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Solvent Dependence of the Reaction of $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ with Aryldiazonium Ions. Synthesis and Characterization of Mono- and Diiridium Carbonyl Complexes Including the X-ray Structures of $[\{(\eta^5\text{-}C_5Me_5)Ir(CO)\}_2(1\text{-}\eta^1\text{-}1,2\text{-}\eta^2\text{-}p\text{-}C_6H_4OMe)][BF_4]$ and $[(\eta^5\text{-}C_5Me_5)(CO)_2Ir{-}Ir(CO)(Cl)(\eta^5\text{-}C_5Me_5)][BF_4]$

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Reaction of $Cp^*Ir(CO)_2$ (**3**, $Cp^* = \eta^5\text{-}C_5Me_5$) with $[N_2Ar][BF_4]$ ($Ar = p\text{-}C_6H_4OMe$) in *acetone* at −78 °C affords the nitrogen extrusion product $[Cp^*Ir(CO)_2(Ar)][BF_4]$ (**5**), but *in dichloromethane* it yields a dinuclear product $[Cp^*(CO)_2Ir{-}Ir(Cl)(CO)Cp^*][BF_4]$ (**6**). By carrying out this very reaction in *ethanol* solution, a nitrogen-retained product $[Cp^*Ir(CO)(OEt)(NHNAr)][BF_4]$ (**7**) is obtained, containing an aryldiazene ligand. Deprotonation of **7** gives quantitatively the neutral doubly-bent aryldiazenido complex $Cp^*Ir(CO)(OEt)(N_2Ar)$ (**8**). The IR ν(CO) absorptions measured for the dinuclear compound **6** indicate no bridging carbonyl, but a ^{13}C NMR study in solution shows that **6** is stereochemically nonrigid at ambient temperature; its three carbonyl ligands are all involved in a fast exchange process, and this process is frozen at −86 °C. Exchange of the CO groups via a terminal−bridging−terminal process accompanied by rotation about the Ir−Ir axis is suggested. The molecular structure of **6** in the solid state has been established by single crystal X-ray crystallographic analysis and is consistent with the solution spectra. By reaction of $[N_2Ar][BF_4]$ with the dinuclear complex $[Cp^*Ir(CO)]_2$ (**4**) in acetone, the complex $[\{Cp^*Ir(CO)\}_2(1\text{-}\eta^1\text{-}1,2\text{-}\eta^2\text{-}p\text{-}C_6H_4OMe)][BF_4]$ (**9**) with a rare σ,π-bridging aryl group has been obtained and crystallized. The molecular structure containing an asymmetric bridging aryl group is established for **9** in the solid state by a single crystal X-ray crystallographic analysis. However, the identical ^1H NMR features observed at ambient temperature and −90 °C in solution (i.e., a singlet resonance for the two Cp* ligands and a symmetric AA′BB′ pattern for the $p\text{-}C_6\mathit{H}_4OMe$) indicate a static or time-averaged symmetrical molecular geometry for **9**. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.583(2)$ Å, $b = 14.256(3)$ Å, $c = 16.818(4)$ Å, $\beta = 95.91\ (2)°$, $V = 2523.9$ Å^3, and $Z = 4$. Refinement yielded $R_F = 0.027$ and $R_{wF} = 0.033$ for 3299 observed reflections ($I_o \geq 2.5\sigma(I_o)$) of 4427 unique reflections. Compound **9** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.695(2)$ Å, $b = 19.911(3)$ Å, $c = 12.539(2)$ Å, $\beta = 96.54(1)°$, $V = 2900.8$ Å^3, and $Z = 4$. Refinement yielded $R_F = 0.025$ and $R_{wF} = 0.035$ for 3444 observed reflections ($I_o \geq 2.5\sigma(I_o)$) of 4526 unique reflections.

Introduction

Since the first transition metal complex containing a stable aryldiazenido ligand, $CpMo(CO)_2(N_2Ph)$, was reported by King and Bisnette in 1964,[1] numerous such compounds have been synthesized and an interesting range of coordination geometries for the N_2Ar ligand has been established from their crystallographic studies.[1b,2] With the wealth of the structural chemistry displayed by these compounds, an understanding of the electronic interactions engendering the different geometries of the aryldiazenido ligand is naturally appealing. A valuable theoretical contribution to this has been made by Hoffmann et al. by using $N_2\mathit{H}$ as the modeling ligand, whereby a general correlation of the geometric preference of a diazenido ligand to the electronic structure of the complex has been elucidated.[3]

However, with a synthetic point of view, we are more interested in how the stabilities and reactivities of an *aryl*diazenido ligand in a given complex are influenced by a systematic change of the natures of the metal and the ligands present in the complex. In this latter regard, our recent research efforts, both in the experimental arena and in the theoretical domain, have therefore been directed at investigating the effects exerted on the aryldiazenido ligand by different ancillary ligands L in a complex with a general formula $[Cp^*Ir(L)(p\text{-}N_2C_6H_4\text{-}OMe)]^n$ ($n = 0$, or $+1$).[4−6] Experimentally, we have to date demonstrated that the singly-bent aryldiazenido fragment $Cp^*Ir(p\text{-}N_2C_6H_4OMe)$ prefers to bind a weak π-acid as the ancillary ligand L,[5] and when a π-base ligand is used for L, no stable analogous two-legged piano stool molecule can be obtained. Especially, in the latter case, when the π-basicity of L is strong enough, *e.g.*, iodide, a novel asymmetric bis(aryldiazenido)-bridged diiridium complex is obtained, which is believed to be formed through a doubly-bent aryldiazenido intermediate species

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with a formal 16e metal center.[5c,6] On the other hand, these experimental facts have been successfully rationalized, and in some cases predicted, by the theoretical considerations derived from a combination of symmetry arguments and EHMO calculations carried out on the N_2Ph^+ ligand.[4−7] From this, it was further anticipated that when L is a strong π-acid such as CO or CN^-, both L and the aryldiazenido ligand in the chosen system would have a strong tendency to mutually labilize each other, which might essentially lead to dissociation of one, or even both, of these two ligands in the system.[4,6]

In this work, we report experimental efforts that have attempted to test this theoretical prediction. Specifically, attempted synthesis of the unknown complex [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**), where the carbonyl is a strong π-acid, has been the main target. As possible synthetic routes to **1**, we have examined (i) reactions of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] (**2**) with carbon monoxide under different reaction conditions, (ii) reactions of Cp*Ir$(CO)_2$ (**3**) directly with [*p*-$N_2C_6H_4OMe$][BF_4] under different reaction conditions, and (iii) reactions of [Cp*Ir(CO)]$_2$ (**4**) with [*p*-$N_2C_6H_4OMe$][BF_4]. Despite these different synthetic strategies and numerous attempts, we have had no success in obtaining **1** to date.

On the other hand, the results that have emerged from these attempts are nevertheless interesting and informative. For example, a strong solvent dependence has been observed for the reaction of **3** with [*p*-$N_2C_6H_4OMe$][BF_4], in which the N_2-extrusion products [Cp*Ir$(CO)_2$(*p*-C_6H_4OMe)][BF_4] (**5**) and [Cp*$(CO)_2$Ir−Ir(Cl)(CO)Cp*][BF_4] (**6**)[8,9] were obtained in acetone and CH_2Cl_2, separately, but a N_2-retained aryl*diazene* complex [Cp*Ir(CO)(OEt)(*p*-$NHNC_6H_4OMe$)][BF_4] (**7**) was obtained in ethanol. Furthermore, reaction of **4** with [*p*-$N_2C_6H_4OMe$][BF_4] afforded an interesting N_2-elimination product [Cp*$_2$Ir$_2$(CO)$_2$(1-η^1-1,2-η^2-*p*-C_6H_4OMe)][BF_4] (**9**), which X-ray crystallographic analysis shows to possess a rare bridging aryl group in the solid state. Several new facile synthetic routes to the known compound **4**[10] were developed during this work and are reported.

Experimental Section

All reactions and manipulations were conducted under anhydrous and anaerobic conditions using typical Schlenk-tube techniques under nitrogen. All solvents were dried and freshly distilled under nitrogen by the appropriate procedures.

Infrared spectra for solutions were measured in CaF_2 cells, and solid samples were measured either as KBr pellets or as a thin film on a KBr disk 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 spectrometer. The remaining ^1H NMR and ^{15}N NMR spectra were obtained in the NMR service of Simon Fraser University by Mrs. M. Tracey on a Bruker AMX-400 instrument at operating frequencies of 400.1 and 40.5 MHz for ^1H, and ^{15}N, respectively. Chemical shifts (δ) are reported in parts per million, downfield positive, relative to tetramethylsilane (TMS) for ^1H and relative to external nitromethane for ^{15}N spectra. Coupling constants are reported in hertz. Fast atom bombardment (FAB) or electron impact (EI) mass spectra were obtained by Mr. G. Owen on a Hewlett-Packard Model 5985 GC-MS spectrometer equipped with a fast atom bombardment probe (xenon source, Phrasor Scientific, Inc., accessory) and utilized samples dispersed or dissolved in thioglycerol. The pattern of the envelopes of the fragment ions were matched with that simulated by computer for the species in question, and in all cases the *m/z* value quoted is that for the most intense peak. Microanalyses for C, H, and N were performed by Mr. M.-K. Yang of the Microanalytical Laboratory of Simon Fraser University.

