trans-Ir(PPh$_3$)$_2$(CO)(NHAr) Complexes: Their Syntheses, Characterization, and Reactions with CO

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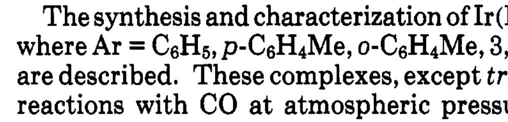
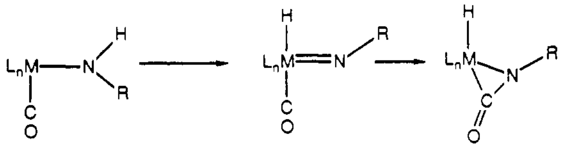
The synthesis and characterization of Ir(I)–arylamido complexes, *trans*-Ir(PPh$_3$)$_2$(CO)(NHAr), where Ar = C_6H_5, *p*-C_6H_4Me, *o*-C_6H_4Me, 3,5-$C_6H_3Me_2$, 2,6-$C_6H_3Me_2$, *p*-C_6H_4Cl, and *p*-$C_6H_4NO_2$, are described. These complexes, except *trans*-Ir(PPh$_3$)$_2$(CO)[NH(*p*-$C_6H_4NO_2$)], undergo rapid reactions with CO at atmospheric pressure and ambient temperatures. For the complexes containing the sterically bulky NH(3,5-$C_6H_3Me_2$) and NH(2,6-$C_6H_3Me_2$) ligands, the CO reactions generate carbamoyl moieties, which result from an insertion of CO into the iridium–nitrogen bond. The end products in the reactions of the other arylamido complexes with CO contain orthometalated carbamoyl moieties, with the generation of hydrido–Ir(III) centers. Intermediates leading to the formation of the orthometalated complexes are discussed. Crystal data for *trans*-Ir(PPh$_3$)$_2$(CO)[NH(3,5-$C_6H_3Me_2$)]·0.5C_6H_6: $C_{48}H_{43}IrNOP_2$; triclinic $P\bar{1}$, $a = 9.072(2)$ Å, $b = 11.667(2)$ Å, $c = 21.133(4)$ Å, $\alpha = 88.74(2)°$, $\beta = 81.24(2)°$, $\gamma = 73.74(2)°$, $V = 2121.9(7)$ Å^3, $Z = 2$, $R(F) = 0.035$, and $R_w(F) = 0.049$ for 5038 ($F > 5\sigma(F)$) reflections.

Introduction

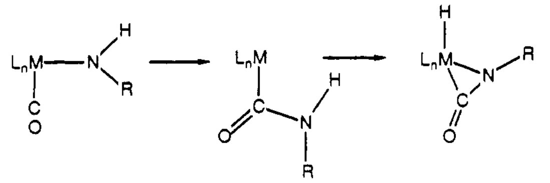
The migratory insertion of CO into metal—carbon bonds is a widely observed phenomenon in organometallic chemistry.[1] This process has been shown to be critical in many industrial processes, such as hydroformylation of alkenes.[2] Insertion reactions involving nitrogen (or oxygen) bases—examples of which are relatively few[3,4]—can also be critical in many catalytic processes. For example, insertion involving an amido group, as shown in eq 1, can model the catalytic formation of ureas from amines and CO. Likewise, metal complexes can potentially catalyze the formation of isocyanates from amines and CO. The formation of a coordinated isocyanate moiety by the insertion of CO into a metal—imido bond has been observed for Cp*Ir═NBu^t.[5] In a catalytic cycle, however, the consumption of an amine will involve either an intermolecular attack on the coordinated CO, or initial N—H bond activation to generate a coordinated amido ligand, which can then participate in a migratory insertion reaction with CO. Two pathways, (2a) and (2b), can be envisioned for the latter possibility. In (2a), after the initial oxidative addition of an amine, the resulting amido ligand can undergo N—H activation to generate a hydrido—imide intermediate, which then can transform to a hydrido–isocyanate species by attack of the imido group on the CO ligand. The amido ligand in (2b) is shown to convert to an isocyanate through a carbamoyl intermediate, which undergoes N—H bond activation (β-hydrogen elimination) to form the product. A consideration of the various oxidation state changes that the metal must go through in these two pathways shows that, in (2a), an increase of +2 units is required in each of the amide and imide formation steps. Reaction 2b requires an increase in the oxidation state of +2 units *only* during the initial amide formation step—β-hydrogen elimination does not involve any formal change in the metal's oxidation state—and thus may kinetically be more favorable. Although the base-promoted conversion of a coordinated carbamoyl moiety to an isocyanate ligand has been observed,[6] a conversion involving activation of the carbamoyl N—H bond is yet to be demonstrated unambiguously.[7] We have begun a study to explore this reaction on low valent late transition metal amido complexes.



$$L_nM(NHR)\text{—}CO \longrightarrow L_nM\text{—}C(O)NHR \xrightarrow{RNH_2} (RHN)_2C{=}O + L_nM\text{-}H \qquad (1)$$



(2a)



(2b)

We present in this paper the syntheses, characterization, and reactivities of the first examples of terminally bound arylamido complexes of Ir(I), *trans*-Ir(PPh$_3$)$_2$(CO)(NHAr),[8] where Ar = C_6H_5 (**1**), *p*-C_6H_4Me (***p*-Me·1**), *o*-C_6H_4Me (***o*-Me·1**), 3,5-$C_6H_3Me_2$ (**3,5-Me$_2$·1**), 2,6-$C_6H_3Me_2$ (**2,6-Me$_2$·1**), *p*-C_6H_4Cl (***p*-Cl·1**) and *p*-$C_6H_4NO_2$ (***p*-NO$_2$·1**). In contrast to other known Ir(I)–amido species,[9] the complexes

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reported here show facile insertion of CO into the iridium–nitrogen bond to form carbamoyl moieties. The observed reactivity bears similarities to the carbonylation reactions of *trans*-Ir(PPh$_3$)$_2$(CO)(OR), where R = alkyl and aryl, to form *trans*-Ir(PPh$_3$)$_2$(CO)$_2$[C(O)OR].[10] While the alkoxycarbonyls react no further, the carbamoyls readily undergo orthometalation reactions. These are rare examples of CO-insertion reactions involving late transition metal amides.

