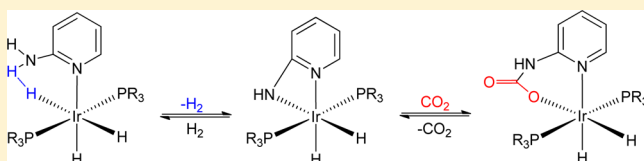


Mild, Reversible Reaction of Iridium(III) Amido Complexes with Carbon Dioxide

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S Supporting Information

ABSTRACT: Unlike some other Ir(III) hydrides, the aminopyridine complex $[(2\text{-NH}_2\text{-C}_5\text{NH}_4)\text{IrH}_3(\text{PPh}_3)_2]$ (**1-PPh₃**) does not insert CO₂ into the Ir–H bond. Instead **1-PPh₃** loses H₂ to form the cyclometalated species $[(\kappa^2\text{-N,N-2-NH-C}_5\text{NH}_4)\text{IrH}_2(\text{PPh}_3)_2]$ (**2-PPh₃**), which subsequently reacts with CO₂ to form the carbamate species $[(\kappa^2\text{-O,N-2-OC(O)NH-C}_5\text{NH}_4)\text{IrH}_2(\text{PPh}_3)_2]$ (**10-PPh₃**). To study the insertion of CO₂ into the Ir–N bond of the cyclometalated species, a family of compounds of the type $[(\kappa^2\text{-N,N-2-NR-C}_5\text{NH}_4)\text{IrH}_2(\text{PR}'_3)_2]$ (R = H, R' = Ph (**2-PPh₃**); R = H, R' = Cy (**2-PCy₃**); R = Me, R' = Ph (**4-PPh₃**); R = Ph, R' = Ph (**5-PPh₃**); R = Ph, R' = Cy (**5-PCy₃**)) and the pyrimidine complex $[(\kappa^2\text{-N,N-2-NH-C}_4\text{N}_2\text{H}_3)\text{IrH}_2(\text{PPh}_3)_2]$ (**6-PPh₃**) were prepared. The rate of CO₂ insertion is faster for the more nucleophilic amides. DFT studies suggest that the mechanism of insertion involves initial nucleophilic attack of the nitrogen lone pair of the amide on CO₂ to form an N-bound carbamate complex, followed by rearrangement to the O-bound species. CO₂ insertion into **1-PPh₃** is reversible in the presence of H₂ and treatment of **10-PPh₃** with H₂ regenerates **1-PPh₃**, along with Ir(PPh₃)₂H₅.



■ INTRODUCTION

The catalytic conversion of CO₂ to useful products is attractive owing to its widespread availability, low cost, and nontoxic nature.¹ Desirable products include liquid fuels,² cyclic carbonates,³ and formic acid.⁴ CO₂ is reactive toward strong nucleophiles (e.g., RMgBr and RLi) but in general reactions with weaker nucleophiles require harsh conditions and more effective catalysts still need to be developed. The insertion of CO₂ into M–X bonds is a crucial step in many catalytic cycles for CO₂ conversion and has been studied in various contexts, including CO₂ hydrogenation⁴ and C–C bond formation.⁵ These examples of organometallic reactivity differ considerably from those demonstrated in the organic literature.

One well-studied organic example is the reversible reaction of CO₂ with amines to form carbamic acids, where the resulting acids must be “trapped” with base as the carbamate anion in order to isolate any product.⁶ Indeed, amines find use in current industrial applications for the “scrubbing” or removal of CO₂ from gaseous waste streams.⁷ Far less studied are the analogous reactions with amido complexes to form products containing carbamate ligands. Reactions with metal amido species to form metal carbamate complexes are known,⁸ particularly for the early transition metals, but there are only scattered reports for the platinum group metals, and few mechanistic details have been determined for these reactions. Furthermore, the majority of these examples feature *N,N*-dialkylcarbamato ligands because of the relative solubility of the

resulting compounds and few monosubstituted complexes are known.⁹

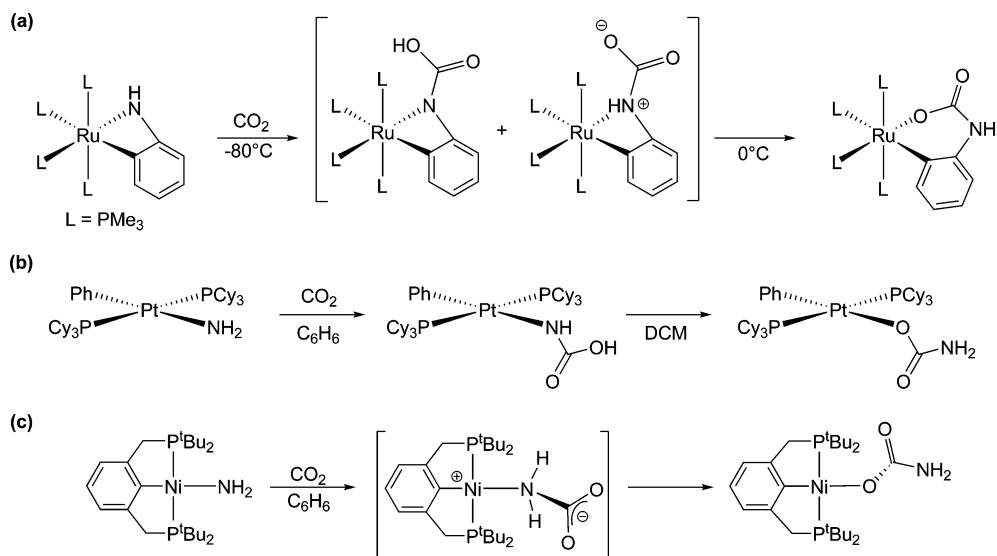
A rare example involving a monosubstituted amido and a platinum group metal was reported by Bergman and Andersen,¹⁰ who found that a ruthenium amido complex underwent facile reaction with CO₂ to form a carbamate complex (Scheme 1a). This reaction occurred without prior ligand dissociation, and based on observations from low temperature NMR spectroscopy, it was postulated that the reaction involved direct electrophilic attack of CO₂ by the nitrogen atom to form an *N*-bound carbamate species, which would rearrange to form the final *O*-bound product. The feasibility of this mechanism was established when Roundhill demonstrated that an isolated Pt *N*-bound carbamate complex, generated from CO₂ and a Pt amido species, readily rearranged to the *O*-bound product in a polar solvent (Scheme 1b).¹¹ Early in 2012, we demonstrated that a Ni amido species supported by a PCP pincer ligand (PCP = bis-2,6-ditert-butylphosphinomethylbenzene) also undergoes CO₂ insertion via a mechanism that involves nucleophilic attack of the amide on CO₂ followed by rearrangement from an *N*-bound carbamate complex to an *O*-bound carbamate complex (Scheme 1c).¹²

In a recent computational study¹³ we compared the relative hydricity of iridium(III) hydrides and used this information to

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Scheme 1. (a) Reaction of a Ru Amido Complex with CO₂,¹⁰ (b) Reaction of a Pt Amido Complex with CO₂,¹¹ (c) Reaction of a Ni Amido Complex with CO₂.¹²



build a model to predict the relative thermodynamic favorability of insertion of CO₂ into the Ir–H bond, a proposed mechanistic step in the hydrogenation of CO₂.¹⁴ We developed a highly active CO₂ hydrogenation catalyst with an N–H hydrogen bond donor in the secondary coordination sphere (Figure 1a); this N–H improved the thermodynamic

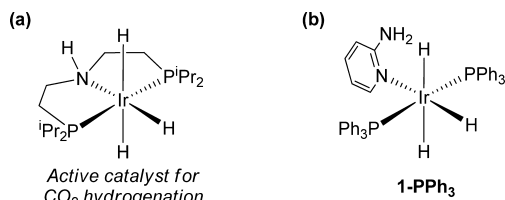


Figure 1. (a) Our prior catalyst for CO₂ hydrogenation.¹³ (b) A related pendant amine compound.¹⁵

favorability of CO₂ insertion. As a continuation of this investigation we were interested in the reactivity of CO₂ with other iridium(III) hydrides having H-bond donors in the secondary coordination sphere.