The [*p*-$N_2C_6H_4OMe$][BF_4] was prepared by the standard procedure using *p*-methoxyaniline (Aldrich) and sodium nitrite and purified periodically by recrystallization from acetone and diethyl ether. The diazonium salt substituted with ^{15}N at the terminal nitrogen (N_α) was prepared by using $Na^{15}NO_2$ (95% ^{15}N, MSD Isotopes) and was employed for the syntheses of ^{15}N-labeled compounds. [Cp*$IrCl_2$]$_2$, Cp*Ir(CO)Cl_2, and Cp*Ir$(CO)_2$ (**3**) were synthesized by the Maitlis method.[11] The known complex [Cp*Ir(CO)]$_2$ (**4**)[10] was made in high yield by four different methods detailed below. The syntheses of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] (**2**), as well as its isotopomer [Cp*Ir(C_2H_4)(*p*-$^{15}N_\alpha NC_6H_4OMe$)][BF_4] (**2a**), have been reported previously.[4,5a]

Four Convenient Synthetic Routes to [Cp*Ir(CO)]$_2$ (4).[10] Method 1. Cp*Ir(CO)Cl_2 (100 mg, 0.234 mmol) and excess predried anhydrous Na_2CO_3 ($\approx$500 mg) in 10 mL ethanol were refluxed for about 2 h with vigorous stirring. During the reaction, the orange yellow suspension of Cp*Ir(CO)Cl_2 slowly disappeared, and a brownish slurry was gradually produced. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2 (*ca*. 20 mL) and filtered through a Celite filter. Evaporating the dark green CH_2Cl_2 extract to dryness afforded the desired product quantitatively as a brownish powder. The product was recrystallized from CH_2Cl_2/hexanes with a typical yield >80%. IR: ν(CO) 1676 cm^{-1} (CH_2Cl_2). ^1H NMR($CDCl_3$): δ 1.79 (s, Cp*). EIMS (*m/z*): 710 (M^+), 680 ($M^+ - CO - 2H$), 648 ($M^+ - 2CO - 6H$), 463 ([Cp*$_2$Ir]$^+$).

Method 2. A reaction similar to method 1, but using a 2:1 molar ratio of Cp*Ir$(CO)_2$ and [Cp*$IrCl_2$]$_2$ under reflux with Na_2CO_3 for 3 h, gave **4** in 92% yield.

Method 3. To a Schlenk tube containing a solution of Cp*Ir(CO)Cl_2 (100 mg, 0.234 mmol) in anhydrous ethanol (20 mL) was added excess zinc dust ($\approx$500 mg). This mixture was degassed twice and then stirred vigorously overnight (*ca*. 14 h) at room temperature. When Cp*Ir(CO)Cl_2 had completely disappeared (monitored by IR), the solution was pumped to dryness, and the residue was extracted with CH_2Cl_2 (3 × 5 mL). Removal of the solvent from the combined extraction solution *in vacuo* gave **4**, generally in >90% yield.

Method 4. A reaction similar to method 3, but using a 2:1 molar ratio of Cp*Ir$(CO)_2$ and [Cp*$IrCl_2$]$_2$, also gave **4** in high yield.

Reaction of Cp*Ir$(CO)_2$ with [*p*-$N_2C_6H_4OMe$][BF_4] in *Acetone*—Formation of [Cp*Ir$(CO)_2$(*p*-C_6H_4OMe)][BF_4] (5). To a vigorously stirred, yellow solution of Cp*Ir$(CO)_2$ (**3**) (20 mg, 0.052 mmol) in acetone (2 mL) at −78 °C (dry ice/ethanol bath) was added an acetone solution ($\sim$1 mL) of [*p*-$N_2C_6H_4OMe$][BF_4] (12 mg, 0.052 mmol) dropwise along the wall of the Schlenk tube. The addition of the diazonium solution should be slow enough to ensure that this solution cools significantly before it mixes with the bulk reaction solution. The color of the reaction solution first changed from yellow to bright red and then to dark brown in a few seconds as the addition proceeded. After the addition was complete, the reaction mixture was stirred for another hour at the same temperature, and then 10 mL of diethyl ether was slowly added with vigorous stirring. A dark brown precipitate formed upon the addition of the diethyl ether. After the precipitate settled, the supernatant solution was carefully removed by pipet and the solid residue was washed three times with cold ether. Still at −78 °C, the dark brown precipitate was dried *in vacuo*, leaving [Cp*Ir$(CO)_2$(*p*-C_6H_4OMe)][BF_4] (**5**) as the product in 80% yield. IR: ν(CO) 2114 (m), 2074 (m) cm^{-1} (acetone). ^1H NMR ($CDCl_3$): δ 2.19 (s, 15H, $C_5(CH_3)_5$), 3.80 (s, 3H, OCH_3), 6.95 (q, AA′BB′ pattern, 4H, C_6H_4). FABMS (*m/z*): 491 (M^+), 463 ($M^+ - CO$), 433 ($M^+ - CO - OCH_2$), 405 ($M^+ - 2CO - OCH_2$). Anal. Calcd: C, 39.50; H, 3.84. Found: C,39.81; H, 3.85.

Reaction of Cp*Ir$(CO)_2$ with [*p*-$N_2C_6H_4OMe$][BF_4] in *CH_2Cl_2*—Formation of [Cp*$(CO)_2$Ir−Ir(Cl)(CO)Cp*][BF_4] (6). To

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a yellow solution of Cp*Ir(CO)$_2$ (**3**) (100 mg, 0.26 mmol) in 3 mL of CH_2Cl_2 at room temperature was directly added solid [*p*-$N_2C_6H_4OMe$][BF_4] (30 mg, 0.13 mmol), and the reaction mixture was stirred vigorously. The color of the reaction mixture changed from yellow to greenish. To completely dissolve the [*p*-$N_2C_6H_4OMe$][BF_4] could take about 1 h. Gas effervescence was obvious initially but gradually diminished over 1 h as all aryldiazonium salt dissolved. After another 3−4 h of stirring, a large amount of fine yellow powder formed. The IR spectrum of the solution after *ca.* 6 h showed that **3** was completely consumed. The solution was concentrated under reduced pressure to *ca.* 1.5 mL, and excess hexane was added to complete precipitation of the yellow powder. The supernatant solution was carefully removed by pipet, and the yellow solid residue was washed twice with diethyl ether, affording the analytically pure product [Cp*(CO)$_2$Ir−Ir(Cl)(CO)Cp*][BF_4] (**6**) (85%). IR: ν(CO) 2058 (m), 2017 (s, br) cm^{-1} (CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 15H, $C_5(CH_3)_5$), 2.23 (s, 15H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.17, 10.39 and 103.05, 106.67 ($C_5(CH_3)_5$), 171.37 (CO). FABMS (*m/z*): 775 (M$^+$), 745 (M$^+$ − CO − 2H), 717 (M$^+$ − 2CO − 2H). Anal. Calcd: C, 31.98; H, 3.50. Found: C, 32.08; H, 3.51.

Alternative Synthesis of 6. Gently bubbling CO into a suspension of [Cp*IrCl_2]$_2$ (300 mg, 0.376 mmol) in 20 mL of freshly distilled benzene changed the color of the reaction mixture completely to yellow in ∼0.5 h. After another 2.5 h, CO was stopped, and Cp*Ir(CO)$_2$ (288 mg, 0.753 mmol) and then AgBF_4 (146 mg, 0.753 mmol) were added. With the addition of AgBF_4, the color of the solution immediately changed to orange and a large amount of orange precipitate was formed. Removal of the solvent *in vacuo* gave an orange residue that was redissolved into acetone. The grey precipitate of AgCl was removed by filtration through Celite, and addition of excess diethyl ether to the filtrate resulted in an orange precipitate. The supernatant solution was carefully removed by pipet, and the orange precipitate was washed twice with diethyl ether, affording the product **6** in 72% yield (310 mg). IR: ν(CO) 2058 (m), 2017 (s, br) cm^{-1} (CH_2Cl_2).

Reaction of Cp*Ir(CO)$_2$ with [*p*-$N_2C_6H_4OMe$][BF_4] in *Ethanol*—Formation of [Cp*Ir(CO)(OEt)(*p*-$NHNC_6H_4OMe$)][BF_4] (7), or 7a. To a solution of Cp*Ir(CO)$_2$ (**3**) (20 mg, 0.052 mmol) in ethanol (10 mL) was added solid [*p*-$N_2C_6H_4OMe$][BF_4] (11.5 mg, 0.052mmol) at room temperature. The color of the solution changed from yellow to orange. IR spectra showed that absorptions (2015 and 1945 cm^{-1}) due to Cp*Ir(CO)$_2$ slowly decreased and a new band at 2058 cm^{-1} increased. After 1 h, the solvent was removed *in vacuo*, affording an orange-colored oily product. The complete characterization of this compound was unsuccessful due to its very poor stability upon complete removal of ethanol or after it was dissolved in other solvents. IR: ν(CO) 2058 cm^{-1} (EtOH). ^{1}H NMR (measured in less than 5 min after dissolving in acetone-d_6): δ 1.12 (t, J_{H-H} = 7, 3H, *Me*CH_2O), 1.96 (s, 15H, $C_5(CH_3)_5$), 3.85 (s, 3H, OMe), 3.97 (b, m, 2H, MeCH_2O), 7.10 (q, AA′BB′ pattern, 4H, C_6H_4). FABMS (*m/z*): 491 (M$^+$ − EtOH), 463 (M$^+$ − EtOH − CO).

The $^{15}N_\alpha$-substituted complex **7a** was synthesized analogously to compound **7** by using [*p*-$^{15}N_\alpha NC_6H_4OMe$][BF_4]. ^{15}N NMR (ethanol): δ −154 (d, $J^{15}{}_{N-H}$ = 88, $^{15}N_\alpha$−H).

