Iridium μ-Imido/Amido A-Frame Complexes[1]

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Received June 23, 1994[®]

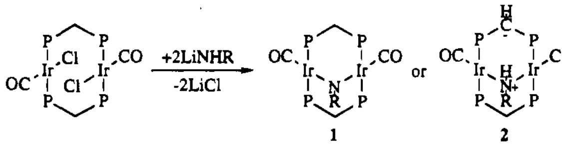
The reaction of $Ir_2Cl_2(CO)_2(\mu\text{-dppm})_2$ (dppm = bis(diphenylphosphino)methane) with 2 equiv of LiNHR yields $Ir_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2$, **1** (R = *p*-tolyl, Ph, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$), or its tautomer $Ir_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$, **2** (dppm-H = bis(diphenylphosphino)methanide; R = Et, Bu^t). NMR data suggest that **1** (R = *p*-tolyl, Ph, *p*-BrC_6H_4) are in equilibrium with small amounts of **2** in polar solvents. An X-ray structural determination of **1** (R = *p*-tolyl) shows that the imido nitrogen atom links two iridium atoms at the apex of an A-frame complex. A very short N−C distance in the imido group suggests extensive N−lone pair donation to the tolyl ring. Crystals of **1** (R = *p*-tolyl) from benzene are tetragonal ($P4_3$) with $a = 21.337(1)$ Å, $c = 14.478(2)$ Å, and $Z = 4$. With the exception of R = *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, and Et, the complexes react with 1 equiv of CO at ambient temperature to form $Ir_2(CO)_3(\mu\text{-dppm})_2$ as the major metal containing product. For R = Et, the reaction generates the unstable isocyanate complex $Ir_2(\mu\text{-EtNCO})(CO)_2(\mu\text{-dppm})_2$. All of the complexes react with excess CO (2 atm) yielding $Ir_2(CO)_4(\mu\text{-dppm})_2$ and amine except for the *p*-$NO_2C_6H_4$ complex, which gives a complex mixture of products.

Introduction

The catalytic oxidation of ammonia on platinum and the catalytic reduction of NO by CO over silica-supported platinum or rhodium are important processes. Mechanistic studies indicate that these catalytic reactions include the formation and cleavage of metal−nitrogen bonds.[2] Additionally, in the catalytic reduction of nitrobenzene, nitrosobenzene and phenylazide by carbon monoxide the formation of an intermediate metal stabilized phenylnitrene is postulated.[3] The study of imido metal complexes could help in understanding these catalytic process and also could result in new methods for the preparation of organonitrogen compounds. Most imido metal complexes are known for the stability and low reactivity of the imido linkage. A few imido metal complexes are reactive. For example, Cp*IrNR,[4] $(RNH)(OEt_2)V{=}NR$,[5] $V(NC_6H_4Me)(OBu^t)_3$[6] and $(Bu^t_3SiNH)_2Zr{=}NSiBu^t_3$[7] exhibit attractive reactivities. Over the last few years we have been exploring the chemistry of rhodium μ-imido dppm[8] A-frame complexes. These complexes also show interesting reactivity,[9] including tautomeric equilibria involving the highly basic imido group and the dppm methylene group, imido/CO coupling reactions, and, for the aryl imido complexes, electrophilic attack on the imido ring. As an extension of our studies and as a comparison of the iridium and rhodium chemistry, we set out to prepare iridium analogs of the Rh A-frame complexes. The synthesis and some chemical characterization of these complexes is reported here.

Results

Syntheses. Treatment of $Ir_2Cl_2(CO)_2(\mu\text{-dppm})_2$ in THF with slightly more than 2 equiv of LiNHR results in the rapid formation of red to red-orange $Ir_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2$ **1** (R = *p*-tolyl, Ph, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$) or its tautomer $Ir_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ **2** (R = Et, Bu^t) (eq 1).[8]