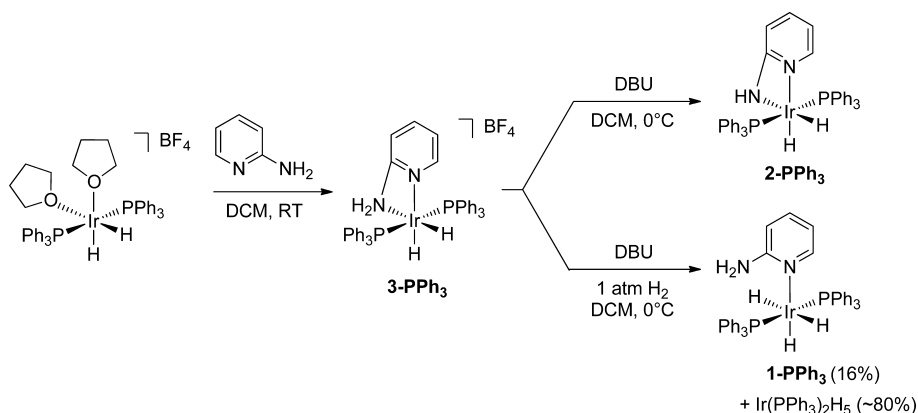
We previously reported a *mer* iridium trihydride complex 1-PPh₃ (Figure 1b)¹⁵ in the context of the H···H dihydrogen

bonding between an Ir–H and the N–H proton of the 2-aminopyridine ligand. This complex was found to lose an equivalent of H₂ thermally to generate an iridium amido species. Here, we report that 1-PPh₃ reacts with CO₂ to form a carbamate complex, rather than the expected formate complex. The reaction proceeds via initial H₂ loss, followed by insertion of CO₂ into the Ir–N bond of the cyclometalated species. Moreover, in some cases the CO₂ can be liberated upon treatment of the carbamate complex with H₂ to regenerate the iridium starting material. We have investigated the CO₂ insertion in detail from DFT calculations and a structure–activity study using a family of related Ir complexes.

RESULTS AND DISCUSSION

Synthesis of Iridium Amido Complexes. Our previous study of 1-PPh₃ revealed that spontaneous loss of H₂ under ambient conditions generated the iridium amido complex, 2-PPh₃;¹⁵ however, this product was not isolated or fully characterized at that time. We have now developed a viable synthesis for 2-PPh₃ (Scheme 2) and have fully characterized this species. Complex 3-PPh₃, formed by treatment of [IrH₂(THF)₂(PPh₃)₂]BF₄¹⁶ with 2-aminopyridine, can be deprotonated by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

Scheme 2. Synthesis of 1-PPh₃ or 2-PPh₃ from a Single Cationic Intermediate 3-PPh₃



to generate **2-PPh₃**. If the deprotonation takes place under an H₂ atmosphere, **1-PPh₃** is formed, along with Ir(PPh₃)₂H₂.¹⁷ In a typical experiment using 1 atm of H₂ only around 16% of **1-PPh₃** is formed but the selectivity is highly dependent on the exact temperature and pressure.

As part of this study the X-ray structure of **1-PPh₃** was elucidated (Figure 2). There is disorder in the position of the

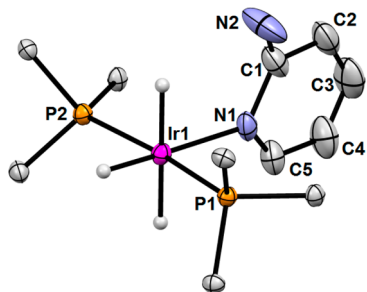


Figure 2. ORTEP of major component of **1-PPh₃** at 30% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–P(1) 2.2693(8), Ir(1)–P(2) 2.2638(8), Ir(1)–N(1) 2.208(9), N(1)–C(1) 1.45(4), N(2)–C(1) 1.122(15), C(1)–C(2) 1.387(19), C(2)–C(3) 1.365(16), C(3)–C(4) 1.322(15), C(4)–C(5) 1.403(19); P(1)–Ir(1)–P(2) 171.38(3), P(1)–Ir(1)–N(1) 92.7(11), P(2)–Ir(1)–N(1) 95.8(11). The phenyl groups of PPh₃ and the disorder in the 2-aminopyridine ligand are hidden for clarity.

pyridyl ligand but it was possible to locate the position of the N–H protons of the major component. One of the N–H protons appears to be forming an H-bond with an Ir–H. Although the hydrides on Ir were found in a difference Fourier map, an unambiguous assignment is impossible due to disorder in the ligands and residual electron density around the Ir center. Nevertheless the crystal structure clearly shows that the coordination sphere around Ir contains two *trans* PPh₃ ligands, three hydrides, and a κ^1 -bound aminopyridine.

The complexes **2-PPh₃** (Figure 3a) and **3-PPh₃** (Figure 3b) were also characterized by X-ray crystallography. To the best of our knowledge they are the first crystallographically charac-

terized examples of 2-aminopyridine ligands κ^2 -coordinated to Ir, although there are many examples both for other transition metals and the lanthanides.¹⁸ The two complexes have very similar overall geometries. For example, **2-PPh₃** features a 4-membered chelating ring with an N(1)–Ir(1)–N(2) angle of 59.3(2)°, while the corresponding angle in **3-PPh₃** is 60.8(3)°. Unsurprisingly the Ir(1)–N(2) bond length in **2-PPh₃**, 2.190(5) Å, is significantly shorter than the Ir(1)–N(2) bond length in **3-PPh₃**, 2.284(8) Å, consistent with the ligand changing from neutral L type in **3-PPh₃** to anionic X type in **2-PPh₃**. However, comparison of the Ir–N bond lengths in **2-PPh₃** reveals that the Ir–N_{pyridine} bond length (Ir(1)–N(1) 2.158(4) Å) is shorter than the Ir–N_{amide} bond length (Ir(1)–N(2) 2.190(5) Å). The bond length difference can be rationalized in terms of a contribution from a resonance form in which the negative charge is localized on the pyridyl nitrogen (Figure 4a). This is confirmed by analyzing the bond lengths in

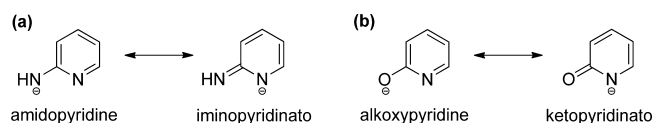


Figure 4. Two limiting resonance forms for deprotonated (a) 2-aminopyridines and (b) 2-hydroxypyridines.