Preparation of Cp*Ir(CO)(OEt)(*p*-$N_2C_6H_4OMe$) (8), or 8a. To an orange solution of freshly synthesized **7** *in situ* in 5 mL of ethanol was added *ca.* 0.2 mL (3 drops) of Et_3N. The color of the reaction solution changed immediately to red. The solvent was removed *in vacuo*, and an excess of hexanes was added to extract the neutral product. After removing the insoluble [Et_3NH][BF_4] through a Celite filter, the filtrate was then evaporated to dryness, resulting in a red oily product **8** in ∼80% yield (based on the amount of Cp*Ir(CO)$_2$ used). IR: ν(CO) 2025 (EtOH), 2029 cm^{-1} (hexanes). ^{1}H NMR (benzene-d_6): δ 1.15 (t, J_{H-H} = 7, 3H, *Me*CH_2O), 1.68 (s, 15H, $C_5(CH_3)_5$), 3.28 (s, 3H, OMe), 4.17 (dq, $^2J_{H-H}$ = 10, $^3J_{H-Me}$ = 7, 1H, MeCH_2O), 4.35 (dq, $^2J_{H-H}$ = 10, $^3J_{H-Me}$ = 7, 1H, MeCH_2O), 6.83 (q, AA′BB′ pattern, 4H, C_6H_4). EIMS (*m/z*): 536 (M$^+$), 508 (M$^+$ − CO), 491 (M$^+$ − EtO), 463 (M$^+$ − EtO − CO), 433 (M$^+$ − EtO − CO − OCH_2). Anal. Calcd: C, 44.85; H, 5.08; N, 5.23. Found: C, 45.01; H, 5.12; N, 5.41.

The $^{15}N_\alpha$-substituted complex **8a** was synthesized analogously to compound **8** by using **7a**. ^{15}N NMR (benzene-d_6): δ 223.5 (s, $^{15}N_\alpha$).

Table 1. Crystallographic Data for the Structure Determination of Complexes **6** and **9**

complex	**6**	**9**
formula	$Ir_2F_4O_3ClC_{23}BH_{30}$	$Ir_2F_4O_3C_{29}BH_{37}$
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	10.583(2)	11.695(2)
b (Å)	14.256(3)	19.911(3)
c (Å)	16.818(4)	12.539(2)
β (deg)	95.91(2)	96.54(1)
Z	4	4
V (Å^3)	2523.9	2900.8
ρ (g/cm^3)	2.266	2.072
μ(Mo Kα) (mm^{-1})	10.66	9.19
cryst size (mm)	0.30 × 0.30 × 0.17	0.10 × 0.32 × 0.33
l(Mo Ka$_1$) (Å)	0.709 30	0.709 30
transmn	0.169−0.300	0.150−0.514
min − max 2θ (deg)	4−50	4−48
scan type	$\omega - 2\theta$	$\omega - 2\theta$
scan range (deg)	1.00 + 0.35 tan θ	0.75 + 0.35 tan θ
scan speed (deg/min)	0.82−5.49	0.70−5.50
R_F[a]	0.027	0.025
R_{wF}[b]	0.033	0.035
GOF[c]	2.57	1.29

[a] $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$ for observed data ($I_o \geq 2.5\sigma(I_o)$). [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for observed data ($I_o \geq 2.5\sigma(I_o)$). [c] GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom})^{1/2}$

X-ray Structure Determination of [Cp*(CO)$_2$Ir−Ir(Cl)(CO)Cp*][BF_4] (6).[12] The crystallization of [Cp*(CO)$_2$Ir−Ir(Cl)(CO)Cp*][BF_4] (**6**) was conducted with the slow diffusion of a large amount of diethyl ether into a saturated CH_2Cl_2 solution of the complex. A suitable yellow crystal was mounted on a glass fiber. Data were acquired using an Enraf-Nonius CAD-4F diffractometer employing graphite monochromatized Mo K$_\alpha$ radiation. Crystallographic data for **6** are summarized in Table 1.

Anisotropic thermal motion, based on indications from the electron density difference Fourier maps, was refined for Ir, Cl, O, and F atoms in the structure, to yield physically reasonable values. All hydrogen atom positions were assigned by calculation using a C−H distance of 0.96 Å and were input as fixed contributions in the subsquent calculations; their idealized positions were recalculated between cycles of refinement. Isotropic thermal parameters were assigned to these hydrogen atoms, on the basis of those of their attached carbon atoms.

A weighting scheme based on counting statistics was used in the final refinement, where the weight w was calculated from $w = [(\sigma(F_o))^2 + 0.00035F_o{}^2]^{-1}$. A final full matrix least-squares refinement of 187 parameters, for 64 atoms, converged to R_F = 0.027 and R_{wF} = 0.033 with a maximum shift of less than 0.05 σ. In the final difference Fourier map, the highest peak had an electron density 1.2(2) e/Å^3 and was located in the anion region at a distance of 0.38 Å from one F atom.

Scattering factors for neutral atoms were used in the calculation of the structure factors, including anomalous dispersion terms for all non-hydrogen atoms.[13] All calculations were performed on a micro VAX-II computer by using the NRC VAX Crystal Structure System.[14]

Preparation of [Cp*$_2$Ir$_2$(CO)$_2$(1-η^1-1,2-η^2-*p*-C_6H_4OMe)][BF_4] (9). A solution of [*p*-$N_2C_6H_4OMe$][BF_4] (16 mg, 0.07 mmol) dissolved in *ca.* 2 mL of acetone was added dropwise to a solution of [Cp*Ir(CO)]$_2$ (**4**) (50 mg, 0.07 mmol) in 5 mL of acetone at −78 °C. The color of the reaction solution changed immediately from deep green-yellow to dark red. After stirring for 30 min, the IR spectrum of the solution showed only one broad absorption at 1964 cm^{-1}. The solvent was then removed under reduced pressure, leaving a dark red foam. Recrystallization of this dark red residue from CH_2Cl_2/hexanes at −10 °C yielded dark red crystals (<10% yield), suitable for X-ray

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(12) Detailed X-ray single crystallographic analyses for **6** and **9** are given in Supporting Information.

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

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crystallographic analysis, covered by the dark red oil. ^{1}H NMR spectra of the crystals and the oil showed identical spectral features. IR: ν(CO) 1964 (s), 1990 (w, sh), cm^{-1} (acetone); 1964 (s), 1995 (w, sh) cm^{-1} (ethanol), and 1968 (s), 1993 (w) cm^{-1} (CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 30H, Cp*), 3.85 (s, 3H, OMe), 6.52 d and 6.92 d (4H, AA′BB′ pattern, C_6H_4). FABMS (*m/z*): 819 (M$^+$), 789 (M$^+$ − CO), 763 (M$^+$ − 2CO). Anal. Calcd: C, 38.50; H, 4.12. Found: C, 38.30; H, 4.00.

X-ray Structure Determination of [Cp*$_2$Ir$_2$(CO)$_2$(1-η^1-1,2-η^2-*p*-C$_6$H$_4$OMe)][BF$_4$] (9).[12] Crystals were obtained from CH_2Cl_2/hexane at −15 °C. A red crystal of **9** was mounted in a Lindemann capilliary tube using vacuum grease as adhesive. Intensity data (Mo K_α/graphite monochromator) were collected using an Enraf-Nonius CAD-4F diffractometer. Data reduction included corrections for Lorentz and polarization effects and intensity scale variations. Crystallographic data for compound **9** are summarized in Table 1.

The BF_4^- ion displayed considerable orientational disorder/thermal motion and was ultimately modeled as three BF_4^- groups with refined partial occupancies restrained to total one and subject to restraints which imposed regular tetrahedral bonding about the boron sites. A single isotropic thermal parameter was refined for all fluorine atoms and one for boron. All hydrogen atoms were placed in calculated positions (C−H, 0.95 Å) and were assigned isotropic thermal parameters dependent on those for the corresponding carbon atoms. During refinement, the phenyl hydrogen atom parameter shifts were linked with those for the corresponding parameters of the carbon atoms to which they were bound. Each CH_3 group was refined as a rigid group subject to restraints which maintained axial symmetry for the CCH_3 fragment. A single parameter was refined for the isotropic thermal motion of all methyl hydrogen atoms. Anisotropic thermal parameters were refined for those ordered atoms which showed evidence of significant anisotropic motion in electron density difference maps, namely, iridium, oxygen atoms of the carbonyl groups, and the carbon atoms of the Cp* ligands. An extinction coefficient was also refined. Final full matrix least-squares refinement included 342 parameters for 3444 data ($I_o \geq 2.5\sigma(I_o)$) and 64 restraints. A weighting scheme, based on counting statistics, was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $\sin(\theta/\lambda)$.

Complex scattering factors for neutral atoms[13] were used in the calculation of structure factors. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX Crystal Structure System.[14] The program suite CRYSTALS[15] was employed in the final refinement of **9**. All computations were carried out on a MicroVAX-II computer.

Attempts To Synthesize [Cp*Ir(CO)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (1) by Four Methods: (a) Reaction of [Cp*Ir(C$_2$H$_4$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2) with Excess Carbon Monoxide in Acetone. In a typical reaction, CO gas was bubbled through an acetone solution of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4$OMe)][BF_4] (**2**) (50 mg, 0.09 mmol) at room temperature. The IR spectrum of the reaction solution showed that Cp*Ir$(CO)_2$ (**2**) (ν(CO) = 1939 and 2009 cm^{-1}) was immediately formed as the major product.

(b) Reaction of [Cp*Ir(C$_2$H$_4$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2) with an Equimolar Amount of Carbon Monoxide in Acetone. An acetone solution of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4$OMe)][BF_4] (**2**) in a Schlenk tube equipped with a rubber serum stopper was injected with an equimolar amount of carbon monoxide gas. After stirring overnight (*ca.* 10 h), the IR spectrum of the solution showed that Cp*Ir$(CO)_2$ (**2**) (ν(CO) = 1939 and 2009 cm^{-1}) was the only observed product. After removing the solvent *in vacuo*, the ^{1}H NMR spectrum of the residue in acetone-d_6 showed Cp*Ir$(CO)_2$ (**3**) and unreacted compound **2** as the major components.