Experimental Section

All preparations were carried out under N$_2$ using standard drybox or Schlenk line techniques. Solvents were purified twice before use and stored under N$_2$ over 4-Å molecular sieves. Hexanes were distilled from CaH$_2$, methylene chloride was distilled from P$_4$O$_{10}$, and toluene and THF were distilled from Na/K alloy and benzophenone. All of the lithium amides, except LiNH(*p*-C$_6$H$_4$NO$_2$), were prepared by reacting equivalent amounts of Bu^{n}Li with the corresponding amines in toluene. LiNH(*p*-C$_6$H$_4$NO$_2$) was prepared by reacting LiN(SiMe$_3$)$_2$ with *p*-nitroaniline in diethyl ether. *trans*-Ir(PPh$_3$)$_2$(CO)Cl was prepared by a published method.[11]

Infrared spectra were recorded on a Nicolet 6000 series FT-IR instrument. ^{1}H, ^{13}C, ^{31}P, and ^{15}N NMR spectra were obtained using either a 250- or a 500-MHz Bruker instrument. To obtain the ^{15}N NMR spectra, a pulse width of 58 μs and a relaxation time of 5 s were used; chemical shift values were referenced against NH$_4$^{15}NO$_3$ (in D$_2$O, $\delta = 0$), which was used as an external standard. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried over 4-Å molecular sieves. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ, and Galbraith Laboratories, Knoxville, TN.

Syntheses. A common procedure was employed for the syntheses of all of the arylamido complexes. In each case, 0.20 g (0.25 mmol) of *trans*-Ir(PPh$_3$)$_2$(CO)Cl was dissolved in THF (30 mL) inside a drybox. The corresponding lithium amide (2–3 equiv), also dissolved in THF (10 mL), was added to the solution containing the iridium complex, and the solution was allowed to stir for 10 min (a slightly longer reaction time was allowed during the preparation of ***p*-NO$_2$·1**). During this period, the color of the solution turned from pale yellow to bright orange. Once the completion of the reaction was ascertained from an IR spectrum of the reaction mixture, the solution was evacuated to dryness to leave a dark orange, waxy solid. Extraction of the solid with toluene, filtration through Celite (to remove the excess lithium amide and LiCl), and concentration of the extract precipitated bright orange microcrystalline solids. Further precipitation was accomplished by cooling the mixture to −10 °C for 10 h. The dark brown supernatant was syringed off and discarded, and the orange solid was washed with hexane and pumped to dryness. The yield ranged from 70 to 83%. Anal. Calcd (found) for **1**: C, 61.70 (61.22); H, 4.33 (4.46); N, 1.67 (1.65). Calcd (found) for ***p*-Me·1**: C, 62.09 (61.72); H, 4.50 (4.71); N, 1.64 (1.44). Calcd (found) for ***o*-Me·1**: C, 62.13 (62.00); H, 4.50 (4.44); N, 1.65 (1.68). Calcd (found) for ***p*-Cl·1**: C, 59.31 (58.78); H, 4.02 (3.91); N, 1.61 (1.57). Calcd (found) for ***p*-NO$_2$·1**: C, 58.45 (57.97); H, 3.99 (4.18); N, 3.17 (3.15). Calcd (found) for **2,6-Me$_2$·1**: C, 62.48 (62.75); H, 4.66 (4.74); N, 1.61 (1.47). Calcd (found) for **3,5-Me$_2$·1**: C, 62.05 (61.78); H, 4.62 (4.52); N, 1.62 (1.59).

Spectroscopic Data. 1: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1944; ^{1}H NMR (C$_6$D$_6$, δ relative to TMS) 7.89, 6.96 (m, 30H, P(C$_6$*H*$_5$)$_3$, 6.74, 6.35 (m, 5H, NH(C$_6$*H*$_5$)), 2.62 (s, 1H, N*H*(C$_6$H$_5$)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ relative to H$_3$PO$_4$) 24.8. *p*-**Me·1**: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1942; ^{1}H NMR (C$_6$D$_6$, δ) 7.89, 6.98 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.54, 6.34 (d, 4H, NHC$_6$*H*$_4$Me)), 2.67 (s, 1H, N*H*(C$_6$H$_4$-Me)), 2.12 (s, 3H, NH(C$_6$H$_4$*Me*)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ) 25.5. *o*-**Me·1**: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1940; ^{1}H NMR (C$_6$D$_6$, δ) 7.85, 6.95 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.70, 6.35 (m, 4H, NH(C$_6$*H*$_4$Me)), 2.50 (s, 1H, N*H*(C$_6$H$_4$Me)), 1.30 (s, 3H, NH(C$_6$H$_4$*Me*)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ) 25.7. *p*-**Cl·1**: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1947; ^{1}H NMR (C$_6$D$_6$, δ) 7.85, 6.97 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.67, 6.13 (d, 4H, NH(C$_6$*H*$_4$-Cl)), 2.45 (s, 1H, N*H*(C$_6$H$_4$Cl)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ) 24.8. *p*-**NO$_2$·1**: IR (CH$_2$Cl$_2$, cm^{-1}) 1962; ^{1}H NMR (C$_6$D$_6$, δ) 7.75, 6.95 (d, br, 4H, NH(C$_6$*H*$_4$NO$_2$)), 7.68, 6.95 (m, 30H, P(C$_6$*H*$_5$)$_3$), 3.06 (s, 1H, N*H*(C$_6$H$_4$NO$_2$). **2,6-Me$_2$·1**: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1940; ^{1}H NMR (C$_6$D$_6$, δ) 7.82, 6.99 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.82, 6.29 (d, t, 3H, NH(C$_6$*H*$_3$Me$_2$)), 2.10 (s, 6H, NH(C$_6$H$_3$*Me*$_2$)), 1.81 (s, 1H, N*H*(C$_6$H$_3$Me$_2$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ) 23.2. **3,5-Me$_2$·1**: IR (CH$_2$Cl$_2$, cm^{-1}) ν(CO) = 1941; ^{1}H NMR (C$_6$D$_6$, δ) 7.85, 7.00 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.02, 5.98 (s, 3H, NH(C$_6$*H*$_3$Me$_2$)), 2.61 (s, 1H, N*H*(C$_6$H$_3$Me$_2$)), 1.92 (s, 6H, NH(C$_6$H$_3$*Me*$_2$)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ) 24.9.