the pyridine ring. Two of the C–C bond lengths (C(2)–C(3) 1.322(8) Å and C(4)–C(5) 1.342(9) Å) are significantly shorter than the other C–C bond lengths (C(1)–C(2) 1.392(7) Å and C(3)–C(4) 1.387(9) Å), in agreement with some contribution coming from the iminopyridinato resonance form (see Figure 4). Recently, Kempe and co-workers have speculated that the iminopyridinato resonance form is favored for late transition metals, especially for the heavier homologues of the triads,¹⁸ and our results are consistent with this hypothesis. In **3-PPh₃**, where the 2-aminopyridine ligand is neutral, the C–C bond lengths in the pyridine ring are identical (within error) and the Ir–N_{pyridine} bond length (Ir–N1 2.184(8) Å) is significantly shorter than the Ir–N_{amide} bond length (Ir–N1 2.282(8) Å). The anion in **3-PPh₃** appears to be

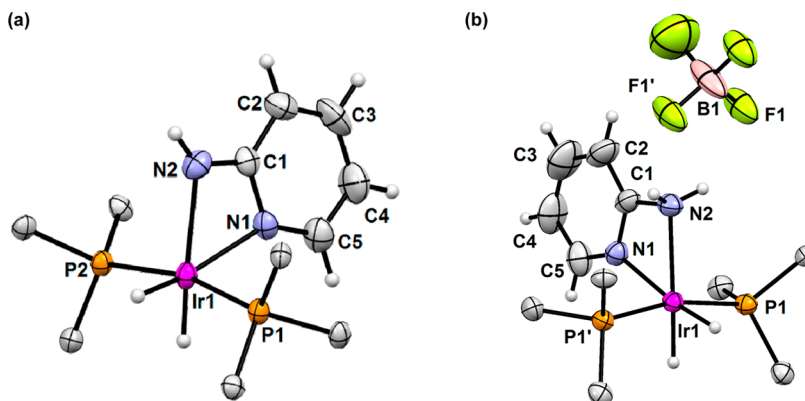


Figure 3. (a) ORTEP of **2-PPh₃** at 50% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–P(1) 2.243(1), Ir(1)–P(2) 2.255(1), Ir(1)–N(1) 2.158(4), Ir(1)–N(2) 2.190(5), N(1)–C(1) 1.342(7), N(2)–C(1) 1.303(6), C(1)–C(2) 1.392(7), C(2)–C(3) 1.322(8), C(3)–C(4) 1.387(9), C(4)–C(5) 1.342(9); P(1)–Ir(1)–P(2) 166.51(4), P(1)–Ir(1)–N(1) 92.8(1), P(1)–Ir(1)–N(2) 103.3(1), P(2)–Ir(1)–N(1) 98.0(1), P(2)–Ir(1)–N(2) 89.2(1), N(1)–Ir(1)–N(2) 59.3(2), Ir(1)–N(1)–C(1) 95.9(3). The phenyl groups of PPh₃ are hidden for clarity. (b) ORTEP of **3-PPh₃** at 50% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–P(1) 2.295(2), Ir(1)–N(1) 2.184(8), Ir(1)–N(2) 2.282(8), N(1)–C(1) 1.324(12), N(2)–C(1) 1.475(12), C(1)–C(2) 1.364(14), C(2)–C(3) 1.367(19), C(3)–C(4) 1.361(20), C(4)–C(5) 1.366(16); P(1)–Ir(1)–N(1) 93.82(4), P(1)–Ir(1)–N(2) 96.14(4), N(1)–Ir(1)–N(2) 61.1(3), Ir(1)–N(1)–C(1) 99.5(6). The phenyl groups of PPh₃ and the cocrystallized solvent molecules are hidden for clarity.

closely associated with the cationic iridium fragment; **3** exhibits two short $\text{BF}_4 \cdots \text{H}-\text{N}$ interactions, with a $\text{N} \cdots \text{F}$ distance of 2.98 Å. A similar interaction has been observed between a BF_4 anion and an NH proton in an Ir(III) complex by Morris and co-workers, although in that case only one H-bond was present.¹⁹

To assess which factors control reactivity with CO_2 , a variety of complexes related to **1-PPh₃** and **2-PPh₃** were prepared (Figure 5). The PCy_3 analogue of **2-PPh₃**, **2-PCy₃**, was

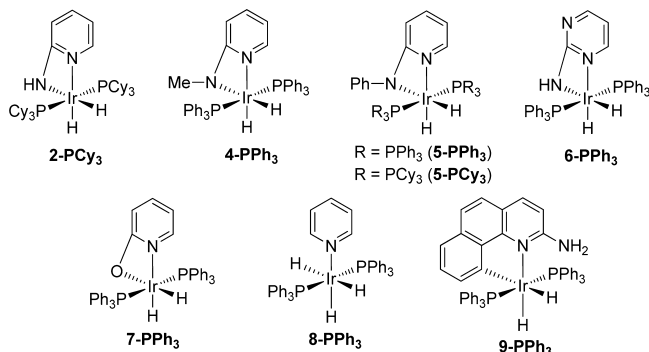


Figure 5. Complexes prepared for screening with CO_2 .

synthesized using a different route than the PPh_3 compound, because steric effects preclude the generation of $[(\text{PCy}_3)_2(\text{cod})-\text{Ir}]^+$.²⁰ Instead, the neutral polyhydride $\text{Ir}(\text{PCy}_3)_2\text{H}_5$ ²¹ was treated with 2-aminopyridine at reflux in toluene. This route was also used for the preparation of **5-PCy₃**, which contains a 2-*N*-phenylaminopyridine ligand. Similarly, **4-PPh₃**, **5-PPh₃**, **6-PPh₃**, and the previously synthesized compound **7-PPh₃**²² were prepared through the treatment of $\text{Ir}(\text{PPh}_3)_2\text{H}_5$ ¹⁷ with 2-*N*-methylaminopyridine, 2-*N*-phenylaminopyridine, 2-aminopyrimidine, and 2-hydroxypyridine respectively. The pyridine supported trihydride, **8-PPh₃**, which cannot cyclometallate, was prepared through the reaction of pyridine with $\text{Ir}(\text{PPh}_3)_2\text{H}_5$, while the benzo[*h*]quinoline-2-amine complex **9-PPh₃** was prepared through literature methods.²³ All of the new complexes prepared as part of this work were fully characterized.

The complex **7-PPh₃** (Figure 6) was characterized by X-ray crystallography. The structure has a geometry nearly identical to that of **2-PPh₃** (e.g., $\text{N1}-\text{Ir1}-\text{O1}$ bond angle of **7-PPh₃** is $59.2(2)^\circ$, $\text{N1}-\text{Ir1}-\text{N2}$ angle of **2-PPh₃** is $59.3(2)^\circ$). The $\text{Ir(1)}-\text{N(1)}$, 2.169(6), and $\text{Ir(1)}-\text{O(1)}$, 2.254(4), bond lengths are consistent with those observed in other Ir(III) complexes supported by 2-hydroxypyridyl ligands²⁴ and suggest some contribution from both the pyridinato and ketopyridonato resonance form (see Figure 4b). This is again confirmed by analyzing the C–C bond lengths in the pyridine ring. There are two short C–C bonds ($\text{C(2)}-\text{C(3)}$ 1.358(10) Å and $\text{C(4)}-\text{C(5)}$ 1.362(10) Å) and two long C–C bonds ($\text{C(1)}-\text{C(2)}$ 1.404(10) Å and $\text{C(3)}-\text{C(4)}$ 1.369(9) Å), although the difference is not as pronounced as in **2-PPh₃**.