(c) Reaction of [Cp*Ir(C$_2$H$_4$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2) with Excess Carbon Monoxide in Ethanol. Carbon monoxide was slowly bubbled through an ethanol solution of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4$OMe)][BF_4] (**2**) for *ca.* 5 min. The color of the solution changed rapidly from yellow to orange-yellow. The IR spectrum of this solution showed a strong band at 2058 cm^{-1} due to compound **7** and two weak, equal intensity, peaks at 1945, 2015 cm^{-1} due to Cp*Ir$(CO)_2$ (**3**). After removing the solvent *in vacuo*, the ^{1}H NMR spectrum of the residue confirmed the presence of **3** and **7** but showed no signals due to the starting material **2**.

(d) Reaction of [Cp*Ir(CO)]$_2$ (4) with 2 Equiv of [*p*-N$_2$C$_6$H$_4$OMe][BF$_4$]. In a similar reaction to that described above for the synthesis of **9**, but using 2 equiv [*p*-$N_2C_6H_4$OMe][BF_4], compound **9**, together with some unreacted aryldiazonium salt, were found, as indicated by the IR and ^{1}H NMR spectra, in the final dark tar residue.

Results and Discussion

Reactions of Cp*Ir(CO)$_2$ with [*p*-N$_2$C$_6$H$_4$OMe][BF$_4$]. Previously, we have shown that Cp*Ir$(C_2H_4)_2$ can readily react with the aryldiazonium salt, [*p*-$N_2C_6H_4$OMe][BF_4], to produce the corresponding aryldiazenido complex **2**.[5a,b] Hence, its analogue Cp*Ir$(CO)_2$ (**3**) was initially thought to be a convenient entry to [Cp*Ir(CO)(*p*-$N_2C_6H_4$OMe)][BF_4] (**1**). However, despite numerous repetitions of this reaction under different conditions, varying the reaction temperature, solvents, and the stoichiometries of the starting materials, no [Cp*Ir(CO)(*p*-$N_2C_6H_4$OMe)][BF_4] (**1**) was ever obtained. A dark red tar was usually produced, which contained no nitrogen but otherwise gave irreproducible microanalysis results. However, a few of these attempts did produce reproducible products, and these are discussed next.

Formation of the Nitrogen Extrusion Products 5 and 6. Mixing equivalent quantities of **3** and [*p*-$N_2C_6H_4$OMe][BF_4] in *acetone* at −78 °C gave a bright red solution, which may be indicative of the coordination of the aryldiazenido ligand.[1b,16] However, this highly colored species did not survive long and the solution underwent a rapid further color change to dark red in a few seconds. From the resulting solution, a dark brown precipitate was isolated upon the addition of diethyl ether, which was then characterized by spectroscopy and elemental analysis as [Cp*Ir$(CO)_2$(*p*-C_6H_4OMe)][BF_4] (**5**), a nitrogen extrusion product. It should be noted here that although the IR, ^{1}H NMR, and mass spectroscopic features observed for **5** could also possibly be consistent with a product of formula [Cp*Ir(CO)(N_2)(*p*-C_6H_4OMe)][BF_4], a potential dinitrogen compound, the absence of nitrogen revealed by elemental analysis rules this out. The higher ν(CO)'s observed for **5**, at 2074 and 2114 cm^{-1} in acetone, compared to those observed for Cp*Ir$(CO)_2$ (**3**) (ν(CO) = 1939, 2009 cm^{-1} in acetone) are consistent with the higher oxidation state of the iridium in **5**. Similar IR shifts to higher wavenumbers for carbonyl ligands have been observed for other Ir(III) derivatives.[17]

By way of contrast, reaction of **3** with 0.5 equiv of [*p*-$N_2C_6H_4$OMe][BF_4] in *CH_2Cl_2* produces the diiridium complex [Cp*$_2$Ir$_2(CO)_3$Cl][BF_4] (**6**) in high yield. The solid state structure of complex **6** has been unequivocally established by single crystal X-ray crystallographic analysis (see Figure 1). The infrared spectral features exhibited by **6** in solution are also consistent with the molecular structure in the solid state. The observed ν(CO) bands in CH_2Cl_2 fall within the terminal carbonyl range. The absorption at 2058 cm^{-1} shows no unusual feature, but the strong band at 2017 cm^{-1} is broad and asymmetric, likely indicative of a superposition of two near-coincident peaks. The most structurally interesting feature for this compound in solution is that its ^{13}C NMR spectrum at room temperature shows only one signal, at δ 171.37 ppm, in the terminal carbonyl range. This clearly indicates that **6** is nonrigid in solution at room temperature, and the carbonyl ligands are rapidly exchanging on the NMR time scale. This has been further

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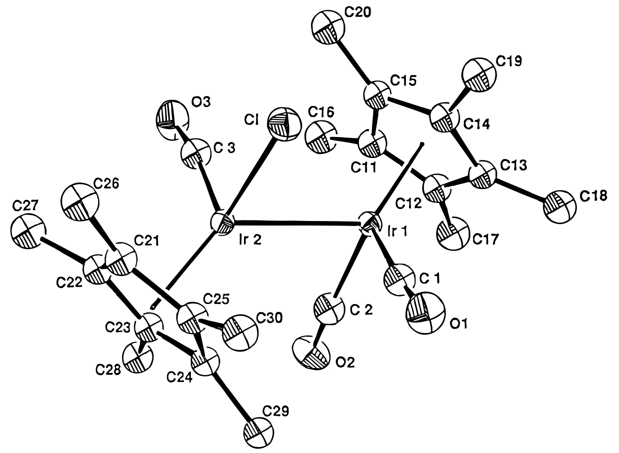
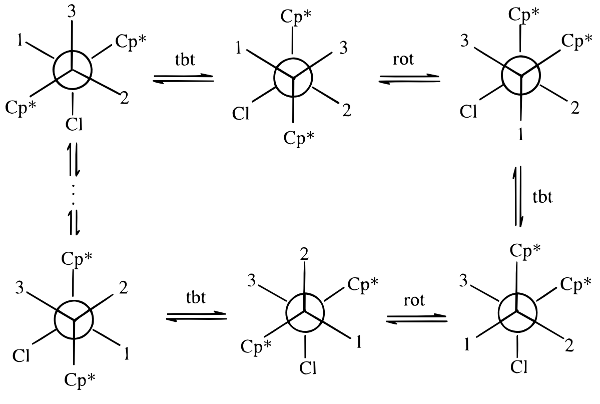


Figure 1. Perspective view of the cation of **6** showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are not shown.

Scheme 1. Proposed Fluxional Process Interconverting CO Groups in **6**



tbt = terminal-bridging-terminal transfer of the trans related carbonyls
rot = rotation of the metal-metal bond 120 degrees

confirmed by low temperature ^{13}C NMR spectroscopy. At −86 °C the singlet at δ 171.37 ppm decoalesces to two singlet signals at δ 173.0 and 168.2 ppm with an intensity ratio of 2:1. The first is assigned to the two CO groups of the Cp*Ir(CO)$_2$ fragment and the second to the CO of the Cp*Ir(CO)Cl fragment. While the former are diastereotopic and should ideally give separate resonances, their distance from the chiral center may be the reason for the single resonance observed. Since two chemically different Cp* groups can be clearly identified in both ambient temperature ^{1}H and ^{13}C NMR spectra, it can be concluded that the chloro ligand is not likely involved in the fluxional process. Consequently, we propose that the exchange of the carbonyl ligands of **6** occurs in a terminal−bridging−terminal fashion together with rotation relative to the metal−metal bond axis. This is illustrated in Newman projections in Scheme 1.

Formation of complexes **5** and, especially, **6** in the reactions clearly indicates a radical process is involved. Ready one-electron oxidation of Cp*Ir(CO)$_2$ (**3**) has been previously demonstrated by us in its reaction with [C(Ph)$_3$]$^+$, where the diiridium dication [Cp*(CO)$_2$Ir−Ir(CO)$_2$Cp*]$^{2+}$, formally a product of one-electron oxidation followed by radical coupling, was obtained.[8] The aryldiazonium ion was also known to be an excellent one-electron oxidizing agent long before it was shown to act as a ligand.[18] To account for this radical process, a mechanism of one electron oxidation of Cp*Ir(CO)$_2$ by the aryldiazonium ion is suggested (eqs 1−4). The neutral radical,

$$\text{Cp*Ir(CO)}_2 + [p\text{-N}_2\text{C}_6\text{H}_4\text{OMe}]^+ \rightarrow [\text{Cp*Ir(CO)}_2]^{\bullet+} + p\text{-N}_2\text{C}_6\text{H}_4\text{OMe}^\bullet \tag{1}$$

p-N$_2$C$_6$H$_4$OMe$^\bullet$, generated in eq 1, would readily lose N$_2$ to give the radical [p-C$_6$H$_4$OMe]$^\bullet$. This can then recombine with the cation radical [Cp*Ir(CO)$_2$]$^+$, in acetone, to yield the product **5** (eq 2). When the solvent is CH$_2$Cl$_2$, either p-N$_2$C$_6$H$_4$OMe$^\bullet$

$$[\text{Cp*Ir(CO)}_2]^{+\bullet} + [p\text{-C}_6\text{H}_4\text{OMe}]^\bullet \rightarrow \underset{(\mathbf{5})}{[\text{Cp*Ir(CO)}_2(p\text{-C}_6\text{H}_4\text{OMe})]^+} \tag{2}$$

or p-C$_6$H$_4$OMe$^\bullet$, can react with solvent to generate Cl$^\bullet$, which in turn could combine with [Cp*Ir(CO)$_2$]$^{\bullet+}$ to form the 18e cation [Cp*Ir(CO)$_2$Cl]$^+$ (eq 3). With excess of the nucleophile

$$[\text{Cp*Ir(CO)}_2]^{\bullet+} + \text{Cl}^\bullet \rightarrow [\text{Cp*Ir(CO)}_2\text{Cl}]^+ \tag{3}$$