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The ^{31}P NMR spectra of **2** (R = Bu^t, Et) show AA′BB′ symmetric patterns approaching A_2B_2 quartets at high field. Similar results were observed for the Rh analogs of **2** but with the additional complication of Rh−P coupling.[9a] Complex **1** (R = *p*-$NO_2C_6H_4$) shows a sharp singlet in C_6H_6. For the other R groups (R = *p*-BrC_6H_4, Ph, *p*-tolyl), solvent-dependent behavior is observed. A single sharp peak is found for spectra in C_6H_6. In CH_2Cl_2, broadened signals are observed. The temperature dependence of the ^{31}P NMR spectrum of the *p*-tolyl derivative in CH_2Cl_2 was investigated. At ambient temperatures (25 °C) a broad peak with a width of 189 Hz (width at half maximum) is observed. At −50 °C, the peak sharpens to a width of 10 Hz. The toluene-d_8 spectra are temperature invariant. These same derivatives (R = *p*-BrC_6H_4, Ph, *p*-tolyl) also display broadened ^1H NMR spectra in CD_2Cl_2 but sharp spectra in C_6D_6. The sharp C_6D_6 spectra of these derivatives and the *p*-$NO_2C_6H_4$ derivative are as expected for the symmetric A-frame structure of the imido tautomer **1**. ^1H NMR spectra of **2** (R = Bu^t, Et) are also as expected and show nonaromatic peaks for the NH, PCH_2P, PCHP and R groups.

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

[1] This paper is dedicated to the memory of Elmer O. Schlemper. Part 15: Late Transition Metal Oxo and Imido Complexes. Part 14: Ge, Y.-W.; Ye, Y.; Sharp, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 8384−8385.

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[8] dppm = bis(diphenylphosphino)methane; dppm-H = bis(diphenylphosphino)methanide.

[9] (a) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796−3797. Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632−2640. (b) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234−2236. Ge, Y.-W.; Sharp, P. R. *Inorg. Chem.* **1992**, *31*, 379−384. (c) Ge, Y.-W.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 3667−3668. Ge, Y.-W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 94−100.

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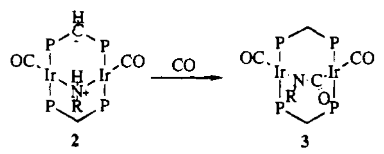
The amido tautomers **2** (R = Et, Bu^t) exhibit carbonyl absorptions in CH_2Cl_2 at ca. 1954 and 1930 cm^{-1}. The p-$NO_2C_6H_4$ imido complex has higher energy absorptions at 1953 and 1937 cm^{-1} while the other imido derivatives (R = p-BrC_6H_4, Ph, p-tolyl) show peaks at ca. 1925 and 1910 cm^{-1}.

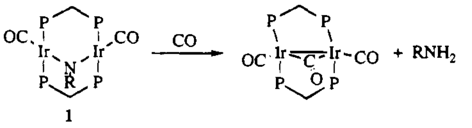
CO Reactions (1:1). The reactivities of the complexes towards CO depends on the properties of the R group. Only the complexes with the more electron-donating R groups react with 1 equiv of CO. The reactions take from seconds to days and follow the reactivity order Et > Bu^t > p-tolyl > Ph. There is no reaction for the complexes with electron-withdrawing groups p-$NO_2C_6H_4$ and p-BrC_6H_4, even after 48 h. However, these complexes do react with excess CO (see below).

The amido complex **2** (R = Et) reacts rapidly with 1 equiv of CO giving the green isocyanate complex $Ir_2(\mu\text{-}EtNCO)(CO)_2(\mu\text{-}dppm)_2$ **3** (eq 2, R = Et). The ^{31}P NMR spectra of **3** in CD_2Cl_2 exhibit two triplets corresponding to the two magnetically inequivalent sets of phosphorus atoms. ^1H NMR spectra show a pair of methylene multiplets consistent with the A-frame structure. In addition, transfer of the amido proton to the PCHP is indicated by the loss of coupling between this proton and the methylene of the NEt group. IR spectra show carbonyl absorptions at 1926 and 1950 cm^{-1}, slightly red shifted as compared with the parent complex. The expected μ-RNCO band is not observed possibly due to overlap with CH_2Cl_2 absorptions. Complex **3** is analogous to previously reported Rh isocyanate complexes and as with the Rh analogues,[9b] attempts to isolate **3** result in decomposition. Solutions of **3** also readily decompose, mostly to $Ir_2(CO)_3(\mu\text{-}dppm)_2$,[10] at ambient temperatures but only slowly at low temperatures (−78 °C). CO addition to **2** (R = Bu^t) also gives a green complex, but it is very unstable and decomposes in less than a minute, also generating $Ir_2(CO)_3(\mu\text{-}dppm)_2$ and other decomposition products.