CO_2 Incorporation. The reaction of the trihydride **1-PPh₃** with CO_2 in DCM was slow at ambient temperature. Over 24 h, a precipitate formed that was insoluble in most common solvents but sparingly soluble in DCM (Scheme 3). X-ray crystallographic analysis showed that this is the neutral pyridyl carbamate complex, **10-PPh₃** (Figure 7a). The carbamate ligand is O-bound with an $\text{Ir(1)}-\text{O(1)}$ bond length of 2.165(3) Å. The $\text{Ir(1)}-\text{N(1)}$ bond length is 2.126(4) Å, which means that both the Ir–N and Ir–O bonds are shorter than those in

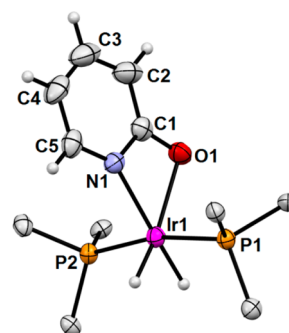
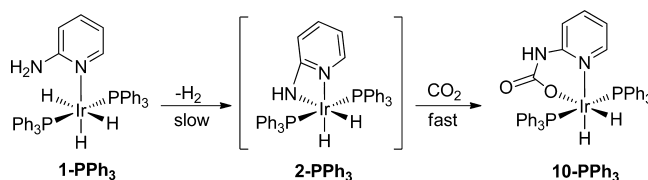


Figure 6. ORTEP of dihydrido(2-hydroxypyridine- κ^2 -O,N)bis(triphenylphosphine)iridium(III) (**7-PPh₃**) at 50% probability. Selected bond lengths (Å) and angles (deg): $\text{Ir(1)}-\text{P(1)}$ 2.281(1), $\text{Ir(1)}-\text{P(2)}$ 2.284(1), $\text{Ir(1)}-\text{O(1)}$ 2.254(4), $\text{Ir(1)}-\text{N(1)}$ 2.169(6), $\text{O(1)}-\text{C(1)}$ 1.283(7), $\text{N(1)}-\text{C(1)}$ 1.337(7), $\text{C(1)}-\text{C(2)}$ 1.404(10), $\text{C(2)}-\text{C(3)}$ 1.358(10), $\text{C(3)}-\text{C(4)}$ 1.369(9), $\text{C(4)}-\text{C(5)}$ 1.362(10); $\text{P(1)}-\text{Ir(1)}-\text{P(2)}$ 168.19(5), $\text{P(1)}-\text{Ir(1)}-\text{O(1)}$ 93.5(1), $\text{P(1)}-\text{Ir(1)}-\text{N(1)}$ 99.1(1), $\text{P(2)}-\text{Ir(1)}-\text{O(1)}$ 96.0(1), $\text{P(2)}-\text{Ir(1)}-\text{N(1)}$ 91.8(1), $\text{O(1)}-\text{Ir(1)}-\text{N(1)}$ 59.2(2), $\text{Ir(1)}-\text{O(1)}-\text{C(1)}$ 92.5(3). The phenyl groups of PPh_3 are hidden for clarity.

Scheme 3. Proposed Pathway for the Generation of the Carbamate Complex **10-PPh₃**



7-PPh₃. This is presumably because there is significantly less strain associated with the 6-membered metallacyclic ring in **10-PPh₃**, compared with the 4-membered metallacyclic ring in **7-PPh₃**. The phosphine ligands are *trans* to one another, and the hydride ligands are mutually *cis*, consistent with the ^1H NMR couplings observed for the hydride resonances (triplets of doublets at δ –20.67, J = 16.8, 7.1 Hz, and δ –26.41 J = 17.1, 7.4 Hz). The crystal lattice of **10-PPh₃** reveals an intermolecular hydrogen bonding interaction that involves a six membered ring composed of two $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds with an $\text{N} \cdots \text{O}$ distance of 2.82 Å (Figure 7b).

A net loss of H_2 must occur in order to form **10-PPh₃** from **1-PPh₃**. Given that spontaneous loss of H_2 from **1-PPh₃** to **2-PPh₃** has previously been observed,¹⁵ we hypothesized that **2-PPh₃** is the true active intermediate which reacts with CO_2 (Scheme 3). The reaction of a DCM solution of isolated **2-PPh₃** with CO_2 resulted in the immediate formation of a precipitate identified as **10-PPh₃**, and the reaction appeared to be complete in less than 5 min at room temperature. This indicates that **2-PPh₃** is a plausible intermediate. It also suggests that if **2-PPh₃** is an intermediate, then the rate determining step in the reaction of **1-PPh₃** with CO_2 is the loss of H_2 , which is consistent with the observation that **2-PPh₃** is not seen as an intermediate by ^1H or ^{31}P NMR spectroscopy in the reaction of **1-PPh₃** with CO_2 . Further support for an initial cyclometallation with formation of an Ir amide came from the lack of reactivity of CO_2 with **9-PPh₃**. Due to geometric constraints **9-PPh₃** cannot cyclometallate²⁵ and even at elevated temperatures no reaction was observed between **9-PPh₃** and CO_2 . An alternative pathway for the formation of **10-PPh₃** from **1-PPh₃** and CO_2 involves initial insertion of CO_2 into a hydride of **1-PPh₃**,

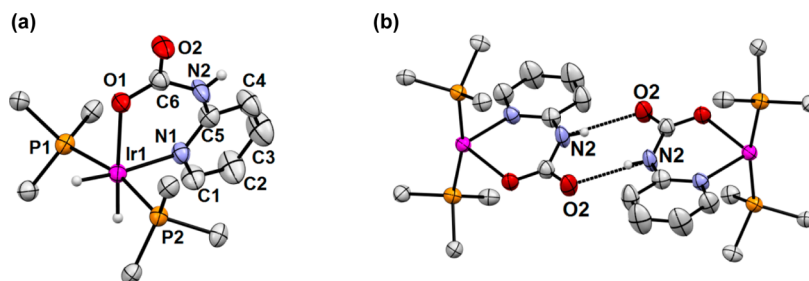


Figure 7. (a) ORTEP of **10-PPh₃** at 50% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–P(1) 2.275(2), Ir(1)–P(2) 2.271(2), Ir(1)–O(1) 2.165(3), Ir(1)–N(1) 2.126(4), O(1)–C(6) 1.254(5), O(2)–C(6) 1.231(7), N(2)–C(6) 1.391(7); P(1)–Ir(1)–P(2) 167.38(5), P(1)–Ir(1)–O(1) 90.4(1), P(1)–Ir(1)–N(1) 95.1(1), P(2)–Ir(1)–O(1) 98.6(1), P(2)–Ir(1)–N(1) 94.2(1), O(1)–Ir(1)–N(1) 87.1(2), O(1)–C(6)–O(2) 124.0(5), O(1)–C(6)–N(2) 119.2(5), O(2)–C(6)–N(2) 116.8(5). Selected hydrogen atoms and the phenyl groups of PPh₃ are hidden for clarity. (b) Solid state hydrogen bonding interaction in **10-PPh₃** between two units in the crystal lattice. The N(2)–O(2) bond length is 2.815 Å. Selected hydrogen atoms and the phenyl groups of PPh₃ have been removed for clarity.

followed by H₂ loss. Given our previous studies on the difficulty of CO₂ insertion into Ir(III) hydrides¹³ and the fact that the control compound **8-PPh₃** (which cannot form a carbamate complex) does not react with CO₂, this route seems unlikely.