(or electron-rich metal base) Cp*Ir(CO)$_2$ present, a carbonyl substitution reaction may then occur to give complex **6** (eq 4).

$$\text{Cp*Ir(CO)}_2 + [\text{Cp*Ir(CO)}_2\text{Cl}]^+ \rightarrow \underset{(\mathbf{6})}{[\text{Cp*Ir(CO)}_2{\rightarrow}\text{Cp*Ir(CO)Cl}]^+} + \text{CO} \tag{4}$$

So, in compound **6** the non-bridged metal−metal bond could be formally considered as a donor-acceptor dative bond[8,9] between Ir(I) and Ir(III). In this regard, compound **6** has also been subsequently synthesized from Cp*Ir(CO)$_2$ and Cp*Ir(CO)Cl$_2$ in the presence of AgBF$_4$. This alternative synthesis may simply be viewed as proceeding by the formation of the unsaturated (or solvated) 16-electron intermediate [Cp*Ir(CO)Cl]$^+$ which is then attacked by the base Cp*Ir(CO)$_2$ (eq 5).

$$\text{Cp*Ir(CO)}_2 + \text{Cp*Ir(CO)Cl}_2 \xrightarrow{\text{Ag}^+} \underset{(\mathbf{6})}{[\text{Cp*Ir(CO)}_2{\rightarrow}\text{Cp*Ir(CO)Cl}]^+} + \text{AgCl} \tag{5}$$

Reactions similar to the formation of **5** and **6** are known for other transition metal complexes. For example, aryl complexes resulted from reactions of [KCo{P(OMe))$_3$}$_4$][19a] and [CpFe(CO)$_2$]$^-$ [19b] with [N$_2$Ar]$^+$, and in a chlorinated solvent the reaction of [Tp′Mo(CO)$_3$]$^-$, Tp′ = BH(3, 5-dimethylpyrazolyl)$_3$,[19c] with [N$_2$Ar]$^+$ resulted in [Tp′Mo(CCl)(CO)$_2$], a product involving abstraction and coupling of a solvent-based radical. This type of radical process, initiated by one electron-transfer from the metal to N$_2$Ar$^+$, has, in fact, been known since

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Cp^*{}_2Ir_2(CO)_3Cl][BF_4]$ (**6**)

	Bond Lengths		
Ir(1)−Ir(2)	2.8266(6)	Ir(1)−Ir(2)	2.855[a]
Ir(1)−C(1)	1.907(10)	Ir(2)−Cl	2.3939(24)
Ir(1)−C(2)	1.901(11)	Ir(2)−C(3)	1.849(10)
Ir(1)−C(11)	2.239(10)	Ir(2)−C(21)	2.221(10)
Ir(1)−C(12)	2.235(10)	Ir(2)−C(22)	2.206(10)
Ir(1)−C(13)	2.257(9)	Ir(2)−C(23)	2.198(9)
Ir(1)−C(14)	2.241(10)	Ir(2)−C(24)	2.301(9)
Ir(1)−C(15)	2.323(10)	Ir(2)−C(25)	2.262(10)
Ir(1)−Cp*(1)[b]	1.904	Ir(2)−Cp*(2)[b]	1.879
O(1)−C(1)	1.129(13)	O(3)−C(3)	1.152(13)
O(2)−C(2)	1.119(13)		
	Bond Angles		
Ir(2)−Ir(1)−C(1)	79.2(3)	Ir(1)−Ir(2)−C(3)	85.3(3)
Ir(2)−Ir(1)−C(2)	85.3(3)	Ir(1)−Ir(2)−Cl	85.10(6)
Ir(2)−Ir(1)−Cp*(1)[b]	130.5	Ir(1)−Ir(2)−Cp*(2)[b]	133.2
C(1)−Ir(1)−Cp*(1)[b]	126.6	C(3)−Ir(2)−Cp*(2)[b]	124.2
C(2)−Ir(1)−Cp*(1)[b]	124.4	Cl−Ir(2)−Cp*(2)[b]	118.6
C(1)−Ir(1)−C(2)	96.7(4)	Cl−Ir(2)−C(3)	99.0(3)
Ir(1)−C(1)−O(1)	174.7(9)	Ir(2)−C(3)−O(3)	170.3(9)
Ir(1)−C(2)−O(2)	173.2(9)		

[a] Upper limit value corrected for thermal motion. [b] Cp* here signifies the center of mass of the respective C_5 rings.

the discovery of the Sandmeyer reaction in 1884.[20] However, despite the extensive use, and the significant success, of this type of reaction in preparative organic chemistry,[2a,d,e,18] the mechanism involved, whether an outer-sphere[18b,21] or an inner-sphere electron transfer,[18a] is still under debate. To account for this type of radical process in our system, a direct, or outer-sphere, electron transfer from the complex to the aryldiazonium ion appears unfavored. According to the Marcus theory,[22] the efficiency (or rate) of electron transfer in an outer-sphere mechanism is directly related to the thermodynamic driving force, *i.e.*, reduction potential, of the reductant, but relative to $Cp^*Ir(C_2H_4)_2$, the complex $Cp^*Ir(CO)_2$ has a lower metal-centred HOMO in energy, due to its strong π-electron withdrawing CO ligands, and hence it would be expected to be a poorer reductant than $Cp^*Ir(C_2H_4)_2$. In other words, if the radical decomposition was caused by a direct electron transfer from $Cp^*Ir(CO)_2$ to the aryldiazonium ion, the same process should also occur even more favorably when $Cp^*Ir(C_2H_4)_2$ is used. This latter situation, however, contrasts with our experimental observation that the reaction of $Cp^*Ir(C_2H_4)_2$ with aryldiazonium ion resulted in $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$, an obvious ligand substitution product.[4,5a,b]

Molecular Structure of 6. In the solid state, the crystal structure of **6** consists of discrete cations $[Cp^*{}_2Ir_2(CO)_3Cl]^+$ and the counter ions $[BF_4]^-$, separated by the normal van der Waals distances. There are no unusually short interionic contacts. The structure of the cation of **6** is shown in Figure 1. The selected interatomic distances and angles for **6** are listed in Table 2.

The two iridium atoms in the cation $[Cp^*{}_2Ir_2(CO)_3Cl]^+$ are both in the typical three-legged piano-stool coordination environment by sharing a common leg as a metal−metal bond. The Ir(1)−Ir(2) distance of 2.827(1) Å in **6** is the second longest Ir−Ir distance to be found in similar bis(pentamethylcyclopentadienyl)diiridium complexes. Complex $[Cp^*Ir(CO)_2]_2[BF_4]_2$ synthesized in this laboratory has the longest Ir−Ir bond length of 2.839(2) Å.[8] Since **6** and $[Cp^*Ir(CO)_2]_2[BF_4]_2$ are the only two known examples containing an Ir−Ir single bond without any bridging ligand, the long Ir−Ir single bonds observed in these two compounds are thus most likely due to the lack of supportive bridging ligands. The M−C and C−O distances in this compound are comparable with those of the dication complex.[8]

Formation of the Nitrogen-Retained Products 7 and 8. In *ethanol* solution, $Cp^*Ir(CO)_2$ reacted rapidly with an equivalent amount of $[p\text{-}N_2C_6H_4OMe][BF_4]$ at room temperature to produce an orange-yellow solution, from which an oily product could be obtained upon removal of the solvent. This orange oil was identified on the basis of IR, ^1H NMR, and ^{15}N NMR spectroscopies as the aryldiazene complex $[Cp^*Ir(CO)(OEt)(p\text{-}NHNC_6H_4OMe)][BF_4]$ (**7**), which was futher verified by deprotonation of the compound to yield a much more stable neutral aryldiazenido complex $Cp^*Ir(CO)(OEt)(p\text{-}N_2C_6H_4OMe)$ (**8**), containing a doubly bent aryldiazenido ligand (eqs 6 and 7).

$$Cp^*Ir(CO)_2 + [N_2Ar]^+ \xrightarrow[-CO]{EtOH} \underset{(\mathbf{7})}{[Cp^*Ir(CO)(OEt)(NHNAr)]^+} \tag{6}$$

$$\underset{(\mathbf{7})}{[Cp^*Ir(CO)(OEt)(NHNAr)]^+} + NEt_3 \rightarrow \underset{(\mathbf{8})}{Cp^*Ir(CO)(OEt)(N_2Ar)} + [NHEt_3]^+ \tag{7}$$

$$Ar = p\text{-}C_6H_4OMe$$

Since complex **7** is not stable in the ethanol-free state, it has been only partially characterized. The IR spectrum of **7** in EtOH shows a strong absorption at 2058 cm^{-1} for $\nu(CO)$. The N−H vibration was unobservable due to overlap with solvent O−H. No $\nu(NN)$ band could be assigned, even when the ^{15}N-enriched sample was used. However, the ^{15}N NMR spectrum of the $^{15}N_\alpha$-enriched sample of **7a** showed a doublet with a chemical shift at δ −154 ppm and a coupling constant of 88 Hz. Both the position of the resonance and the coupling constant indicate the presence of a terminally coordinated aryldiazene ligand in **7**.[5a,23] The ^1H NMR spectrum of this compound was measured immediately after it was dissolved in acetone-d_6. Except for the proton directly bonded to N_α, all other proton signals were observed in the appropriate resonance range and with the correct integration. Notably, the highest mass values (*m/z*: 489, 491) observed in the FABMS spectrum of **7** were not those of the parent, but the fragment from loss of EtOH, *i.e.*, $[Cp^*Ir(CO)(p\text{-}N_2C_6H_4OMe)]^+$ (ironically, the species we have been trying to obtain by synthesis).