(2)

The imido complexes **1** (R = Ph, p-tolyl) react with 1 equiv of CO in CH_2Cl_2 giving mostly $Ir_2(CO)_3(\mu\text{-}dppm)_2$ without detectable formation of an intermediate (eq 3). ^{31}P NMR spectra at the beginning of the reaction show starting material, $Ir_2(CO)_3(\mu\text{-}dppm)_2$ and $Ir_2(CO)_4(\mu\text{-}dppm)_2$.[10] As the reaction proceeds, the amount of $Ir_2(CO)_3(\mu\text{-}dppm)_2$ increases at the expense of the starting complex and $Ir_2(CO)_4(\mu\text{-}dppm)_2$, until $Ir_2(CO)_3(\mu\text{-}dppm)_2$ is the major product. The main organic product is RNH_2 (^1H NMR spectroscopy). The source of the hydrogens is likely solvent as found for similar reactions with the Rh analogs.[9b]



(3)

CO Reactions (Excess). The reactions of the complexes (R = p-BrC_6H_4, Ph, p-tolyl, Bu^t, Et) with excess CO (1:5 ratio) in CH_2Cl_2 give $Ir_2(CO)_4(\mu\text{-}dppm)_2$. The reactivity order is Et > Bu^t > p-tolyl > Ph > p-BrC_6H_4. There is no reaction of **1** (R = p-$NO_2C_6H_4$) under these conditions. However, under CO pressure (2 atm) in CH_2Cl_2 the complex does react to give a complex mixture of products.

Table 1. Crystallographic Data for Imido Complex **1** (R = p-Tolyl)

formula	$Ir_2P_4O_2NC_{59}H_{47}$	V, Å^3	6591.4
fw	1307.33	Z	4
space group	$P4_3$ (No. 78)	d_{calc}, g cm^{-3}	1.317
T, °C	22	μ, cm^{-1}	87.6
λ, Å	1.54056	transm range, %	0.760−0.999
a, Å	21.337(1)	$R(F_o)^a$	0.042
c, Å	14.478(2)	$R_w(F_o)^b$	0.064

^{a} $R(F_o) = (\Sigma||F_o| - |F_c||)/\Sigma F_o$. ^{b} $R_w(F_o) = [(\Sigma w(||F_o| - |F_c||)^2)/\Sigma wF_o^2]^{1/2}$; $w = 4F_o^2/(\Sigma F_o^2)^2$.

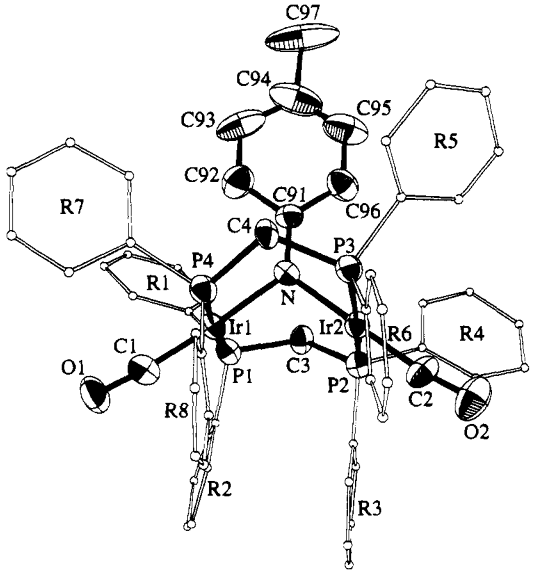


Figure 1. ORTEP drawing of imido complex **1** (R = p-tolyl). Phenyl ring carbons with arbitrary spheres, all other atoms with 50% probability ellipsoids. Hydrogen atoms omitted.

To explore the organic products from the CO reactions, the R = p-BrC_6H_4 derivative was treated with CO at 2 atm. After this mixture was stirred at room temperature for 20 h, the CO was released and the reaction mixture was analyzed by IR spectroscopy. The isocyanate RNCO, a product formed in analogous Rh reactions,[9b] was not detected. Moreover, the CH_2Cl_2 was removed and dimethyl-d_6 sulfoxide was added to the residue. The ^1H NMR spectrum indicated a 70% yield of p-$BrC_6H_4NH_2$. The urea RNHC(O)NHR, also a product in analogous Rh reactions,[9b] was not detected in the residue. A similar procedure was applied to the reaction of the Ph derivative with CO (2 atm). Only aniline was detected (68% yield).