To further understand the factors controlling the reactivity of the amido species with CO₂, all of the cyclometalated complexes prepared as part of this work were exposed to CO₂ in DCM. The results are summarized in Table 1. Several

we suggest that this reaction is slower as a result of electronic effects.

Other complexes tried were completely unreactive under ambient conditions. The *N*-phenyl analogues **5-PPh₃** and **5-PCy₃** are totally unreactive toward CO₂, as is the charged complex **3-PPh₃**, which contains a cyclometalated amine ligand rather than a cyclometalated amide ligand. The 2-hydroxypyridyl supported species **7-PPh₃** also does not react with CO₂, despite its structural similarities with **2-PPh₃**.

The complexes **10-PCy₃** and **11-PPh₃** were characterized by X-ray crystallography (Figure 8). The structure of **10-PCy₃** is

Table 1. Reactivity of Cyclometalated Ir Amides with 1 atm CO₂ in DCM

R = PPh ₃ (10-PPh₃) R = PCy ₃ (10-PCy₃)	
compound	reactivity with CO ₂
2-PPh₃	instant reaction at room temperature (product 10-PPh₃)
2-PCy₃	instant reaction at room temperature (product 10-PCy₃)
3-PPh₃	no reaction
4-PPh₃	instant reaction at room temperature to give a 9:1 mixture of product and starting material (product 11-PPh₃)
5-PPh₃	no reaction
5-PCy₃	no reaction
6-PPh₃	slow reaction at room temperature (product 12-PPh₃)
7-PPh₃	no reaction

of our amido complexes react with CO₂ to form carbamate complexes, analogous to **2-PPh₃**. The PCy₃ complex, **2-PCy₃**, and a *N*-Me species, **4-PPh₃**, undergo facile reaction with CO₂ under ambient conditions to form **10-PCy₃** and **11-PPh₃**, respectively. The reactivity of **4-PPh₃** demonstrates that CO₂ incorporation is not dependent on the presence of an *N*-H proton. However, in this case complete conversion of **4-PPh₃** to **11-PPh₃** was not observed and under 1 atm of CO₂ at room temperature a 9:1 mixture of product to starting material was present. Furthermore, the product **11-PPh₃** could not be isolated on a reasonable scale, as exposure to vacuum resulted in the loss of CO₂ and the regeneration of **4-PPh₃**. It was possible to grow crystals of **11-PPh₃** for X-ray diffraction under an atmosphere of CO₂ (vide infra) but exposure of these crystals to vacuum resulted in loss of CO₂. In contrast to these rapid reactions, the reaction between the pyrimidine complex **6-PPh₃** and CO₂ took several hours at room temperature, and

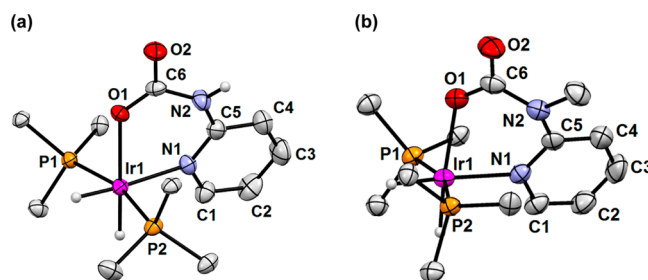


Figure 8. (a) ORTEP of **10-PCy₃** at 50% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–P(1) 2.3123(16), Ir(1)–P(2) 2.3259(16), Ir(1)–O(1) 2.198(3), Ir(1)–N(2) 2.189(5), O(1)–C(1) 1.253(7), O(2)–C(1) 1.251(6), N(2)–C(1) 1.401(8); P(1)–Ir(1)–P(2) 164.83(6), P(1)–Ir(1)–O(1) 88.25(11), P(1)–Ir(1)–N(1) 97.08(14), P(2)–Ir(1)–O(1) 98.42(11), P(2)–Ir(1)–N(1) 97.15(14), O(1)–Ir(1)–N(1) 84.24(15), O(1)–C(1)–O(2) 124.7(6), O(1)–C(1)–N(2) 120.8(4), O(2)–C(1)–N(2) 114.5(5). Selected hydrogen atoms and the cyclohexyl groups of PCy₃ are hidden for clarity. (b) ORTEP of **11-PPh₃** at 50% probability. Ir(1)–P(1) 2.271(2), Ir(1)–P(2) 2.265(2), Ir(1)–O(1) 2.168(5), Ir(1)–N(1) 2.123(4), O(1)–C(6) 1.259(10), O(2)–C(6) 1.222(10), N(2)–C(6) 1.396(8); P(1)–Ir(1)–P(2) 162.37(5), P(1)–Ir(1)–O(1) 98.56(16), P(1)–Ir(1)–N(1) 101.07(18), P(2)–Ir(1)–O(1) 88.05(16), P(2)–Ir(1)–N(1) 96.09(19), O(1)–Ir(1)–N(1) 80.75(17), O(1)–C(6)–O(2) 124.2(6), O(1)–C(6)–N(2) 119.3(7), O(2)–C(6)–N(2) 116.5(7). Selected hydrogen atoms and the phenyl groups of PPh₃ are hidden for clarity.

analogous to **10-PPh₃**, although presumably due to steric factors, the Ir–P bond lengths are longer in **10-PCy₃** (Ir(1)–P(1) = 2.3123(16) and Ir(1)–P(2) = 2.3259(16)) compared with **10-PPh₃** (Ir(1)–P(1) = 2.275(2) and Ir(1)–P(2) = 2.271(2)). In a comparable fashion to **10-PPh₃**, two intramolecular N–H⋯O hydrogen bonding interactions are present in **10-PCy₃** to form a dimer (as shown for **10-PPh₃** in Figure

7b). The N...O bond distance is 2.89 Å. In contrast **11-PPh₃** does not contain any N–H bonds, and no solid state intramolecular hydrogen bonding is apparent. This may explain why CO₂ insertion into **4-PPh₃** does not appear to be as thermodynamically favorable as insertion into **2-PPh₃** or **2-PCy₃**. In other regards the structure of **11-PPh₃** is similar to **10-PPh₃**.

Computational Studies of the Mechanism of CO₂ Insertion into **1-PPh₃** and Cyclometalated Ir Species.

To understand the pathway for CO₂ insertion into **1-PPh₃**, a computational study was performed. A model system where PPh₃ was replaced by PH₃ was utilized. The validity of this model was confirmed by performing selected calculations with PPh₃ and these are reported in the Supporting Information. The DCM solvent used in the experiments was included in the calculations using a continuum model. Two possibilities were considered: direct reaction of CO₂ with **1-PH₃**, and reaction of CO₂ with the intermediate **2-PH₃**, which is obtained by H₂ elimination of **1-PH₃**.²⁶

CO₂ insertion has previously been observed with the complex (PNP)IrH₃ (PNP = HN(ⁱPr₂PC₂H₄)₂) shown in Figure 1a and the insertion of CO₂ into an Ir–H bond of **1-PH₃** was calculated (see Figure 9).¹³ The Gibbs free energy