As a matter of contrast, the complex $Cp^*Ir(CO)(OEt)(p\text{-}N_2C_6H_4OMe)$ (**8**), obtained by deprotonation of **7** *in situ*, showed a much higher stability either in solution or in the solid state. The infrared spectra of **8** exhibited $\nu(CO)$ at 2025 cm^{-1} in ethanol, which is 23 cm^{-1} lower than the corresponding $\nu(CO)$ observed in its parent compound **7**. This decrease in wavenumber, upon removal of the N_α proton, clearly indicates the sensitivity of the $\nu(CO)$ position to the N_α lone pair electrons of the aryldiazenido ligand in this three-legged piano-stool structure. Correlations of this kind have been previously

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discussed in detail in terms of the electronic interactions involved in this type of complex.[4−6] The ^{1}H NMR spectrum of **8** was recorded in C_6D_6. In addition to the resonances corresponding to the protons in the Cp* and *p*-$N_2C_6H_4OMe$ ligands, two well-resolved multiplets due to the two diastereotopic methylene protons of the OEt group were also observed. Most convincingly, the ^{15}N NMR spectrum of **8a** shows a far downfield singlet at δ 224, indicating the presence of a doubly-bent aryldiazenido ligand,[23] which sharply contrasts with the doublet observed at δ −154 ppm for the $^{15}N_\alpha$-labeled aryldiazene ligand of **7a**.

Reactions of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] (2) with Carbon Monoxide. Previously, we have shown that a simple substitution of the labile ethylene ligand in compound **2** has provided a convenient entry to a variety of aryldiazenido complexes.[5,6] Logically, a similar substitution of the ethylene ligand of **2** by carbon monoxide was expected to lead to the target complex [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**). Hence, **2** was reacted first with excess carbon monoxide in acetone solution at different temperatures, but always resulted in Cp*Ir(CO)$_2$ as the only isolable organometallic species. The failure to obtain an aryldiazenido derivative was thought possibly to be due to the excess of carbon monoxide. Consequently, a stoichiometrically controlled reaction was carried out, in which equivalent amounts of **2** and carbon monoxide were used. After a much longer reaction time, the IR and ^{1}H NMR spectra again revealed that, in addition to the unreacted **2**, Cp*Ir(CO)$_2$ was the only detectable product. Hence, it is concluded that no stable compound [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**) can be formed by this method.

A similar reaction of **2** and CO in ethanol solution resulted in [Cp*Ir(CO)(OEt)(*p*-$NHNC_6H_4OMe$)][BF_4] (**7**) and Cp*Ir(CO)$_2$ (**3**), instead of the target complex [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**).

In the reactions of complex **2** with CO, the replacement of ethylene by a CO ligand is evident. However, in acetone solution these reactions apparently did not stop at the stage of [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**), the target complex, but instead continued to give Cp*Ir(CO)$_2$ (**3**), even when the stoichiometric amount of CO was used. Cp*Ir(CO)$_2$ (**3**) was also produced by the reaction in ethanol. However, in addition to it, a nitrogen-retained complex, [Cp*Ir(CO)(OEt)(*p*-$NHNC_6H_4OMe$)][BF_4] (**7**), was formed. Complex **7** is clearly a form of [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**) stabilized by the solvent ethanol, and its formation unequivocally shows that CO is capable of being added without immediate loss of the N_2Ar ligand and points to the target complex [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**) being an intermediate in the reaction pathway. These observations, together with the repeated failures to obtain **1** by use of this reaction in the absence of EtOH indicate that [Cp*Ir(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (**1**) itself must be either very reactive or very unstable. This view is consistent with our predictive argument that in such a system there is an unfavorable electronic arrangement that leads to destabilization of a singly-bent aryldiazenido ligand. Because of the critical role of π-bonding in the stabilization of a singly-bent aryldiazenido ligand in a late transition metal complex, sharing the same pair of metal d_π-electrons with a trans-arranged strong π-acid, CO, would significantly weaken the π-bonding between a singly-bent aryldiazenido ligand and a late transition metal, such as Ir(I).[4,5a,6] A further note to this is that, while numerous carbonyl aryldiazenido complexes of the late transition metals have been synthesized and structurally characterized,[2] to the best of our knowledge, there has been no example of such a compound of a late transition metal in the literature in which a singly-bent aryldiazenido ligand is trans to a carbonyl ligand and thus competes for the same metal d_π-electrons.

Reaction of [Cp*Ir(CO)]$_2$ with [*p*-$N_2C_6H_4OMe$][BF_4]. It was at first thought that the reaction of [Cp*Ir(CO)]$_2$ with [*p*-$N_2C_6H_4OMe$][BF_4] might provide an alternative synthetic route to [Cp*$_2$Ir$_2$(CO)$_2$(η^2-μ-*p*-$N_2C_6H_4OMe$)][BF_4],[5b,6] that had been synthesized in a rather low yield from the reaction of [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] (**2**) with Cp*Ir(CO)$_2$ (**3**) in ethanol.

Instead, treatment of a dark green acetone solution of [Cp*Ir(CO)]$_2$ with [*p*-$N_2C_6H_4OMe$][BF_4] at −78 °C resulted in a dark red solution, from which [Cp*$_2$Ir$_2$(CO)$_2$(1-η^1-1,2-η^2-*p*-C_6H_4-OMe)][BF_4] (**9**), a nitrogen elimination product, was isolated in a fairly good yield. Presumably similar to the formation of **5**, the formation of compound **9** is also initiated by an addition of aryldiazonium ion to the unsaturated metal−metal bond, followed by a nitrogen extrusion from the adduct to give the bridging aryl complex as the final product. A symmetrical bridge−terminal transfer of the two carbonyl ligands to the two metal centers must also be involved in this process. Chemistry closely related to this has been seen in the reactions of diazoalkanes with complexes containing an unsaturated metal−metal bond, in which bridging carbene complexes are often generated.[24−26] However, to the best of our knowledge, compound **9** is the first instance where the bridging aryl group is introduced from an aryldiazonium ion.

Compound **9** is very soluble in polar solvents such as chloroform, acetone, dichloromethane, and ethanol. However, it is not very stable in solution at room temperature. It slowly decomposes to [Cp*Ir(CO)]$_2$, Cp*Ir(CO)$_2$, and other unidentified products. The elemental analysis for **9** immediately negated the possibility of the presence of nitrogen in this compound. The FABMS of **9** exhibits the appropriate molecular ion, as well as the ions corresponding to a sequential loss of two CO ligands. The IR spectrum of **9** in CH_2Cl_2 exhibits bands at 1968 and 1993 cm^{-1} (1964 and 1990 cm^{-1} in ethanol), with the band at higher frequency much weaker than the lower one. Consequently, these two bands were assigned to two terminal carbonyls. The relative intensities and positions of the two absorption bands indicated that the two carbonyls were, most likely, separated with a large 2θ angle.[27] The most chemically interesting feature for **9** was its rather simple ^{1}H NMR spectrum. At room temperature the 100 MHz ^{1}H NMR spectrum showed a singlet at δ 1.95 attributed to Cp*, also a singlet at δ 3.85 and an AA′BB′ pattern in the aromatic proton range corresponding to the *p*-C_6H_4OMe group. Integration of the signals indicated a relationship of two Cp*'s and one *p*-C_6H_4OMe ligand, in agreement with the molecular formula [Cp*$_2$Ir$_2$(CO)$_2$(C_6H_4OMe)][BF_4]. One single signal observed for the two Cp* ligands indicated that they are either chemically equivalent or undergoing exchange. In an attempt to distinguish these two possibilities, a low-temperature (−90 °C) ^{1}H NMR spectrum in a different solvent (CD_2Cl_2) was recorded on a higher field (400 MHz) spectrometer. However, the features displayed by the low-temperature ^{1}H NMR spectrum were identical to that observed at ambient temperature in $CDCl_3$, except for a slight broadening and slightly different chemical shifts. It was then obvious that a single-crystal X-ray structural analysis would be helpful to establish the molecular structure

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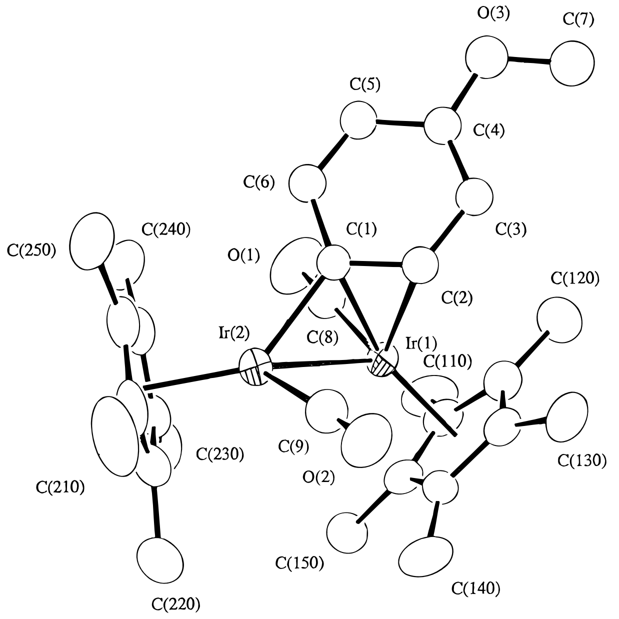

Figure 2. Perspective view of the cation of **9** showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are not shown.

of **9**. After many various attempts, crystals suitable for X-ray crystallographic study were obtained from CH_2Cl_2/hexane at −10 °C.