Carbonylation Reactions. The reactions of ***p*-Me·1**, ***o*-Me·1**, and ***p*-Cl·1** with CO were carried out on a preparative scale using identical methods. In each case, 0.15 g of the arylamido complex was dissolved in benzene (20 mL) under nitrogen in a Schlenk flask, fitted with a rubber septum. The N$_2$ inlet to the flask was then closed and the solution was frozen at 0 °C. CO gas (2–3 equiv) was introduced into the flask via a gastight syringe, and the solution was gradually allowed to warm to room temperature. During this period, the bright orange color of the solution began to turn pale yellow. After stirring it for ca. 0.5 h, the solution was reduced in volume by ca. two-thirds, causing precipitation of a pale-yellow solid. An analytically pure sample could be obtained by recrystallizing the crude product from benzene. Yield: 65–70%.

Ir(PPh$_3$)$_2$(CO)(H)[C(O)NH(*p*-MeC$_6$H$_3$)], *p*-Me·1·CO. Anal. Calcd (found): C, 61.43 (60.75); H, 4.35 (4.19); N, 1.60 (1.16). IR (CH$_2$Cl$_2$, cm^{-1}): ν(Ir–H) = 2094, ν(CO) = 2017, ν(–C(O)–) = 1598. ^{1}H NMR (C$_6$D$_6$): δ 8.05, 6.75, 6.21 (s, d, d, 3H, –C(O)NH(C$_6$*H*$_3$-Me)), 7.75, 7.25, 6.90 (m, 30H, P(C$_6$*H*$_5$)$_3$)), 2.10 (s, 3H, –C(O)-NH(C$_6$H$_3$*Me*)), −9.12 (d of d, 1H, $J_{\mathrm{P-H}}$ = 127 and 19 Hz, 1H, Ir–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 0.1, 5.2 (d, $J_{\mathrm{P-P}}$ = 18 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$) of ^{13}CO-enriched sample: δ 190.9 (m, Ir–*C*O), 178.9 (m, Ir–*C*(O)NH(C$_6$H$_3$Me)).

Ir(PPh$_3$)$_2$(CO)(H)[C(O)NH(*o*-MeC$_6$H$_3$)], *o*-Me·1·CO. Anal. Calcd (found): C, 61.31 (61.17); H, 4.35 (4.24); N, 1.59 (1.60). IR (CH$_2$Cl$_2$, cm^{-1}): ν(N–H) = 3393, ν(Ir–H) = 2098, ν(CO) = 2018, ν(–C(O)–) = 1594. ^{1}H NMR (C$_6$D$_6$): δ 7.85, 7.30, 6.85 (m, 30H, P(C$_6$*H*$_5$)$_3$), 6.75, 6.60, (d, t, 2H, partial –C(O)NH(C$_6$*H*$_3$Me)), 1.80 (s, 3H, –C(O)NH(C$_6$H$_3$*Me*)), −9.22 (d of d, 1H, $J_{\mathrm{P-H}}$ = 126 and 21 Hz, Ir–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −3.1, −7.6 (d, $J_{\mathrm{P-P}}$ = 22 Hz).

Ir(PPh$_3$)$_2$(CO)(H)[C(O)NH(*p*-ClC$_6$H$_3$)], *p*-Cl·1·CO. Anal. Calcd (found): C, 57.81 (57.91); H, 3.92 (3.86); N, 1.55 (1.56). IR (CH$_2$Cl$_2$, cm^{-1}): ν(Ir–H) = 2095, ν(CO) = 2021, ν(–C(O)–) = 1601. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.51 (s, 1H, –C(O)N*H*(C$_6$H$_3$Cl)), 7.30 7.00 (m, 30H, P(C$_6$*H*$_5$)$_3$)), 6.42, 6.20, 6.00 (s, d, d, 3H, –C(O)NH(C$_6$*H*$_3$-Cl)), −9.16 (d of d, 1H, $J_{\mathrm{P-H}}$ = 120 and 19 Hz, Ir–*H*).

Carbonylation of 2,6-Me$_2$·1. CO gas was bubbled through a solution of 0.15 g (0.17 mmol) of the complex in toluene (20 mL) for 5 min. At this time, an IR spectrum of the reaction mixture indicated completion of the reaction. The yellow solution was then reduced in volume to ca. 5 mL, and hexane was added to precipitate the complex Ir(PPh$_3$)$_2$(CO)$_2$[C(O)NH(2,6-C$_6$H$_3$Me$_2$)] as a microcrystalline solid, which was collected by filtration, washed with hexane, and pumped to dryness. A second crop from the supernatant could be obtained in a similar fashion. Combined yield: 0.11 g, 78%. Anal. Calcd (found): C, 61.87 (61.20); H, 4.51 (4.44); N, 1.57 (1.65). IR (CH$_2$Cl$_2$, cm^{-1}): ν(N–H) = 3425, ν(CO) = 1975 (m), 1923 (s), ν(–C(O)–) = 1624 (w), ν(^{13}CO) = 1928 (m), 1878 (s), ν(–^{13}C(O)–) = 1573. ^{1}H NMR (C$_6$H$_6$): δ 7.50, 6.41 (m, 34H, P(C$_6$*H*$_5$)$_3$, –C(O)N*H*(C$_6$*H*$_3$Me$_2$)), 2.15 (s, 6H, –C(O)NH(C$_6$H$_3$*Me*$_2$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 2.31. Ir(PPh$_3$)$_2$-(^{13}CO)$_2$[^{13}C(O)NH(C$_6$H$_3$Me$_2$)]: ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ) 158.9 (t,

