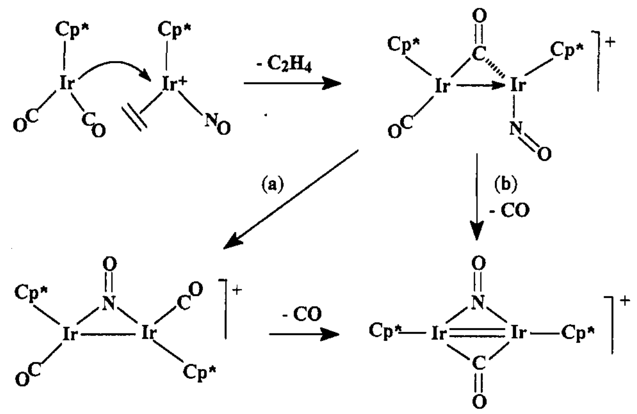
^{a} CH_2Cl_2. ^{b} $CDCl_3$. ^{c} Nujol. ^{d} CD_2Cl_2. ^{e} Acetone-d_6. ^{f} Data not reported. ^{g} KBr.

cobalt group that we have been able to find are CpCo(NO)X (X = Br, I), which were formed by reactions of $Cp_2Co_2(NO)_2$ with X_2.[31,32] Each of the iridium nitrosyl halides transforms in solution to products characterized by ^{1}H NMR Cp* methyl resonances in the range δ 1.54–1.66, and for X = Br or I X-ray crystallography has shown that the species with δ near 1.66 are the binuclear Ir(III) complexes *trans*-$Cp^*_2Ir_2X_2$(μ-X)(μ-NO). Surprisingly, in spite of the considerable literature on binuclear cyclopentadienyl nitrosyl compounds of cobalt, rhodium, and iridium, there do not seem to be any previous reports of direct analogs of these complexes.

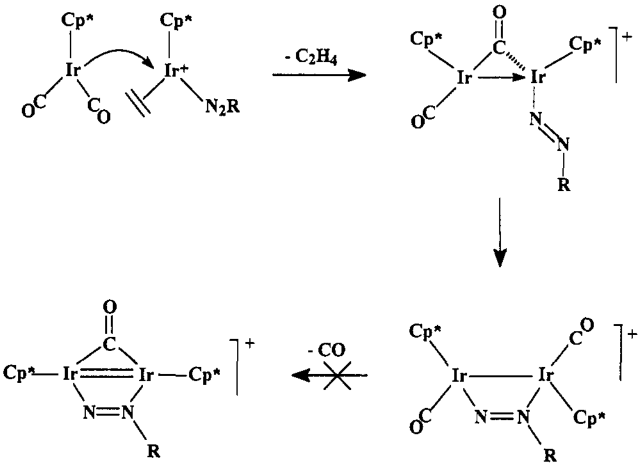
The nucleophile OEt^- is observed to undergo nucleophilic attack at the coordinated ethylene ligand in **1** with formation of the ethoxyethyl complex **4**. This reaction is similar to other instances where alkoxides have been observed to attack coordinated ethylene, such as the reaction of [CpPd(PPh_3)(C_2H_4)]$^+$ [33] or [CpFe(CO)$_2$(C_2H_4)]$^+$.[34,35]

As indicated in Table 10, the binuclear nitrosyl carbonyl complexes of the type [(η-C_5R_5)$_2$$M_2$($\mu$-CO)($\mu$-NO)]$^+$ have been synthesized previously for both cobalt and rhodium with both Cp and Cp* ligands,[24-26,30] though the complex [Cp_2Co_2(μ-CO)(μ-NO)]$^+$ does not appear to have been isolated in a pure state.[25,26] No corresponding iridium complex has been synthesized other than [$Cp^*_2Ir_2$(μ-CO)(μ-NO)]$^+$ described here. The cobalt[30] and rhodium[24,25] compounds have been prepared by the reaction of (η^5-C_5R_5)M(CO)$_2$ (M = Co, Rh; R = H, Me) with $NOBF_4$ or $NOPF_6$, and the structure of [$Cp^*_2Rh_2$(μ-CO)(μ-NO)]$^+$ has been determined by X-ray diffraction.[25] The analogous reaction of Cp*Ir(CO)$_2$ with $NOBF_4$ did not result in any observable formation of [$Cp^*_2Ir_2$(μ-CO)(μ-NO)]$^+$ or any other nitrosyl complex under the conditions employed. Instead, the binuclear complex [$Cp^*_2Ir_2$(CO)$_3$Cl]$^+$ was formed (by using CH_2Cl_2 as the solvent) and the NO^+ appeared to function solely as an oxidant, as did also arenediazonium ion which gave the same product.[36]