Molecular Structure of 9 in the Solid State. The structure of the cation of **9** in the crystal is shown in Figure 2. The molecule consists of a binuclear bis(pentamethylcyclopentadienyl) Ir−Ir structural frame, with two terminal carbonyls bonded to two iridium centers separately, and a *p*-methoxyphenyl as a bridging ligand between the two iridiums. There are no unusual interionic distances in the crystal structure. The selected bond distances and bond angles for compound **9** are listed in Table 3.

The iridium−iridium bond distance of 2.7294(5) Å found in **9** is comparable to 2.723(4) Å found in the μ^2-η^2-bridging aryldiazenido analogue, $[Cp^*_2(CO)_2Ir_2(\eta^2\text{-}\mu\text{-}p\text{-}N_2C_6H_4OMe)][BF_4]$,[6] and 2.7166(2) Å found in $[Cp_2(CO)_2Ir_2](\eta^2\text{-}\mu\text{-}C_6H_4)$,[29] indicating a metal−metal single bond. The bridging *p*-methoxyphenyl ligand in **9** coordinates to Ir(2) by an apparent η^1- (or σ−) linkage from C(1) of the phenyl ring and to Ir(1) by η^2- (or π−) binding from C(1) and C(2) of the aromatic ring. The C_6 ring is planar (see Table 4), and the Ir(2) atom is approximately coplanar with the C_6 ring, with only a slight deviation of 0.050(11) Å from the least-squares plane through the six ring atoms. Furthermore, the bond angle C(2)−C(1)−Ir(2) (122.5(5)°) is very close to the angle C(6)−C(1)−Ir(2) (123.8(5)°). It is then clear that the ligand *p*-C_6H_4OMe is σ-bonded to Ir(2), apparently through an sp^2 hybridized atom C(1). The Ir(2)−C(1) distance of 2.054(7) Å is similar to the previously reported σ-bond lengths between iridium and phenyl carbon. For example, Ir-C(phenyl) is 2.070(15) Å in $Ir(C_2H_4)_2(PPh_3)PPh_2C_6H_4$[28] and Ir-C(phenylene) 2.045(3) Å in $[Cp_2(CO)_2Ir_2](\eta^2\text{-}\mu\text{-}C_6H_4)$.[29] It should be also noted that as a result of the σ−π coordination of the bridging *p*-C_6H_4OMe, the η^2 coordination bond is not symmetric. The Ir(1)−C(2) distance of 2.394(7) Å is slightly longer than Ir(1)−C(1) of 2.324(7) Å, and the internal dihedral angle between plane C(1)−C(2)−Ir(1) and the C_6-ring is not 90° but 116.2(3)°. The bonds Ir(1)−Ir(2) and C(1)−C(2) make a torsional angle of −62.4(4)° for Ir(1)−Ir(2)−C(1)−C(2). The bond angle C(2)−C(1)−C(6) (113.7(7)°), compared to C(1)−C(2)−C(3) (123.3(7)°), presumably reflects a larger stereochemical influence of the σ-bound iridium atom at C(1) relative to that of the hydrogen atom at C(2). In the phenyl ring, the bond lengths of C(3)−C(4) and C(5)−C(6), both 1.35(1) Å, are marginally shorter than the other intraring C−C bond distances, 1.40(1)−1.43(1) Å, but the alternating pattern of these intraring C−C bond distances is interesting. Note that the bond lengths of 1.35(1) Å are shorter than the carbon-carbon bonds (1.39 Å) in benzene itself,[30] and very close to the bond length of an isolated C=C bond in ethene (1.34 Å).[31] So it is indicative that, as a consequence of the π-bonding to iridium from C(1) and C(2), the aromaticity of the phenyl ring is disrupted and an alternating multiple bond character is produced in the ring.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Cp^*_2Ir_2(CO)_2(1\text{-}\eta^1\text{-}1,2\text{-}\eta^2\text{-}p\text{-}C_6H_4OMe)][BF_4]$ (**9**)

	Bond Lengths		
Ir(1)−C(1)	2.324(7)	Ir(2)−Ir(1)	2.7294(5)
Ir(1)−C(2)	2.394(7)	Ir(2)−C(1)	2.054(7)
Ir(1)−C(8)	1.857(9)	Ir(2)−C(9)	1.858(9)
Ir(1)−Cp*1[a]	1.902	Ir(2)−Cp*2 [b]	1.898
Ir(1)−C(11)	2.192(7)	Ir(2)−C(21)	2.207(7)
Ir(1)−C(12)	2.242(8)	Ir(2)−C(22)	2.251(8)
Ir(1)−C(13)	2.331(8)	Ir(2)−C(23)	2.293(7)
Ir(1)−C(14)	2.335(8)	Ir(2)−C(24)	2.272(8)
Ir(1)−C(15)	2.197(7)	Ir(2)−C(25)	2.237(8)
O(1)−C(8)	1.13(1)	O(2)−C(9)	1.127(9)
O(3)−C(4)	1.367(9)	O(3)−C(7)	1.41(1)
C(1)−C(2)	1.43(1)	C(1)−C(6)	1.43(1)
C(2)−C(3)	1.40(1)	C(3)−C(4)	1.35(1)
C(4)−C(5)	1.41(1)	C(5)−C(6)	1.35(1)
	Bond Angles		
C(1)−Ir(1)−Ir(2)	47.1(2)	C(1)−Ir(2)−Ir(1)	56.0(2)
C(2)−Ir(1)−C(1)	35.2(2)	C(9)−Ir(2)−C(1)	88.8(3)
C(8)−Ir(1)−Ir(2)	91.2(3)	C(9)−Ir(2)−Ir(1)	89.4(3)
Cp*1[a]−Ir(1)−Ir(2)	130.6	Cp*2[b]−Ir(2)−Ir(1)	134.4
Cp*1[a]−Ir(1)−C(8)	127.2	Cp*2[b]−Ir(2)−C(9)	127.5
Cp*1[a]−Ir(1)−C(2)	115.8	Cp*2[b]−Ir(2)−C(1)	136.1
C(2)−Ir(1)−Ir(2)	73.2(2)	C(2)−C(1)−Ir(1)	75.1(4)
C(8)−Ir(1)−C(1)	81.9(3)	Ir(2)−C(1)−Ir(1)	76.8(2)
C(8)−Ir(1)−C(2)	105.2(3)	C(2)−C(1)−Ir(2)	122.5(5)
Cp*1[a]−Ir(1)−C(1)	148.7	C(6)−C(1)−Ir(1)	120.8(5)
C(3)−C(2)−Ir(1)	120.9(5)	C(6)−C(1)−Ir(2)	123.8(5)
C(1)−C(2)−Ir(1)	69.7(4)	O(1)−C(8)−Ir(1)	174.2(8)
C(6)−C(1)−C(2)	113.7(7)	O(2)−C(9)−Ir(2)	174.3(8)
C(3)−C(2)−C(1)	123.3(7)	C(3)−C(4)−O(3)	125.4(7)
C(4)−C(3)−C(2)	119.6(7)	C(5)−C(4)−O(3)	115.2(7)
C(5)−C(4)−C(3)	119.4(7)	C(7)−O(3)−C(4)	114.6(7)
C(6)−C(5)−C(4)	121.5(8)	C(5)−C(6)−C(1)	122.4(7)

[a] The center of mass of Cp* 1. [b] The center of mass of Cp* 2.

Table 4. Least-Squares Plane for Aryl Group of $[Cp^*_2Ir_2(CO)_2(1\text{-}\eta^1\text{-}1,2\text{-}\eta^2\text{-}p\text{-}C_6H_4OMe)][BF_4]$ (**9**).

Equation of the Plane		$3.80(4)X + 7.45(6)Y + 10.356(23)Z = 6.818(18)$	
	Distances (Å) to the Plane from the Atoms in the Plane		
C(1)	−0.013(9)	C(2)	0.016(9)
C(3)	−0.006(9)	C(4)	−0.007(10)
C(5)	0.007(10)	C(6)	0.004(10)
χ^2 for this plane		6.887	
	Distances (Å) to the Plane from the Atoms out of the Plane		
Ir(1)	−2.015(8)	Ir(2)	−0.050(11)
O(3)	0.015(11)	C(7)	−0.020(15)

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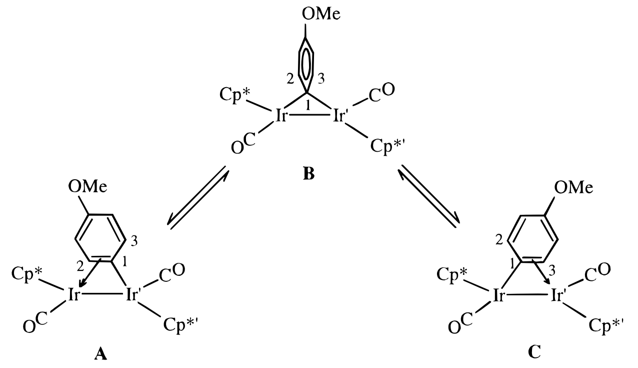
Scheme 2. Possible Fluxional Process for Compound **9** in Solution



Furthermore, the difference of the bond orders between C(3)−C(4) and C(4)−C(5) would be expected to have some effect on the −OMe group at C(4). Notably, the bond angle C(3)−C(4)−O(3) (125.4(7)°) is unusually much more obtuse than C(5)−C(4)−O(3) (115.2(7)°).

Another interesting structural feature of **9** is that despite the asymmetrically coordinated bridging aryl group, the molecular framework of Cp*Ir(CO)−Cp*Ir(CO) approximates C_2 symmetry. This is illustrated by the barely significant difference in the molecular dimensions of the two Cp*Ir(CO) fragments, *e.g.*, Ir−CO distances: 1.857(9) *vs* 1.858(9) Å; and angles of Cp*(centroid)−Ir−CO, 127.2 *vs* 127.5°, C(O)−Ir−Ir, 91.2(3) *vs* 89.4(3)°, and Cp*(centroid)−Ir−Ir, 130.6 *vs* 134.4°. In other words, the asymmetrical coordination of the aryl ring through a simultaneous σ and π bonding to the two different iridium atoms clearly does not cause any significant difference in the configurations of the two Cp*Ir(CO) fragments.