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Table 1. Crystallographic Data for *trans*-Ir(PPh_3)$_2$(CO)[NH(3,5-$C_6H_3Me_2$)]·0.5C_6H_6

formula	$C_{48}H_{43}IrNOP_2$
fw	904.02
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.072(2)
b, Å	11.667(2)
c, Å	21.133(4)
α, deg	88.74(2)
β, deg	81.24(2)
γ, deg	73.74(2)
V, Å^3	2121.9(7)
Z	2
μ(Mo Kα), cm^{-1}	32.56
D(calc), g cm^{-3}	1.410
$R(F)$, %	3.47
$R_w(F)$,^{a} %	4.92
δ/σ (max)	0.001
GOF	1.23

[a] $w^{-1} = \sigma^2(F) + 0.001(F)^2$.

J_{P-C} = 36 Hz, Ir–C(O)NH($C_6H_3Me_2$)), 188.4 (unrslv t, Ir–CO); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.31 (d, of t, J_{P-C} = 36 and 6 Hz).

Carbonylation of 3,5-Me$_2$·1. The procedure described above for **2,6-Me·1** was adopted to obtain Ir(PPh_3)$_2$(CO)$_2$[C(O)NH(3,5-$C_6H_3Me_2$)]. However, this complex shows decomposition in solution, which precluded us from obtaining an analytically pure sample. IR data (CH_2Cl_2, cm^{-1}): ν(CO) = 1980 (m), 1927 (s), ν(–C(O)–) = 1604. ^{1}H NMR (C_6D_6): δ 7.55, 7.00 (m, 31H, P(C_6H_5)$_3$, –C(O)N*H*($C_6H_3Me_2$)), 6.75, 6.50 (m, 3H, –C(O)NH($C_6H_3Me_2$)), 2.05 (s, 6H, –C(O)NH($C_6H_3Me_2$)).

Crystallographic Studies of *trans*-Ir(PPh_3)$_2$(CO)[NH(3,5-$C_6H_3Me_2$)]·0.5C_6H_6. The crystallographic data are summarized in Table 1. X-ray quality crystals of the complex were grown from benzene. A yellow needle of approximate dimensions 0.20 × 0.25 × 0.35 mm was covered with epoxy resin and was placed at the tip of a glass fiber. The cell constants and orientation matrix for data collection were based on 25 centered reflections in the range 20° < 2θ < 30°. The data revealed a triclinic system and the centrosymmetric space group $P\bar{1}$ was initially chosen. Final data refinement confirmed the accuracy of the choice. The position of the Ir atom was determined by the Patterson method, and the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. A correction for absorption was applied to the diffraction data by empirical methods. Following anisotropic refinement of all non-hydrogen atoms, the H attached to the nitrogen atom was assigned to the largest peak in the Fourier map and was refined independently. The remaining hydrogens were placed at calculated positions. All computations used SHELXTL-PC software (G. Sheldrick, Siemens, Madison, WI).

Results

Synthesis and Characterization. The amido complexes were synthesized in high yields by reacting the lithium salts of the arylamides with Vaska's complex, *trans*-Ir(PPh_3)$_2$(CO)Cl. A 2–3-fold excess of the lithium salt was used in each case to obtain rapid completion of the reaction, which was deemed necessary to avoid secondary reactions. Extraction of the reaction mixture with toluene and crystallization from the same solvent yielded solids of high purity. All of the complexes are stable for months at room temperature and under a dry nitrogen atmosphere.

The carbonyl stretching bands in the IR spectrum fall in the range 1944–1940 cm^{-1} for the anilide and methyl-substituted anilide complexes—these values are similar to that observed for the structurally analogous Ir–alkoxy complex *trans*-Ir(PPh_3)$_2$(CO)(OPh)[10]—and reflect the presence of a greater amount of Ir-to-CO back-bonding than in Vaska's complex. As expected, substitution in the phenyl ring of the amido ligand by electron withdrawing groups, as in ***p*-Cl·1** and ***p*-NO$_2$·1**, gives rise to higher ν(CO) values (1948 and 1962 cm^{-1}, respectively).

With the exception of **2,6-Me$_2$·1** and ***p*-NO$_2$·1**, all of the amido complexes display a broad singlet resonance for the amido proton (N*H*Ar) at δ ~2.4 in the ^{1}H NMR spectrum. The resonance for the same proton in ***p*-NO$_2$·1** is shifted downfield to δ 3.06, whereas that for **2,6-Me$_2$·1** is shifted upfield to δ 1.81. The aromatic region of the spectra is dominated by the resonances due to the phenyl protons of the two PPh_3 ligands. The number of observed resonances and their multiplicity patterns associated with the aromatic protons of the amido ligands imply fast rotation of the aromatic rings around the C(ipso)–N bond on the NMR time scale.

The nature of the amido nitrogen in *trans*-Ir(PPh_3)$_2$(CO)(^{15}NHPh) was probed by ^{15}N NMR spectroscopy, which produces a sharp doublet at δ –298.7 (vs $NH_4{}^{15}NO_3$ at δ 0 as the external reference). The chemical shift value, when referenced against $^{15}NH_2Ph$, and the observed J_{N-H} of 75 Hz are very similar to those observed for *trans*-Pt(PEt_3)$_2$(H)(^{15}NHPh).[12] Coupling between the ^{15}N atom and the two PPh_3 ligands was not observed. Comparing to the known values for aromatic amines,[13] the observed N–H coupling constant in *trans*-Ir(PPh_3)$_2$(CO)(^{15}NHPh) implies sp^3 hybridization at nitrogen.