Structure of Imido Complex 1 (R = p-Tolyl). A crystal grown from a benzene solution containing **1** (R = p-tolyl) was subjected to an X-ray crystal structure analysis. Crystal and data collection parameters are summarized in Table 1. An ORTEP diagram is shown in Figure 1. Selected atomic coordinates are given in Table 2, and selected interatomic distances and angles are provided in Table 3. The complex is the imido tautomer **1** (R = p-tolyl) and has the expected A-frame geometry where two iridium atoms are linked by the imido nitrogen. The most remarkable features of the structure are the planarity of the imido nitrogen (angles total 360°) and the short N−C distance 1.35(2) Å in the imido group (N−C91). A single bond C(sp^2)−N(sp^3) distance is expected to be ca. 1.43 Å. The observed distance is almost as short as the N−C distance (1.316(5) Å) in $Rh_2(\mu\text{-}NC_6H_4NO_2)(CO)_2(\mu\text{-}dppm)_2$ where resonance forms involving N−C double bonds are readily invoked.[9a] Resonance forms for **1** (R = p-tolyl) involve charge density on the ring carbons as in **A**, **B**, and **C** (Scheme 1). We have previously observed electrophilic addition of carbon-based

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Table 2. Atomic Parameters for Imido Complex **1** (R = *p*-Tolyl)

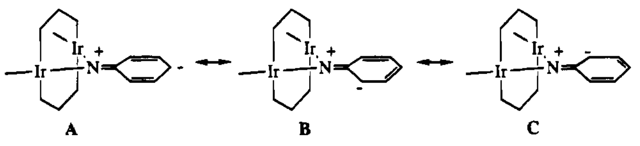
	x	y	z	B,[a] Å^2
Ir1	0.56640(3)	0.88544(3)	0.87713	3.32(3)
Ir2	0.48587(3)	0.78029(3)	0.77626(6)	3.307(25)
P1	0.52748(19)	0.96099(17)	0.7796(3)	3.54(16)
P2	0.43917(19)	0.86185(18)	0.7008(3)	3.49(16)
P3	0.54514(18)	0.70263(18)	0.8451(3)	3.48(16)
P4	0.60797(19)	0.80430(18)	0.9620(3)	3.65(16)
O1	0.5782(7)	0.9715(6)	1.0408(11)	6.7(7)
O2	0.3655(6)	0.7055(6)	0.7819(12)	7.1(7)
N	0.5681(6)	0.8278(6)	0.7657(9)	3.7(5)
C1	0.5704(8)	0.9376(7)	0.9762(12)	4.2(7)
C2	0.4134(7)	0.7376(7)	0.7871(15)	4.5(7)
C3	0.4903(7)	0.9276(7)	0.6760(11)	3.9(7)
C4	0.6183(7)	0.7328(6)	0.8960(11)	3.4(6)
C91	0.6143(7)	0.8177(7)	0.7034(12)	3.7(6)
C92	0.6749(9)	0.8472(9)	0.7100(15)	5.8(9)
C93	0.7233(9)	0.8361(12)	0.6475(20)	8.6(14)
C94	0.7132(14)	0.7953(12)	0.5727(17)	8.8(14)
C95	0.6567(11)	0.7663(10)	0.5658(17)	7.8(13)
C96	0.6099(9)	0.7778(8)	0.6278(14)	5.1(9)
C97	0.7640(14)	0.7808(18)	0.5000(25)	13.9(23)

[a] B is the mean of the principal axes of the thermal ellipsoid.

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for Imido Complexex **1** (R = *p*-Tolyl)

Ir1−P1	2.299(4)	P3−C51	1.830(16)
Ir1−P4	2.301(4)	P3−C61	1.824(17)
Ir1−N	2.029(12)	P4−C4	1.813(14)
Ir1−C1	1.817(17)	P4−C71	1.812(18)
Ir2−P2	2.283(4)	P4−C81	1.857(18)
Ir2−P3	2.310(4)	O1−C1	1.194(21)
Ir2−N	2.031(12)	O2−C2	1.232(19)
Ir2−C2	1.802(14)	N−C91	1.354(20)
P1−C3	1.841(16)	C91−C92	1.442(24)
P1−C11	1.801(16)	C91−C96	1.39(3)
P1−C21	1.818(16)	C92−C93	1.39(3)
P2−C3	1.813(14)	C93−C94	1.41(4)
P2−C31	1.851(16)	C94−C95	1.36(4)
P2−C41	1.801(18)	C94−C97	1.54(3)
P3−C4	1.843(14)	C95−C96	1.37(3)
P1−Ir1−P4	174.36(15)	Ir1−N−C91	129.7(10)
P1−Ir1−N	86.7(4)	Ir2−N−C91	126.9(10)
P1−Ir1−C1	94.2(5)	N−C91−C92	122.7(16)
P4−Ir1−N	87.8(4)	N−C91−C96	124.9(15)
P4−Ir1−C1	91.2(5)	C92−C91−C96	112.4(15)
N−Ir1−C1	176.3(6)	C91−C92−C93	123.2(20)
P2−Ir2−P3	172.62(14)	C92−C93−C94	119.5(21)
P2−Ir2−N	87.7(4)	C93−C94−C95	118.3(20)
P2−Ir2−C2	93.0(5)	C93−C94−C97	122(3)
P3−Ir2−N	85.3(4)	C95−C94−C97	118(3)
P3−Ir2−C2	94.0(5)	C94−C95−C96	121.3(22)
N−Ir2−C2	179.1(7)	C91−C96−C95	125.3(18)
Ir1−N−Ir2	103.1(5)		