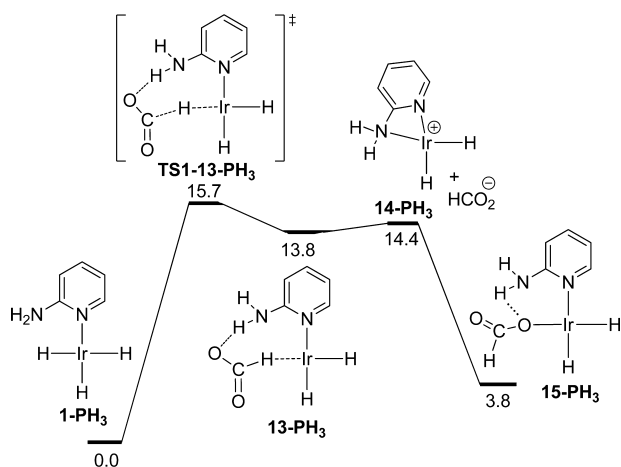


Figure 9. ΔG_{DCM} energy profiles, in kcal mol^{−1}, for CO₂ insertion into Ir–H bond of **1-PH₃**. PH₃ ligands have been omitted for clarity.

barrier for CO₂ insertion into one of the *trans* hydrides of **1-PH₃** is 15.7 kcal mol^{−1}, which is similar to the energy barrier observed with (PNP)IrH₃ (12.4 kcal mol^{−1}). However the reaction with **1-PH₃** is slightly endothermic ($\Delta G_{\text{DCM}} = 3.8$ kcal mol^{−1}), while it is exothermic ($\Delta G_{\text{THF}} = -4.8$ kcal mol^{−1}) using (PNP)IrH₃. This is probably a consequence of the lower acidity of the NH₂ group compared with the metal bound NH group of (PNP)IrH₃, which stabilized the HCO₂[−] anion far more effectively through hydrogen bonding. This hypothesis is supported by the higher energy of **14-PH₃** + HCO₂[−] ($\Delta G_{\text{DCM}} = 14.4$ kcal mol^{−1}) compared with the analogous complex with the PNP ligand ($\Delta G_{\text{THF}} = 6.3$ kcal mol^{−1}). After formation of **15-PH₃**, elimination of H₂ should occur in order to form the final product **10-PH₃**. However all the pathways tried were unsuccessful. From **1-PH₃**, a pathway where nucleophilic attack of NH₂ to CO₂ is concurrent to the H₂ formation was also calculated but it has high energy barriers (see Supporting Information).

The insertion of CO₂ into the NH group of **2-PH₃** appears to be a more likely process according to calculation (consistent

with our experimental results). Two different pathways were obtained for the insertion: one concerted and the other stepwise (Figure 10). In the concerted mechanism the Ir–O

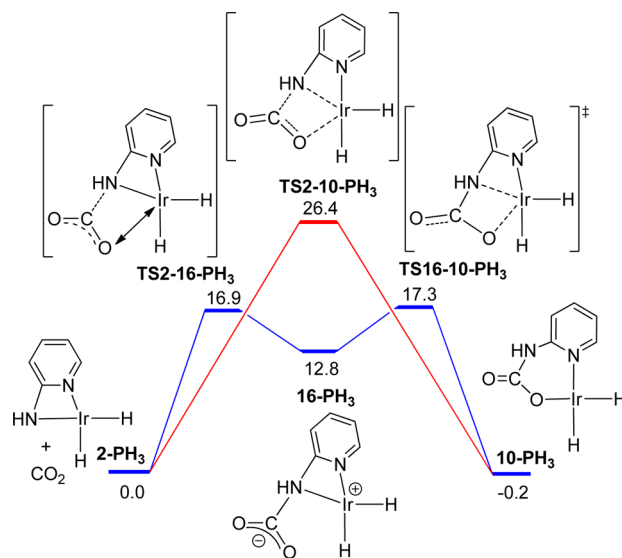


Figure 10. ΔG_{DCM} energy profiles, in kcal mol^{−1}, for the CO₂ insertion into the Ir–NH bond of **2-PH₃**. PH₃ ligands have been omitted for clarity.

and N–C bonds are formed simultaneously in **TS2–10-PH₃** (Ir...O=2.87 and N...C=2.50 Å), while in the stepwise pathway this happens in two steps. The N–C bond is formed first in **TS2–16-PH₃** (N...C=1.95 Å) yielding the N-bound carbamate species **16-PH₃**. Subsequently, this species undergoes a rearrangement from the N-bound to the O-bound complex via **TS16–10-PH₃** (Ir...N = 2.85 Å, Ir...O = 3.10 Å) to give the final product **10-PH₃**.

Comparing the energy barriers for the concerted and stepwise processes, the latter is preferred by 9.1 kcal mol^{−1}. Hence, the stepwise mechanism seems to be the one responsible for the insertion of CO₂ in **2-PH₃**. The low Gibbs free energy obtained for the transition states of this process, of 16.9 and 17.3 kcal mol^{−1}, is consistent with a fast reaction of CO₂ with **2-PH₃**. This picture also explains why intermediate **2-PPh₃** is not observed in the reaction of **1-PPh₃** with CO₂, as suggested in Scheme 3. The almost thermoneutral process, with **10-PH₃** being only 0.2 kcal mol^{−1} below the reactants (**2-PH₃** + CO₂), is in agreement with a reversible insertion of CO₂ in the absence of hydrogen bonding. Calculations on this mechanism (see Supporting Information) using PPh₃ instead of PH₃ as spectator ligand lead to similar relative energies.

Calculations of the reaction of CO₂ with **4-**, **5-**, and **6-PH₃** were also performed in order to check the experimental observations shown in Table 2. The trend observed in the energy barriers of these systems ($\Delta G_{\text{DCM}}^{\ddagger} = 21.0, 31.1,$ and 22.3 kcal mol^{−1}, respectively) matches quite well with the experimental results. For instance, the lack of CO₂ insertion with **5-PH₃**, using the Py–NPh ligand, is in agreement with a relatively high energy barrier of 31.1 kcal mol^{−1}. In this case the transition state of the stepwise process could not be found, and only a transition state analogous to **TS2–10-PH₃** was obtained. This is probably due to the low nucleophilicity of NPh compared to NH and NMe present in the other compounds.

Table 2. Crystal and Refinement Data for Complexes 1-PPh₃, 2-PPh₃, 3-PPh₃, 7-PPh₃, 10-PPh₃, 10-PCy₃, and 11-PPh₃

	1-PPh ₃	2-PPh ₃	3-PPh ₃	7-PPh ₃
empirical formula	C ₄₁ H ₃₉ IrN ₂ P ₂	C ₄₁ H ₃₇ IrP ₂ N ₂	IrP ₂ N ₂ BF ₄ C ₄₁ H ₃₈ ·1.21 (CH ₂ Cl ₂)	C ₄₁ H ₃₆ IrP ₂ ON
formula weight	813.88	811.92	1002.50	812.91
temperature (K)	223	223	223	223
<i>a</i> (Å)	11.5834(16)	10.760(7)	19.2265(14)	9.111(4)
<i>b</i> (Å)	12.2221(16)	12.160(7)	15.8767(12)	11.977(6)
<i>c</i> (Å)	13.2838(18)	13.764(9)	15.0485(11)	16.669(7)
α (deg)	90.472(6)	101.791(11)	90	70.480(11)
β (deg)	106.509(7)	94.401(10)	90	81.580(10)
γ (deg)	102.999(7)	111.133(10)	90	73.712(13)
volume (Å ³)	1751.6(4)	1621.9(17)	4593.6(6)	1642.7(13)
<i>Z</i>	2	2	4	2
crystal system	triclinic	triclinic	orthorhombic	triclinic
space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>Pnma</i> (#62)	<i>P</i> $\bar{1}$ (#2)
<i>d</i> _{calc} (Mg/m ³)	1.543	1.866	1.449	1.643
θ range (deg)	3.21–30.51	0.997–27.49	0.996–27.10	0.990–27.48
μ (mm ^{−1})	3.934	4.260	3.171	4.208
abs. correction	semiempirical	semiempirical	semiempirical	semiempirical
GOF	1.092	1.095	1.184	1.106
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0415, 0.0624	0.0411, 0.0657	0.0589, 0.1174	0.0477, 0.0759