Crystals suitable for X-ray structural analyses were obtained for the ***p*-Me·1**, ***o*-Me·1**, and **3,5-Me$_2$·1** complexes. The structure of ***p*-Me·1** has been communicated earlier[8] and will not be discussed any further. The structural analysis of **3,5-Me$_2$·1** allowed detection of the –NH– hydrogen from a difference Fourier map, thus revealing the geometry around the amido nitrogen. This and other structural features will be discussed here. Table 1 summarizes the crystallographic data, and Table 3 lists pertinent bond distances and angles. An ORTEP diagram with partial atom numbering scheme is provided in Figure 1. The geometry around the d^8 Ir center is nearly planar, as expected, with normal Ir–P(C_6H_5)$_3$ and Ir–CO distances. The Ir–N distance of 2.046(6) Å and the Ir–N–C(2) angle of 130.1(6)° are very similar to those observed for ***p*-Me·1**. The plane generated by the aromatic ring of the amido ligand is twisted by ~10° with respect to the Ir–N–C(2) plane and is also deviated by ~29° from being perpendicular to the square plane around iridium. Both these features are probably a result of steric interaction between this ring and the phenyl rings of the two PPh_3 ligands. The amido hydrogen was located in the final difference Fourier map, and its independent refinement yielded an N–H distance of 1.14(9) Å. Interestingly, the position of this hydrogen atom makes the nitrogen environment planar. Planar nitrogen atoms in coordinated amido ligands have been observed in late transition metal complexes in the past.[12,14,15] Despite the apparent planarity, the observed J_{N-H} values, determined for *trans*-Ir(PPh_3)$_2$(CO)(^{15}NHPh) and *trans*-Pt(PEt_3)$_2$(H)(^{15}NHPh), suggest sp^3 hybridization at the nitrogen atom. Unlike *trans*-Pt(PEt_3)$_2$(H)(NHPh), our molecule lacks any in-

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(13) Martin, G. J.; Martin, M. L.; Gouesnard, J.-P. *^{15}N-NMR Spectroscopy*; Springer-Verlag: Berlin, 1981; Chapter 7.

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for *trans*-Ir(PPh$_3$)$_2$(CO)[NH(3,5-C$_6$H$_3$Me$_2$)]·0.5C$_6$H$_6$

	x	*y*	*z*	*U*(eq)
Ir	374(1)	2071(1)	1967(1)	32(1)
P(1)	425(2)	89(2)	1882(1)	38(1)
P(2)	180(2)	4108(2)	2002(1)	36(1)
O	2762(7)	1925(5)	808(3)	72(3)
N	−1240(7)	2118(5)	2763(3)	45(2)
C(1)	1824(9)	1978(6)	1267(4)	46(3)
C(2)	−1277(9)	2488(6)	3387(3)	46(3)
C(3)	−46(10)	2739(6)	3587(3)	53(3)
C(4)	−173(11)	3196(7)	4220(4)	63(4)
C(5)	−1499(14)	3337(8)	4632(4)	77(5)
C(6)	−2736(13)	3029(8)	4446(4)	76(4)
C(7)	−2646(10)	2637(7)	3832(3)	58(3)
C(8)	1228(15)	3507(10)	4397(5)	108(6)
C(9)	−4271(14)	3193(11)	4911(5)	113(6)
C(11)	1462(8)	−907(6)	2459(3)	41(3)
C(12)	1228(10)	−472(8)	3081(4)	62(4)
C(13)	1970(12)	−1219(10)	3547(5)	84(5)
C(14)	2881(12)	−2355(9)	3368(6)	83(5)
C(15)	3108(11)	−2758(8)	2752(5)	73(4)
C(16)	2426(9)	−2056(6)	2294(4)	56(3)
C(17)	1303(10)	−673(6)	1113(3)	52(3)
C(18)	2865(11)	−789(7)	890(4)	63(3)
C(19)	3548(14)	−1366(9)	307(5)	88(5)
C(20)	2708(21)	−1816(11)	−48(5)	124(7)
C(21)	1189(19)	−1709(11)	146(6)	116(7)
C(22)	457(13)	−1124(9)	737(4)	82(4)
C(23)	−1529(8)	−107(6)	2032(3)	42(3)
C(24)	−2684(10)	693(8)	1760(4)	64(4)
C(25)	−4191(10)	581(9)	1858(6)	80(4)
C(26)	−4526(11)	−307(10)	2244(6)	87(5)
C(27)	−3391(11)	−1095(9)	2518(5)	79(5)
C(28)	−1875(10)	−1019(8)	2400(4)	64(4)
C(29)	2097(8)	4368(6)	1827(4)	43(3)
C(30)	3233(9)	3726(7)	2162(5)	64(4)
C(31)	4723(11)	3881(9)	2039(6)	82(5)
C(32)	5074(10)	4638(11)	1589(6)	87(5)
C(33)	3957(13)	5264(11)	1257(5)	88(5)
C(34)	2464(10)	5135(8)	1377(4)	59(3)
C(35)	−871(7)	4917(6)	1386(3)	39(3)
C(36)	−1010(8)	4313(7)	851(3)	48(3)
C(37)	−1797(10)	4905(9)	379(4)	68(4)
C(38)	−2472(10)	6133(9)	439(5)	72(4)
C(39)	−2327(12)	6745(9)	951(5)	83(5)
C(40)	−1530(11)	6147(8)	1423(5)	70(4)
C(41)	−759(8)	5042(6)	2703(3)	40(3)
C(42)	−25(9)	5716(7)	3013(4)	51(3)
C(43)	−788(11)	6421(8)	3550(4)	65(4)
C(44)	−2307(12)	6428(8)	3790(4)	74(4)
C(45)	−3048(9)	5770(8)	3491(4)	60(3)
C(47)	−2291(8)	5084(7)	2952(4)	51(3)
C(48)[a]	3309(23)	295(17)	5117(11)	173(7)
C(49)[a]	4268(24)	252(16)	4471(9)	163(6)
C(50)[a]	4119(27)	25(18)	5610(11)	188(8)