Scheme 1



electrophiles at the para-ring position of the Rh analogs of **1** and used these reonance forms to explain this reactivity.[9c] The present results now lend structural support to this explanation. The Ir−N distances (2.029(12) and 2.031(12) Å) are comparable to those observed in the Rh complexes $Rh_2(\mu\text{-}NC_6H_4NO_2)(CO)_2(\mu\text{-}dppm)_2$ (2.042(2) Å) and $Rh_2(\mu\text{-}NHMe)(CO)_2(\mu\text{-}dppm)(\mu\text{-}dppm\text{-}H)$ (2.098(5) and 2.092(5) Å)[9a] and to the Ir−O distances found in $Ir_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-}dppm)_2$ (2.06(2) and 2.07(2) Å).[10] The Ir−P distances (2.283(4)−2.310(4) Å, 2.30 Å average) are somewhat shorter than analogous distances found in other dppm bridged Ir complexes (e.g., 2.32 Å average in $Ir_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-}dppm)$). Other features of the structure are common to A-frame complexes.

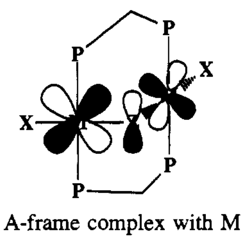
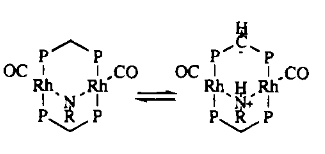


Figure 2. HOMO of A-frame complex with M = Rh or Ir and Y = S, O, NR.

Discussion

We began this chemistry expecting to find that the Ir chemistry was essentially identical to the analogous Rh chemistry. There are, however, notable differences. The first of these is the apparently lower basicity of the imido nitrogen in the Ir complexes. This is suggested by the lower tendency of Ir to form the amido tautomers. For Rh, we found substantial amounts of the amido tautomer in equilibrium with the imido tautomer for R = Ph, *p*-tolyl, *p*-BrC_6H_4, and other aryl R groups (eq 4).[9a] Here for Ir and these R groups, the only evidence we find for the amido tautomer is the broadening of the NMR spectra. IR spectra and low temperature ^{31}P NMR show no detectable amounts of the amido tautomer. The observed spectral broadening occurs in polar CH_2Cl_2 but not in C_6H_6 consistent with the formal zwiterionic character of the amido tautomer. Although we cannot totally discount possible changes in the acidity of the dppm C−H bond on going from Rh to Ir it seems most likely that the major factor in the lower tendency to form the amido tautomer is a reduction in the imido group basicity. The N−M σ-interaction is likely to be similar for both Rh and Ir. The difference is probably therefore in the π-interaction.



(4)

This conclusion is consistent with the MO diagram[11] developed from the model complex $[Rh_2(\mu\text{-}S)Cl_2(\mu\text{-}dppm)_2]^{2-}$. The HOMO (Figure 2) is an antibonding combination of Rh d-orbitals and a S^{2-} p-orbital and has ca. 45% S character. Replacement of S^{2-} with NR^{2-} with its higher energy p-orbitals results in greater N character in the HOMO, enhanced e$^-$ density on N, and high basicity. (A similar analysis explains the high basicity of $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-}dppm)_2$.)[12] If we now replace Rh with Ir and its higher energy d-orbitals, the HOMO loses N character and gains Ir character resulting in less e$^-$ density on N and lower basicity. Note, however, that there is still substantial e$^-$ density on the N as evidenced by the high sensitivity of the complexes to protic compounds and the structural data for **1** (R = *p*-tolyl) presented above. The electron density is, however, reduced enough to discourage internal deprotonation of the CH_2 group for all but the most electron donating R groups, Et and Bu^t.