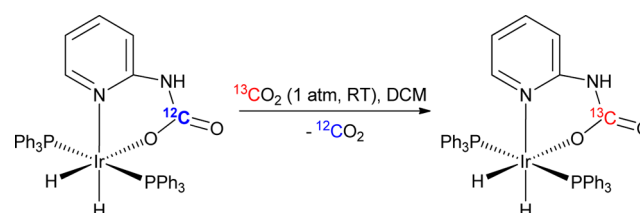
	10-PPh ₃	10-PCy ₃	11-PPh ₃
empirical formula	IrP ₂ O ₂ N ₂ C ₄₂ H ₃₇ ·2(CH ₂ Cl ₂)	IrC ₄₃ H ₇₃ O ₂ N ₂ P ₂ ·(CH ₂ Cl ₂)	IrP ₂ O ₂ N ₂ C ₄₃ H ₃₉ ·2.5(CH ₂ Cl ₂)
formula weight	1025.80	977.15	1082.29
temperature (K)	223	223	223
<i>a</i> (Å)	11.729(4)	10.9796(7)	13.269(9)
<i>b</i> (Å)	12.900(5)	12.2163(7)	13.481(8)
<i>c</i> (Å)	15.653(6)	18.3145(13)	14.591(11)
α (deg)	96.745(9)	96.882(7)	66.345(20)
β (deg)	101.430(8)	105.104(7)	71.92(2)
γ (deg)	109.434(8)	102.724(7)	78.945(19)
volume (Å ³)	2145.7(14)	2272.1(3)	2145.7(14)
<i>Z</i>	2	2	2
crystal system	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)
<i>d</i> _{calc} (Mg/m ³)	1.588	1.586	1.586
θ range (deg)	3.25–27.98	3.08–27.16	3.15–27.79
μ (mm ^{−1})	3.482	3.170	3.359
abs. correction	semiempirical	semiempirical	semiempirical
GOF	1.089	1.040	1.055
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0552, 0.0812	0.0541, 0.0922	0.0559, 0.1150

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Calculations on 7-PH₃, a model for the hydroxypyridyl complex 7-PPh₃, reveals that insertion into the Ir–O bond is thermodynamically uphill ($\Delta G = 17.9$ kcal mol^{−1}), which explains the observed lack of reactivity.

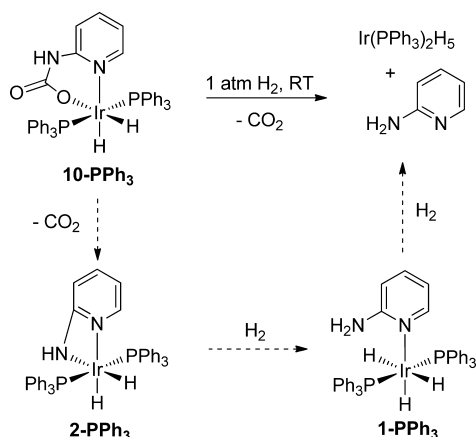
Overall, the stepwise mechanism for the CO₂ insertion in 2-PH₃ resembles the insertion mechanism observed with the Ru complex shown in Scheme 1a.¹⁰ This process is also similar to the mechanism proposed by our group for the insertion of CO₂ into the Ni–N bond of complex [(PCP)Ni–NH₂].¹² However, it should be noted that Chisholm and Extine observed that CO₂ insertion into the W amide bond of W(NMe₂)₆ and W₂(NEt₂)₄Me₂ was catalyzed by fortuitous amine.²⁷ Elemental analysis suggests that our complexes are pure and do not contain free amine, and the reactions are performed in the absence of water. In addition, the fact that 3-PPh₃, which contains a cyclometalated amine ligand, does not react with CO₂ strongly suggests that a reaction involving a free amine is not occurring.

Reversibility of CO₂ Insertion into 2-PPh₃. Treatment of a DCM solution of the carbamate complex 10-PPh₃ with ¹³C-labeled CO₂ produces a significant quantity of the ¹³C-labeled product over 24 h at room temperature as determined by ¹³C NMR spectroscopy (Scheme 4). This indicates that the CO₂ insertion is likely a reversible process, and depending on conditions, CO₂ could be liberated.

Scheme 4. Isotopic Exchange of the Carbon Atom in the Carbamate Ligand in 10-PPh₃ with ¹³CO₂

Though complex **10-PPh₃** does not lose CO₂ readily at room temperature under vacuum in the solid state (presumably due to the hydrogen bonding), we found that it does react with H₂ even at 1 atm. The reaction of the carbamate complex **10-PPh₃** with H₂ at 1 atm and room temperature results in the Ir(PPh₃)₂H₅ species within a few hours (Scheme 5). The single

Scheme 5. Loss of CO₂ from **10-PPh₃** under an H₂ Atmosphere to Form Ir(PPh₃)₂H₅



hydridic resonance (δ -11.28, triplet, J = 12.0 Hz) present in the ¹H NMR spectrum of the reaction mixture indicates that this is the only iridium hydride-containing product.

Reaction of complex **1-PPh₃** or **2-PPh₃** with H₂ at room temperature also results in the formation of Ir(PPh₃)₂H₅. Before all of **2-PPh₃** is consumed, hydride resonances corresponding to **1-PPh₃** are also visible by ¹H and ³¹P NMR spectroscopy, suggesting that **1-PPh₃** is an intermediate en route to Ir(PPh₃)₂H₅. Peaks corresponding to uncoordinated 2-aminopyridine are also present, confirming the dissociation of the ligand from iridium. Given the reversibility of the CO₂ insertion reaction seen by isotopic labeling, we suggest that **10-PPh₃** loses CO₂ to form the Ir amide **2-PPh₃**, followed by reaction with two equivalents of H₂ to form Ir(PPh₃)₂H₅ (Scheme 5). The hydrogenolysis of **2-PPh₃** is likely only possible if the CO₂ incorporation by **10-PPh₃** is reversible. H₂ has no obvious role in the release of CO₂, and instead we propose that H₂ serves to trap **2-PPh₃** and drive the reaction to completion by the formation of Ir(PPh₃)₂H₅, a thermodynamic sink.

CONCLUSIONS

CO₂ reacts with an Ir(III) trihydride supported by an 2-aminopyridine ligand, but unlike previous hydrides we have studied,¹³ CO₂ does not insert into an Ir–H bond. Instead, the complex undergoes cyclometalation, releasing H₂ and generating a species with an Ir amide bond. This Ir–N bond rapidly inserts CO₂ to form an O-bound carbamate complex. The reaction of late transition metal amide bonds with CO₂ has not been extensively studied^{10–12} and the factors that promote insertion are still unclear. We have performed an experimental structure–activity study and used calculations to propose a reaction pathway. The reaction proceeds via initial nucleophilic attack of the coordinated amide on CO₂ to form an N-bound carbamate species. Ligand rearrangement then occurs to generate the O-bound carbamate complex. The rate of reaction depends on the nucleophilicity of the amide, with more

nucleophilic amides giving faster rates. The reaction with CO₂ is reversible and addition of H₂ results in the release of CO₂ and the formation of the iridium trihydride. Further work will be needed to find an entry into a potential catalytic cycle that incorporates CO₂ into organic reactants via carboxylation.