[a] Atoms C(48)–C(50) are for the benzene molecule.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Ir(PPh$_3$)$_2$(CO)[NH(3,5-C$_6$H$_3$Me$_2$)]·0.5C$_6$H$_6$

Ir–P(1)	2.310(2)	Ir–C(1)	1.807(7)
Ir–P(2)	2.335(2)	O–C(1)	1.178(9)
Ir–N	2.046(6)	N–C(2)	1.388(10)
P(1)–Ir–P(2)	175.7(1)	P(2)–Ir–C(1)	86.5(2)
P(1)–Ir–N	85.0(2)	N–Ir–C(1)	178.1(3)
P(2)–Ir–N	95.2(2)	Ir–N–C(2)	130.1(6)
P(1)–Ir–C(1)	93.4(2)	Ir–C(1)–O	179.5(5)

termolecular contact involving the -NH- hydrogen. To determine whether or not any steric factor might be responsible for the apparent planarity, we searched for "short" contacts within our molecule. As shown in a space-filling diagram of the molecule in Figure 2, the amido hydrogen is nestled between the bulky phosphorus atom (P(1)) of one PPh$_3$ ligand and an ortho C–H of the other

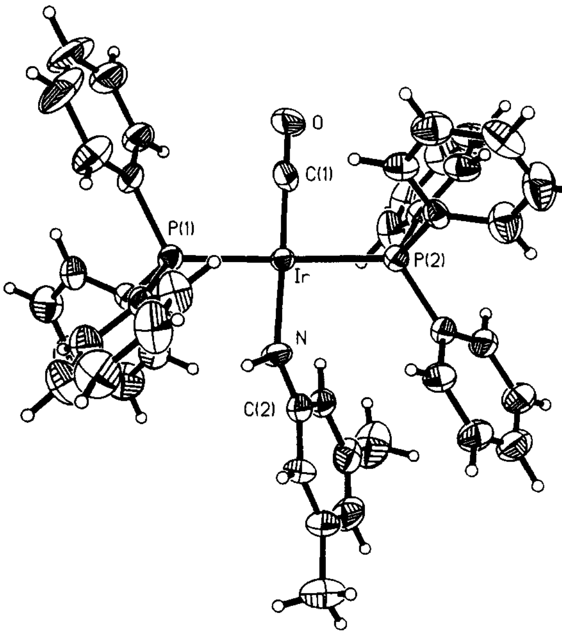


Figure 1. ORTEP diagram (40% thermal probability) of *trans*-Ir(PPh$_3$)$_2$(CO)[NH(3,5-C$_6$H$_3$Me$_2$)], **3,5-Me$_2$·1**.

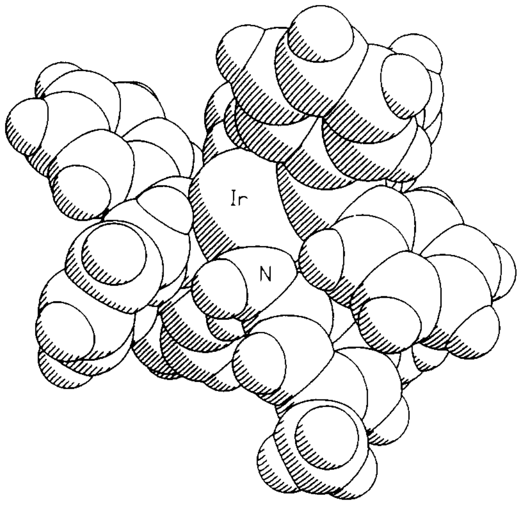
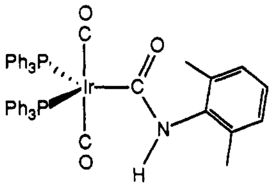


Figure 2. Space filling diagram of *trans*-Ir(PPh$_3$)$_2$(CO)[NH(3,5-C$_6$H$_3$Me$_2$)], **3,5-Me$_2$·1**.

PPh$_3$ ligand. These two interactions might have forced the hydrogen to attain a planar arrangement. In the absence of more structural and spectroscopic data, a concrete assessment of metal–nitrogen bonding in late metal amido complexes cannot be made at present.

Carbonylation Reactions. All of the amido complexes, except ***p*-NO$_2$·1**, undergo rapid reactions with CO at atmospheric pressure and at ambient temperature. When both the ortho sites on the arylamide ligand are blocked, as in *trans*-Ir(PPh$_3$)$_2$(CO)[NH(2,6-Me$_2$C$_6$H$_3$)], **2,6-Me$_2$·1**, the reaction with CO produces the five coordinate carbamoyl complex Ir(PPh$_3$)$_2$(CO)$_2$[C(O)N(H)(2,6-Me$_2$C$_6$H$_3$)], **2,6-Me$_2$·1·CO**, which has been assigned the following structure.

Characterization of this complex was accomplished by IR and NMR spectroscopic methods. The ^{31}P{^{1}H} NMR spectrum of an unlabeled sample shows a singlet at δ 2.35. The coupling between the carbonyl groups and PPh$_3$ ligands results in a doublet of triplet ($^2J_{P-C}$ = 6.0 and 36.0 Hz) splitting pattern for the same resonance when ^{13}CO-labeled sample is used (^{13}CO is observed to incorporate in



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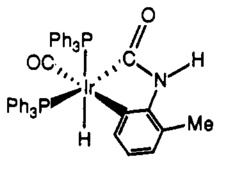
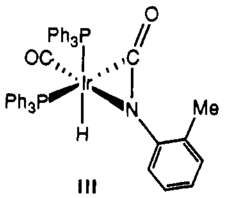