There are also differences in the CO reaction chemistry on going from Rh to Ir. For Rh, the first equivalent of CO gives isocyanate complexes analogous to **3** for all R groups except *p*-$NO_2C_6H_4$.[9b] Only the alkyl group amido complexes give

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evidence of isocyanate complex formation for Ir. In common with Rh, the isocyanate complexes are unstable. However, for Rh they react further with CO giving CO/RN coupling products (dimetallocycloimide complexes, free RNCO, and RNHC(O)NHR) while for Ir further reaction with CO gives only carbonyl complexes and free amines.

Conclusions

While the Ir imido/amido dppm A-frame chemistry resembles that for Rh there are significant differences. Although the Ir imido complexes are still highly basic, they appear to be less basic than the Rh analogs as judged by their tendency to undergo tautomerization between the imido−dppm methylene and the amido−dppm methanide. Moreover, there is a dramatic change in the CO reaction chemistry. Ir, in contrast to Rh, does not give any final products resulting from imido−CO coupling. The reason for this is not clear to us.

Experimental Section

General Methods. All experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corp. drybox or by Schlenk techniques. Solvents were carefully dried under dinitrogen by recommended published techniques[13] and were stored under dinitrogen over 4 Å molecular sieves. $Ir_2Cl_2(CO)_2(\mu\text{-dppm})_2$ was prepared in a 90% yield by a modification of the published procedure in which three steps and alternating solvents are required.[14] In this work, only one solvent (THF) and vigorous reflux for 6 h were necessary. LiNHR reagents were prepared from the corresponding amine and commercial Bu^nLi hexane solution in ether. NMR spectra were recorded on a Nicolet NT 300 or a Bruker AMX 500 using TMS for ^1H and 85% H_3PO_4 for ^{31}P as references. IR spectra were obtained on a Nicolet 20 DXB FTIR spectrometer using NaCl plates. Microanalyses (inert atmosphere) were performed by Desert Analytics. The pressure reactions were conducted in a Fisher-Porter pressure bottle.

Syntheses of Imido/Amido Complexes. $Ir_2[\mu\text{-N}(p\text{-}NO_2C_6H_4)](CO)_2(\mu\text{-dppm})_2$, 1 (R = p-$NO_2C_6H_4$). To a stirred suspension of $Ir_2Cl_2(CO)_2(\mu\text{-dppm})_2$ (102 mg, 0.08 mmol) in 6 mL of THF was added a THF (4 mL) solution of $LiNH(p\text{-}NO_2C_6H_4)$ (26 mg, 0.176 mmol). After this was stirred at room temperature for 0.5 h, a slightly cloudy red solution had formed. The volatiles were removed in vacuo, yielding a red solid. The solid was dissolved in 6 mL of CH_2Cl_2 and filtered to remove the LiCl. Reduction of the solution volume in vacuo to ca. 1 mL followed by addition of ethyl ether (10 mL) produced a red solid. The red solid was purified by a methylene chloride−hexane reprecipitation, collected by filtration, washed twice with ether, and dried in vacuo to yield 94 mg (87%) of product. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.7. ^1H NMR (CD_2Cl_2): δ 2.97, 3.62 (m, 2 each, PCH_2P), 5.66 (d, 2, J_{HH} = 10.0 Hz, $NO_2C_6H_4$), 7.1−7.6 (m, 42, Ph). The second member of the $NO_2C_6H_4$ A_2B_2 pair was obscured by Ph peaks. ^1H NMR (C_6D_6): δ 2.55, 3.95 (m, 2 each, PCH_2P), 6.20, 8.07 (d, 2 each, J_{HH} = 9.1 Hz, $NO_2C_6H_4$), 6.3−7.6 (m, 40, Ph). IR (CH_2Cl_2, cm^{-1}): 1937 (vs), 1953 (vs).

$Ir_2[\mu\text{-N}(p\text{-}BrC_6H_4)](CO)_2(\mu\text{-dppm})_2$, 1 (R = p-BrC_6H_4). A solution of $LiNH(p\text{-}BrC_6H_4)$ (63 mg, 0.352 mmol) in THF (4 mL) was added to a suspension of $Ir_2Cl_2(CO)_2(\mu\text{-dppm})_2$ (205 mg, 0.16 mmol) in 8 mL of THF. This reaction mixture was stirred for 0.5 h. A transparent red solution was generated. Removal of the volatiles in vacuo resulted in a red solid. The solid was dissolved in toluene (10 mL) and filtered to remove the LiCl. The toluene solution volume was reduced in vacuo to ca. 1 mL, and 10 mL of hexane was added, causing the precipitation of a red-orange solid. A methylene chloride−hexane reprecipitation was used for the purification. The product was isolated by filtration, washed twice with hexane, and dried in vacuo to give 188 mg (86%) of product. Anal. Calcd (found) for $C_{58}H_{48}NO_2BrP_4Ir_2$: C, 50.51 (50.15); H, 3.51 (3.44); N, 1.02 (1.16). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.8. ^1H NMR (C_6D_6): δ 2.47, 4.30 (m, 2 each, PCH_2P), 6.35 (d, 2, J_{HH} = 9.0 Hz, BrC_6H_4), 6.75−7.68 (m, 42, Ph). The second member of the BrC_6H_4 A_2B_2 pair was obscured by Ph peaks. IR (CH_2Cl_2, cm^{-1}): 1914 (vs), 1929 (vs).