Scheme 2



Scheme 3



The formation of [$Cp^*_2Ir_2$(μ-CO)(μ-NO)]$^+$probably results from attack of the electron-rich Lewis base[3c] Cp*Ir(CO)$_2$ at the metal of the cationic nitrosyl complex [Cp*Ir(NO)(C_2H_4)]$^+$ (Scheme 2) to form the bent nitrosyl intermediate illustrated. This then transforms to the product *via* loss of CO and C_2H_4 either by way of the binuclear dicarbonylnitrosyl intermediate shown in route a or directly, as in route b. This is essentially similar to the mechanism that was suggested[25] for the formation of the complexes [(η^5-C_5R_5)$_2$$M_2$($\mu$-CO)($\mu$-NO)]$^+$ (M = Co, Rh) from the reaction of (η^5-C_5R_5)M(CO)$_2$ and NO^+; [(η^5-C_5R_5)M(CO)(NO)]$^+$ is first formed and reacts with further (η^5-C_5R_5)M(CO)$_2$. In some instances the binuclear dicarbonylnitrosyl intermediate was isolable.[25] In the iridium case, the reaction is slow and IR or NMR monitoring did not reveal anything definitive as to the nature of possible intermediates. While the stoichiometry of the product requires the loss of one CO group, the prior dissociation of CO from Cp*Ir(CO)$_2$ seems rather unlikely under the reaction conditions employed, since thermolysis, of this dicarbonyl has been reported to require maintaining a temperature of 170 °C for 1 week.[37] Furthermore, a similar reaction of Cp*Ir(CO)$_2$ with the iridium aryldiazenido(ethylene) cation [Cp*Ir(C_2H_4)(p-$N_2C_6H_4OMe$)]$^+$ is known to proceed with loss of ethylene to produce a related binuclear dicarbonyl cation as the observed product (Scheme 3). In this case, however, one CO group has transferred to the adjacent Ir atom, presumably by a terminal–bridge–terminal rearrangement; and the corresponding carbonyl-loss product is not observed.[36]

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(31) (a) Brunner, H.; Wachsmann, H. *J. Organomet. Chem.* **1968**, *15*, 409. (b) Brunner, H.; Loskot, S. *Z. Naturforsch. (B)* **1973**, *28B*, 314.

(32) There is also a report of the suspected formation of (η^5-C_5Ph_5)Rh(NO)I (ν(NO) 1798 cm^{-1}), see: Connelly, N. G.; Raven, S. J.; Geiger, W. E. *J. Chem. Soc. Dalton Trans.* **1987**, 467.

(33) (a) Kurosawa, H.; Asada, N. *Tetrahedron Lett.* **1979**, 255. (b) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996.

(34) (a) Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. *J. Organomet. Chem.* **1970**, *25*, 207. (b) Lennon, P.; Madhavaras, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.

(35) For a review of nucleophilic attack on coordinated alkenes see: (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, NY, 1986; Vol. 1, Chapter 14, pp 897–938. (b) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(36) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424.

(37) Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.

Conclusion

The synthesis and characterization of the half-sandwich iridium nitrosyl ethylene cationic complex [Cp*Ir(NO)(C_2H_4)][BF_4] (**1**) has been described, including the crystal structure. This compound provides a convenient entry into cyclopentadienyl iridium nitrosyl chemistry, which is a hitherto unexplored area. The corresponding cobalt and rhodium analog of **1** is either unknown (Co) or has not been isolated (Rh). We have begun an investigation of the chemistry of **1**. Substitution of ethylene by halide ions occurs readily, but the simple mononuclear product Cp*Ir(NO)X displays an increased tendency to convert to binuclear products of the type $Cp^*_2Ir_2X_2(\mu\text{-}NO)(\mu\text{-}X)$ as the halide is changed from iodide to bromide and chloride. The crystal structures of the iodide **2** and bromide **3** were determined. By way of contrast, ethoxide did not effect ethylene displacement, but attacked it to give the ethoxyethyl complex **4**, an indication that other alkyl(nitrosyl) complexes should be synthesizable in this system. The ethylene in **1** can also be displaced by an electron-rich metal base, in this case Cp*Ir$(CO)_2$, to give a binuclear product. We are continuing to explore further reactions of **1** in an effort to develop this area.

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Supplementary Material Available: Tables of supplementary crystallographic data, atomic coordinates and temperature factors, bond lengths and angles, and selected intramolecular torsion angles for compounds 1-4 (24 pages). Ordering information is given on any current masthead page.

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