II



III

all CO sites of the molecule). We assign the smaller of the two J values to coupling between PPh_3 and the terminal ^{13}CO ligands, while the larger value is assigned to coupling between PPh_3 and the $-^{13}C(O)-$ of the carbamoyl ligand.[16] Consistent with this, we observe in the $^{13}C\{^1H\}$ NMR spectrum a well resolved triplet ($^2J_{P-C}$ = 36.0 Hz), centered at δ 159.8, that we assign to the carbonyl group in the carbamoyl ligand, and an unresolved triplet, at δ 188.4, for the CO ligands. The large coupling between the phosphines and C=O of the carbamoyl is perhaps indicative of their being in the equatorial plane, thus ~120° apart, rather than being 90° apart in a structure with axial PPh_3 ligands (this was pointed out by a reviewer). The relative intensities—one weak and one strong—of the two carbonyl bands in the IR spectrum is also consistent with the CO ligands being trans to each other. The weak band at 1624 cm^{-1} has been assigned to the C=O group of the carbamoyl ligand, and the observed splitting suggests that there may be isomers generated by rotation around the C—N bond. A weak IR band at 3425 cm^{-1} is assigned to ν(N—H). The reaction of **3,5-Me$_2$·1** with CO also affords a similar carbamoyl species, **3,5-Me$_2$·1·CO**, in spite of available ortho protons on the amido aromatic ring (*vide infra*).

The reactions between ***p*-Me·1**, ***o*-Me·1**, and ***p*-Cl·1** and CO produce products, labeled ***p*-Me·1·CO**, ***o*-Me·1·CO**, and ***p*-Cl·1·CO**, which are different from those just discussed. The addition of 2–3 equiv of CO to benzene solutions of the amido complexes afford pale-yellow, microcrystalline solids, whose IR spectra display weak, broad bands in the range 2098–2093 cm^{-1}, strong, sharp bands in the range 2021–2016 cm^{-1}, and strong, but broad bands in the range 1594–1601 cm^{-1}. The lowest energy bands are indicative of carbamoyl type moieties, while the highest energy bands suggest the presence of metal–hydride(s), which was confirmed by ^1H NMR spectroscopy. The hydride resonance for ***o*-Me·1·CO** appears as a doublet of doublets, centered at δ -9.22. The splitting is due to coupling of the hydride to two inequivalent PPh_3 ligands. The large J_{P-H} of 126 Hz suggests that one of the phosphines is trans to the hydride ligand. Consistent with these observations is the appearance of two doublets (J_{P-P} = 22 Hz) in the $^{31}P\{^1H\}$ NMR spectrum for the two inequivalent, and mutually cis, PPh_3 ligands. The use of 99% ^{13}CO in the synthesis of ***o*-Me·1·CO** shows isotopic enrichment in both the terminal CO and $-C(O)N=$ ligands, as evidenced by the appearance of two multiplets at δ 190.8 and 178.9 in the $^{13}C\{^1H\}$ NMR spectrum. Two possible sources for the hydride ligand were considered: the -NH- and ortho CH of the arylamide ligand, giving rise to structures **II** and **III**.

In **II**, the orthometalated ring should display three aromatic resonances in the ^1H NMR spectrum, whereas in **III**, four such resonances are expected. We are able to see only two resonances, a doublet and a triplet, for the $C(O)N(H)(o\text{-}C_6H_3Me)$ moiety. Other resonances, if present, are probably hidden underneath those due to the phenyl protons of the PPh_3 ligands. To resolve the ambiguity with structural assignment, *trans*-$Ir(PPh_3)_2(CO)(NHC_6D_5)$ was reacted with CO. The CO-inserted product shows an Ir–D stretching vibration at 1963 cm^{-1}, a much lower frequency than the Ir–H stretching vibration of the same complex in the fully protio form. The presence of Ir–D was also evident from NMR spectroscopy: the ^1H NMR spectrum shows no sign of any hydride resonance, and a broad doublet at δ -9.4 was observed in the ^2H NMR spectrum. The deuterium labeling study provides unambiguous evidence that the structure of the CO-inserted product is **II**, not **III**. Although the -NH- resonance could not be detected in the ^1H NMR spectrum (possibly due to overlap with PPh_3 proton resonances), the band due to ν(N–H) could be detected at ~3400 cm^{-1} in the IR spectrum for all three complexes. Interestingly, the deuteride complex, $Ir(PPh_3)_2(CO)(D)[C(O)N(H)C_6D_3]$, shows a slow growth of the hydride signal in C_6D_6 over a period of 48 h, possibly due to intramolecular exchange of Ir–D with N–H.

We have examined a few reactivities of the orthometalated complex, ***p*-Me·1·CO**. A slow isomerization in CD_2Cl_2 was observed. The process retains the mutual cis arrangement of the two PPh_3 ligands and their relative disposition with respect to the hydride ligand. We believe the isomerization consists of a rearrangement of the $C(O)NHC_6H_3Me$ moiety, such that the metalated ring, which was originally trans to the CO ligand, is now trans to a PPh_3 ligand. Furthermore, addition of excess CO at atmospheric pressure shows reversible displacement of a PPh_3 ligand to produce $Ir(PPh_3)(CO)_2(H)[C(O)NH(C_6H_3Me)]$. The reaction can be reversed to the bis(phosphine) complex by removing excess CO under reduced pressure. The hydride ligand, as in many other hydride complexes,[17] can be exchanged with a chloride ligand by reaction with $CHCl_3$, which is converted to CH_2Cl_2. The ^1H NMR spectrum of the chloro complex allows a detection of all the aromatic protons of the orthometalated species, and the multiplicity pattern renders further support to our initial structural assignment.