$Ir_2(\mu\text{-NPh})(CO)_2(\mu\text{-dppm})_2$, 1 (R = Ph). The phenyl imido/amido complex was prepared by the same procedure described for the p-BrC_6H_4 imido/amido complex and was isolated as a red-orange solid in a 90% yield. Anal. Calcd (found) with 0.5 equiv of CH_2Cl_2: C, 52.32 (52.20); H, 3.75 (3.72); N, 1.04 (0.96). The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy in $CDCl_3$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.7. ^1H NMR (C_6D_6): δ 2.47, 4.37 (m, 2 each, PCH_2P), 6.36 (t, 1, J_{HH} = 7 Hz, NPh), 6.61 (d, 2, J_{HH} = 7 Hz, NPh), 6.74−7.74 (m, 42, Ph). IR (CH_2Cl_2, cm^{-1}): 1908 (vs), 1926 (vs).

$Ir_2[\mu\text{-N}(p\text{-tolyl})](CO)_2(\mu\text{-dppm})_2$, 1 (R = p-tolyl). The p-tolyl imido/amido complex was prepared by the same procedure described for the p-BrC_6H_4 imido/amido complex except a longer reaction time (1.5 h) was used. The product was isolated in a 91% yield as a deep red solid. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.6. ^1H NMR (C_6D_6): δ 2.32 (s, 3, Me), 2.46, 4.38 (m, 2 each, PCH_2P), 6.54 (d, 2, J_{HH} = 7 Hz, NPh), 6.73−7.73 (m, 42, Ph). IR (CH_2Cl_2, cm^{-1}): 1907 (vs), 1923 (vs).

$Ir_2(\mu\text{-NHBu}^t)(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$, 2 (R = Bu^t). This complex was prepared by the same procedure described for the p-tolyl imido/amido complex. The product was isolated in a 91% yield as a red solid. Anal. Calcd (found) with 0.6 equiv of CH_2Cl_2: C, 51.06 (51.07); H, 4.10 (3.97); N, 1.05 (0.86). The presence of CH_2Cl_2 in product was confirmed by ^1H NMR spectroscopy in $CDCl_3$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 6.2, 18.6 (symmetric AA′BB′ pattern). At low field (36 MHz), a single peak with surrounding small peaks is observed in the ^{31}P. ^1H NMR (C_6D_6): δ 0.91 (s, 9, Bu^t), 1.85 (m, 1, PCHP), 3.90 (m, 2, PCH_2P), 6.94−8.32 (m, 40, Ph). The NH peak was not identified. IR (CH_2Cl_2, cm^{-1}): 1930 (vs), 1954 (vs).

$Ir_2(\mu\text{-NHEt})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$, 2 (R = Et). The ethyl amido complex was synthesized by the same method as for the p-tolyl imido/amido complex. The product was isolated in an 89% yield as a red solid. One unusual feature of the spectrum of the Et derivative is the appearance of the Et methylene as a quintet evidently resulting from combined H−H and H−N coupling. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 11.1, 18.9 (symmetric AA′BB′ pattern). ^1H NMR (C_6D_6): δ 0.48 (t, 3, J_{HH} = 6.9 Hz, $HNCH_2CH_3$), 1.80 (m, 1, PCHP), 3.00 (quin, 2, $J_{HH} \approx J_{HH(N)}$ = 7 Hz, $HNCH_2CH_3$), 3.54 (m, 2, PCH_2P), 6.77−8.27 (m, 40, Ph). A COSY spectrum confirmed the coupling in the Et group. The NH peak was observed in CD_2Cl_2 but not in C_6H_6. ^1H NMR (CD_2Cl_2): δ 0.23 (t, 3, J_{HH} = 6.9 Hz, $HNCH_2CH_3$), 1.42 (br quin, 1, $J_{HH} \approx J_{HN}$ = 7 Hz, $HNCH_2CH_3$), 1.81 (m, 1, PCHP), 2.78 (quin, 2, $J_{HH} = J_{HH(N)}$ = 6.9 Hz, $HNCH_2CH_3$), 3.72 (m, 2, PCH_2P), 7.0−7.95 (m, 40, Ph). IR (CH_2Cl_2, cm^{-1}): 1930 (vs), 1955 (vs).