It should be also pointed out here that although the 1-η^1-1,2-η^2- bridging pattern has often been seen in complexes with a bridging alkenyl or alkynyl ligand that contains an unconjugated π bond,[32] it is rare in a bridged *aryl* complex. Previously, only two examples of 1-η^1-1,2-η^2-bridging aryl complexes have been reported.[33]

Possible Molecular Structure of 9 in Solution. Evidently, the unsymmetrical molecular structure of **9** in the solid state revealed by its X-ray crystallographic analysis is discrepant with the spectroscopic data obtained in solution. In order to confirm that the crystals used for the X-ray crystallographic analysis have the same chemical composition as that of the bulk samples of **9**, further IR and ^{1}H NMR measurements were made on a freshly prepared solution from the same group of crystals used for X-ray structural analysis, and these were identical to the previous ones. This, together with the absence of any short intermolecular distance in the crystal lattice, strongly suggests that a symmetrically bridged aryl ligand required by the spectroscopic data of **9** in solution is most probably the time-averaged result of a fast exchange process involved in the molecule **9**. Consequently, an exchange mechanism of the bridging aryl ligand in **9** is proposed and shown in Scheme 2.

In this mechanism, the bridging aryl ring is rapidly flipping its relative orientation from structure **A**, through **B**, to **C** and *vice versa*. Furthermore, the closely related structure and symmetry of Cp*Ir(CO)−Cp*Ir(CO) in **A** (or **C**) and **B** (*vide supra*) indicates that little distortion of this framework would be expected during the exchange process. In other words, by only flipping the bridging aryl group without severe distortion of the framework of the molecule, this exchange would be energetically facile. This may provide an explanation for the experimental observation that in the low-temperature NMR for compound **9** no decoalescence was observed, even at −90 °C.

Notably, similar fluxionality for other σ−π-bridging ligands has also been observed, for example (μ-σ-$CH_3C{=}CH_2$)(μ-EtS)-$Fe_2(CO)_6$,[34a] (μ-η^1,η^3-$CH{=}C{=}C(CH_3)_2$(μ-*t*-BuS)$Fe_2(CO)_6$,[34b] (μ-H)(μ-σ-π-$CH{=}CH_2$)$Re_2(CO)_7(PPh_3)$,[34c] (μ-η^1,η^3-RC=CRC-(O))M_2(CO)(μ-CO)Cp_2 (M = Fe, Ru),[34d] {μ-EtC=CEt-(CO_2)}$Fe_2(CO)_6$,[34e] (L−L′)$Fe_2(CO)_6$ (L−L′ = μ-$C_6H_5C{=}CC_6H_5S$ or μ-$C_6H_4CH_2NR$),[34f] and (μ-H)(μ-σ-π-$CH{=}CH_2$)$Os_3(CO)_{10}$.[34g]

Although the proposed mechanism above can give us a satisfactory explanation for all of the experimental observations for **9** in solution, we still lack evidence to rule out completely the possibility of structure **B** being the only isomer present in solution. This type of symmetrically bridged aryl ligand has ample precedent in the literature.[35]

Formation of [Cp*Ir(CO)]$_2$ (4). Our interest in **4** was that a stoichiometric reaction of it with 1, or 2, equiv of [*p*-$N_2C_6H_4$-OMe][BF_4] might result in the known bridging aryldiazenido complex [Cp*$_2$Ir$_2$(CO)$_2$(η^2-μ-*p*-$N_2C_6H_4$OMe)][BF_4], or the possible target complex [Cp*Ir(CO)(*p*-$N_2C_6H_4$OMe)][BF_4] (**1**). Considering the exhausting long reaction time (1 week) at 180 °C, and very narrow optimal reaction conditions required by the available literature method,[10] an alternative route to compound **4** was sought, and our efforts were rewarded by several convenient methods for preparation of this compound. Complex **4** can be smoothly synthesized in excellent yield from readily available precursors through procedures that consist essentially of reduction and assembly steps, as shown in Scheme 3.

Considering that the synthetic procedure described in Scheme 3b involves two different precursor compounds, logically, it could be used in the synthesis of unsymmetrical dinuclear complexes by changing either the ligand or the metal center of one precursor. Preliminary trials by using this strategy have resulted in quantitative syntheses of the unsymmetrical compounds Cp*$_2$IrRh(μ-CO)$_2$ from [Cp*RhCl$_2$]$_2$ and Cp*Ir(CO)$_2$, and Cp*CpIr$_2$(μ-CO)$_2$ from [Cp*IrCl$_2$]$_2$ and CpIr(CO)$_2$.[36]

The success of the *reduction-assembly* method in syntheses of the above symmetric and unsymmetrical dinuclear complexes suggests it may have potentially wider utility. It is noticeable that the literature preparative methods for these types of

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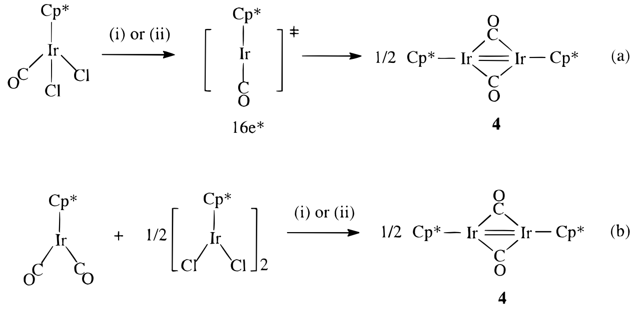
Scheme 3. Facile Synthetic Routes to Compound **4**



(i) Stir with excess Zn dust for 12 h at r.t..

(ii) Reflux with Na_2CO_3 in EtOH for 3 ~ 4 h.

* Formal electron count (neglecting possible solvation).

dinuclear complexes of Co, Rh, or Ir usually always involve vigorous reaction conditions, such as photolysis or thermolysis. For example, Cp*$_2$Co$_2$(μ-CO)$_2$ has been made by thermolysis of Cp*Co(CO)$_2$ in toluene for 24 h, or by photolysis in THF for 4 days,[37] Cp*$_2$Rh$_2$(μ-CO)$_2$ has been synthesized by pyrolizing Cp*Rh(CO)$_2$ at high pressure,[38] and as mentioned above, Cp*$_2$Ir$_2$(μ-CO)$_2$ was previously made by pyrolizing Cp*Ir(CO)$_2$ at 180 °C for 1 week.[10] Evidently, a further extension of the method developed here to make these and other, both known and unknown, dinuclear complexes will be useful, and a study of this aspect is being undertaken.

Conclusion

The majority of the procedures in this study that were tried in order to obtain the target complex [Cp*Ir(CO)(*p*-N$_2$C$_6$H$_4$-OMe)][BF$_4$] (**1**) were frustrated by the formation of products that were not reproducible or isolable. This is perhaps not surprising since there are many instances in the literature in which attempts to obtain aryldiazenido carbonyl complexes by direct reaction of the aryldiazonium ion and metal carbonyl derivatives have failed.[39] Despite this, the results that have emerged from these attempts are nevertheless interesting. Several different products have been isolated from the reactions of Cp*Ir(CO)$_2$ and [*p*-N$_2$C$_6$H$_4$OMe][BF$_4$] in different reaction media, *i.e.*, formation of [Cp*Ir(CO)$_2$(Ar)]$^+$ in acetone, [Cp*Ir(CO)$_2$ $\rightarrow$ Ir(CO)(Cl)Cp*]$^+$ in CH$_2$Cl$_2$, and [Cp*Ir(CO)(OEt)(NHNAr)]$^+$ in EtOH. Also the compound [Cp*$_2$Ir$_2$(CO)$_2$(1-η^1-1,2-η^2-*p*-C$_6$H$_4$OMe)][BF$_4$] (**9**) with a rare σ,π-bridging aryl ligand is obtained from the reaction of [Cp*Ir(CO)]$_2$ and N$_2$Ar$^+$ and provides the first example of a bridging aryl group generated from an aryldiazonium ion.

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Supporting Information Available: For compound **6**, text giving the detailed crystallographic analysis and listings of fractional atomic coordinates and isotropic temperature factors for non-hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2), fractional atomic coordinates and isotropic temperature factors for hydrogen atoms (Table S3), and for compound **9**, text giving the detailed crystallographic analysis and listings of fractional atomic coordinates and isotropic or equivalent isotropic temperature factors for non-hydrogen atoms (Table S4), anisotropic thermal parameters (Table S5), fractional atomic coordinates and isotropic temperature factors for hydrogen atoms (Table S6) (10 pages). Ordering information is given on any current masthead page.

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(36) Spectroscopic data for Cp*$_2$IrRh(μ^2-CO)$_2$. IR: ν(CO) 1703 cm^{-1} (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$): δ 1.55 (s, 15H, Cp*), 1.88 (s, 15H, Cp*′). EIMS (*m/z*): 622 (M$^+$), 592 (M$^+$ − CO − 2H), 564 (M$^+$ − 2CO − 2H), 562 (M$^+$ − 2CO − 4H), 560 (M$^+$ − 2CO − 6H), 463 ([Cp*$_2$Ir]$^+$), 373 ([Cp*$_2$Rh]$^+$). Spectroscopic data for Cp*CpIr$_2$(μ^2-CO)$_2$. IR: ν(CO) 1695 cm^{-1} (CH$_2$Cl$_2$). ^{1}H NMR (C$_6$D$_6$): δ 1.58 (s, 15H, Cp*), 5.14 (s, 5H, Cp).

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