Mechanism of Carbonylation. In an attempt to detect the intermediates involved in the carbonylation of ***p*-Me·1**, a variable temperature IR spectral study was carried out. At -15 °C, the formation of the carbamoyl complex, $Ir(PPh_3)_2(CO)_2[C(O)(NHC_6H_4Me)]$, was evident, as suggested by the appearance of CO bands similar to those observed for **2,6-Me$_2$·1·CO**. The formation of the orthometalated complex began at ~5 °C, and proceeded to yield the dicarbonyl complex (*vide supra*) due to the presence of excess CO. Although the carbamoyl complex is the first species we could detect conclusively, it is, by no means, the first intermediate of the reaction. For its formation, two possible pathways which have precedent in the carbonylation of late transition metal alkoxide

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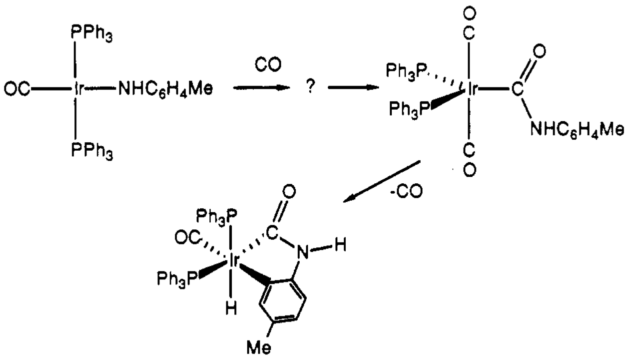
[16] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; Table 2.7.

[17] Schunn, R. A. In *Transition Metal Hydrides*: Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 203.

complexes, can be envisioned: the initial formation of Ir$(PPh_3)_2(CO)_2[NH(C_6H_4Me)]$, followed by intramolecular insertion and addition of CO,[18] or initial formation of the cationic species $Ir(PPh_3)_2(CO)_3^+$, through displacement of the amido ligand, followed by nucleophilic attack by the free amido ligand on one of the CO ligands of the tricarbonyl species.[19] Our experiment was not able to distinguish between these two possibilities. The proposed mechanism is depicted in the following scheme:



Discussion

The arylamido complexes discussed in this paper have structural (iridium–heteroatom bond distances) and spectroscopic (ν(CO)) properties that are very similar to those of *trans*-$Ir(PPh_3)_2(CO)(OPh)$.[10] These observations suggest that the degrees of Ir–O and Ir–N π bonding, if any, in these complexes are similar. The issue of heteroatom to late transition metal π bonding has been discussed recently,[20–22] and a consensus appears to be growing that, although empty orbitals of suitable symmetry and energy are not available to square-planar Ir^I or Pt^{II}, the presence of one or more π-acid ligands in the coordination sphere could produce some degree of π electron delocalization from the heteroatom to the metal center. Even if such "pseudo π bonding" is present, the heteroatom centers in both the alkoxide and amide complexes show a high degree of nucleophilicity, as judged by their reaction with CO. Even the presence of an electron withdrawing Cl substituent on the arylamide ligand does not seem to affect the nucleophilic character of the nitrogen too significantly; however, the NO_2 group as a substituent reduces the nucleophilicity to the point that no reaction with CO is observed at ambient temperature and pressure.

The formation of carbamoyl moieties by the reaction of CO with *trans*-$Ir(PPh_3)_2(CO)(NHAr)$ complexes has, to the best of our knowledge, only one precedent among group 9 and 10 amido species: $(dppe)Pt(Me)[NH(CH_2C_6H_5)]$ was reported to undergo an insertion reaction with CO to afford $(dppe)Pt(Me)[C(O)NH(CH_2C_6H_5)]$.[23] The Ir^I or Rh^I complexes containing the amido ligand $N[Si(Me)_2CH_2PR_2]_2^-$,[9] where the amido nitrogen is part of a chelate ring, does not undergo insertion of CO into the metal–nitrogen bond, presumably due to ring strain or due to electron deficiency at the nitrogen caused by the adjacent silyl groups. The Pt^{II}–amido complex *trans*-$Pt(PEt_3)_2(H)(NHPh)$[12] reductively eliminates aniline and forms $Pt(PEt_3)_2(CO)_2$ upon reaction with CO. A similar reductive elimination of amine was observed in the reaction of Cp*Ir$(PPh_3)(H)(NHPh)$ with CO.[24]

Another noteworthy feature of the carbonylation reactions of ***p*-Me·1·CO**, ***p*-Cl·1·CO**, and ***o*-Me·1·CO** is the facile aromatic C–H bond activation that occurs for the intermediate carbamoyl complexes, but is not observed for $Ir(PPh_3)_2(CO)_2[C(O)(OPh)]$. These are the first examples of orthometalation reactions involving a carbamoyl moiety. Since one of our goals is to obtain intramolecular N–H bond activation from a carbamoyl ligand, the propensity of C–H over N–H bond activation in these complexes was slightly disappointing. However, the observed reactions do show that oxidation of the Ir^I to an Ir^{III} center in the carbamoyl complexes is feasible. Work is underway to examine possible N–H activation in $Ir(PPh_3)_2(CO)_2[C(O)NH(2,6\text{-}Me_2C_6H_3)]$. We have also begun to synthesize arylamido complexes of Ir^I containing phosphines more basic than PPh_3, such as PMe_2Ph, PEt_3, or PMe_3, with the goal of making the metal center more susceptible to oxidative addition by employing strong σ donor ligands. The synthesis and carbonylation reactions of these new complexes will be reported in the future.

Acknowledgment. We wish to thank Johnson Matthey/Aesar for a generous loan of iridium chloride, the Department of Chemistry, University of Vermont, for financial support, and Professor Robert J. Angelici for helpful discussions. Thanks are also due to Henry Murdoch for attempting the preparations of ***p*-Cl·1** and ***p*-NO₂·1** and to Jim Breeyear and Rob Hayes for help with the NMR instruments. The 500-MHz NMR instrument was purchased through a grant from NSF (CHE-9208434).

Supplementary Material Available: Full listings of bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters, an ORTEP diagram with the complete atom numbering scheme, an IR spectrum of **2,6-Me₂·1·CO**, and ^1H NMR spectra of ***p*-Me·1** and ***o*-Me·1·CO** (8 pages). Ordering information is given on any current masthead page.

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[18] A similar mechanism was invoked for the carbonylation of several Pt–alkoxide complexes: (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (c) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.

[19] Such an intermediate was invoked in the carbonylation of *trans*-$Ir(PPh_3)_2(CO)(OPh)$: see ref 10.

[20] Paulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

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[22] Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.

[23] Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.

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