Reaction of Imido/Amido Complexes with CO. Complex:CO = 1:1. An NMR tube was charged with 13 mg (0.01 mmol) of $Ir_2(\mu\text{-NHEt})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ and 0.7 mL of CH_2Cl_2. Carbon monoxide (0.22 mL) was injected. The solution immediately turned green. $^{31}P\{^1H\}$ NMR and IR spectra were recorded at once. A similar operation was used to record the ^1H NMR in C_6D_6. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 6.54 (t), 10.04 (t), J_{AB} = 20 Hz. ^1H NMR (CD_2Cl_2): 0.19 (t, 3, J_{HH} = 7.4 Hz, CH_3CH_2N), 2.45 (quartet, 2, CH_3CH_2N), 3.48 (m, 2, PCH_2P), 3.80 (m, 2, PCH_2P), 7.0−7.96 (m, 40, Ph). ^1H NMR (C_6D_6): 0.64 (t, 3, J_{HH} = 7.4 Hz, CH_3CH_2N), 3.13 (quartet, 2, CH_3CH_2N), 3.46 (m, 2, PCH_2P), 3.82 (m, 2, PCH_2P), 6.79−8.40 (m, 40, Ph). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1926 (vs), 1950 (vs).

Similar operations were applied for the reactions of **1** (R = p-$NO_2C_6H_4$, p-BrC_6H_4, Ph, p-tolyl) with CO. $^{31}P\{^1H\}$ NMR and IR data showed only the formation of $Ir_2(CO)_3(\mu\text{-dppm})_2$[10] except for the p-$NO_2C_6H_4$ and p-BrC_6H_4 complexes which remained unchanged. Complex **2** (R = Bu^t) gave similar results with the formation of a transient green solution.

Complex:CO = 1:5. CO (1.1 mL, 0.05 mmol) was injected into an NMR tube containing 13 mg (0.01 mmol) of **2** (R = Bu^t) dissolved in 0.7 mL of CH_2Cl_2. The solution turned orange in a few minutes. The reactions of **1** (R = p-$NO_2C_6H_4$, p-BrC_6H_4, Ph, p-tolyl) and **2** (R = Et) with CO (1:5) were carried out in the same manner. $^{31}P\{^1H\}$ NMR and IR data for the final products were consistent with the published data for $Ir_2(CO)_4(\mu\text{-dppm})_2$[10] except for the p-$NO_2C_6H_4$ complex which remained unchanged.

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CO Pressure Reactions. A Fischer & Porter pressure bottle was charged with 13 mg (0.01 mmol) of **1** (R = *p*-tolyl) dissolved in 2 mL of CH_2Cl_2. Two atmospheres of CO was introduced. After this mixture was stirred at room temperature for 20 h, the CO was carefully released. $^{31}P\{^1H\}$ NMR and IR spectra showed the product to be $Ir_2(CO)_4(\mu\text{-dppm})_2$. The reactions of the other complexes with 2 atm of CO were performed in a similar way also giving $Ir_2(CO)_4(\mu\text{-dppm})_2$ with the exception of the *p*-nitrophenyl complex, which resulted in a complicated mixture of products.

Structure Analysis of Imido Complex 1 (R = *p*-Tolyl). An outline of crystallographic and data collection parameters is given in Table 1. Crystals of the *p*-tolyl imido complex were grown from a concentrated solution of the compound in benzene. A suitable crystal was mounted in the air on a glass fiber and immediately coated with a layer of epoxy. Further details are provided as supplementary material.

Acknowledgment. We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-88ER13880), for support of this work. Grants from the National Science Foundation provided a portion of the funds for the purchase of the X-ray (Grant CHE-9011804) and NMR (Grants PCM-8115599 and CHE 89-08304) equipment.

Supplementary Material Available: Listings of X-ray crystal, data collection and processing parameters, positional parameters, thermal parameters, and bond distances and angles for **1** (R = *p*-tolyl) (8 pages). Ordering information is given on any current masthead page.

IC9407252