EXPERIMENTAL SECTION

General. The syntheses of the metal complexes were conducted using standard Schlenk or drybox techniques under a dinitrogen atmosphere using dry, degassed solvents unless otherwise indicated. The solvents for air- and moisture-sensitive reactions were dried by passage through a column of activated alumina followed by storage under dinitrogen. Dihydrido(bis(tetrahydrofuran) bis-(triphenylphosphine)iridium(III) tetrafluoroborate,¹⁶ trihydrido(2-aminopyridine) bis(triphenylphosphine)iridium(III),¹⁵ pentahydrido(bis(triphenylphosphine)iridium(III),¹⁷ and pentahydrido(bis(tricyclohexylphosphine)iridium(III)¹⁷ were synthesized according to literature procedures. 2-Aminopyridine was sublimed under high vacuum at room temperature prior to use. All other reagents were purchased commercially from Sigma-Aldrich, Cambridge Isotope Laboratories, Airgas, Alfa-Aesar, or Strem Chemicals and used as received unless otherwise indicated. NMR spectra were recorded at room temperature on a 400 or 500 MHz Bruker or Varian spectrometer. Chemical shifts are reported in ppm with respect to residual internal protio solvent for ¹H and ¹³C{¹H} NMR spectra and to an external standard for ³¹P{¹H} spectra (85% H₃PO₄ in H₂O at δ 0.0 ppm). Coupling constants are reported in Hz. IR spectra were measured using diamond smart orbit ATR on a Nicolet 6700 FT-IR instrument unless noted. Elemental analyses were performed by Robertson Microлит Laboratories (Madison, NJ). The ¹H and ³¹P NMR spectra are provided in the Supporting Information for any compounds that did not have satisfactory elemental analyses.

Synthesis and Characterization of Compounds. *Dihydrido(2-aminopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) (2-PPh₃).* To a flame-dried Schlenk flask was added dihydrido(2-aminopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) tetrafluoroborate (**3-PPh₃**, 200.0 mg, 0.222 mmol, 1.0 equiv) (for preparation of **3-PPh₃** see below). The flask was evacuated and backfilled with dinitrogen three times, and 20 mL of dried degassed DCM was added. The reaction was cooled to -30 °C, and a 1 M solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran (222 μ L, 0.222 mmol, 1.0 equiv) was added dropwise. The reaction was stirred for 30 min, during which time it was allowed to warm to -10 °C and then the solvent was removed under reduced pressure. Ten mL of dried, degassed toluene was added and the resulting suspension was filtered through Celite in vacuo. The filtered solution was evaporated under reduced pressure leaving a light brown residue. This material was recrystallized by layering a concentrated DCM solution with pentane under dinitrogen atmosphere. The solution was decanted off and the solid was dried overnight under vacuum. Crystals suitable for X-ray diffraction were obtained by recrystallization (DCM/pentane, layering, under dinitrogen at RT). Yield 51 mg, 28%. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.61–7.55 (m, 12H, PPh₃), 7.35–7.23 (m, 18H, PPh₃), 6.65 (d, J = 5.3 Hz, 1H, pyridine C–H), 6.52 (t, J = 7.6 Hz, 1H, pyridine C–H), 5.36 (t, J = 6.1 Hz, pyridine C–H), 5.07 (d, J = 8.6 Hz, 1H, pyridine C–H), 3.27 (br s, 1H, –NH), –22.45 to –22.70 (m, 2H, Ir–H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 19.42. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 174.63 (s), 147.32 (s), 136.12 (t, J = 25.4 Hz), 134.77 (t, J = 6.2 Hz), 133.42 (s), 129.82 (s), 128.11 (t, J = 4.8 Hz), 110.23 (s), 103.59 (s). Anal. Calcd for C₄₁H₃₇IrN₂P₂: C, 60.65; H, 4.59; N, 3.45. Found: C, 60.41; H, 4.20; N, 3.37.

Dihydrido(2-aminopyridine- κ^2 -N,N')bis(tricyclohexylphosphine)iridium(III) (2-PCy₃). To a suspension of IrH₅(PCy₃)₂ (47 mg, 0.06 mmol) in 10 mL of dry C₆H₆ in a 50-mL flame-dried Schlenk flask, 2-aminopyridine (34 mg, 0.36 mmol) was added. The mixture was heated at 75 °C for 37 h. The volatiles were removed under vacuum. The resulting residue was triturated with C₆H₆ (2 $\times$ 0.5 mL) to give **2-PCy₃** as a white solid, which was dried under vacuum. Yield: 32 mg, 62%. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.50 (d, J = 8 Hz, 1H, pyridine

C–H), 6.73 (t, $J = 8$ Hz, 1H, pyridine C–H), 5.68 (t, $J = 8$ Hz, pyridine C–H), 5.39 (d, $J = 8$ Hz, 1H, pyridine C–H), 3.43 (br s, 1H, –NH), 1.80 (br s, 18H) and 1.63 (br s, 12H) and 1.53 (br s, 6H) and 1.28 (m, 12H) and 1.08 (m, 18H) (Cy), –25.37 to –25.66 (m, 2H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 22.31. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 173.09 (s), 146.69 (s), 133.40 (s), 133.42 (s), 109.55 (s), 100.60 (s), 36.90 (t, $J = 13$ Hz), 30.59 (br s), 30.51 (br s), 28.47 (br s), 27.48 (s). Anal. Calcd for $\text{C}_{41}\text{H}_{73}\text{IrN}_2\text{P}_2\cdot\text{CH}_2\text{Cl}_2$: C, 54.06; H, 8.10; N, 3.00. Found: C, 55.10; H, 8.02; N, 3.17.

Dihydrido(2-aminopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) tetrafluoroborate (3-PPh₃). To a 100-mL flame-dried Schlenk flask was added dihydridobis(tetrahydrofuran) bis-(triphenylphosphine)iridium(III) tetrafluoroborate ($[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{BF}_4$, 914.0 mg, 0.962 mmol). The flask was evacuated and backfilled with dinitrogen three times, and 5 mL of dried degassed DCM was added. A dry degassed solution of 2-aminopyridine (90.4 mg, 0.962 mmol) in DCM (20 mL) was added dropwise over 5 min via cannula transfer. The reaction was allowed to stir for 1.5 h. The yellow solution was concentrated under reduced pressure, resulting in partial precipitation of the product. Fifteen mL of dried degassed diethyl ether was added, and the solution was decanted off the precipitated solid. The solid was washed with diethyl ether (2 $\times$ 5 mL) and dried overnight under vacuum. Crystals suitable for X-ray diffraction were grown from DCM/diethyl ether (vapor diffusion, RT). Yield 659.9 mg, 76%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.59–7.45 (m, 12H, Ar), 7.43–6.98 (m, 20H, Ar), 6.88–6.82 (m, 1H, pyridine C–H), 6.61 (d, $J = 8.0$ Hz, 1H, pyridine C–H), 3.81 (s, 1H, –NH₂), –23.49 (td, $J_{\text{PH}} = 15.6$ Hz, $J_{\text{HH}} = 8.7$ Hz, 1H, Ir–H), –25.32 (td, $J_{\text{PH}} = 15.8$ Hz, $J_{\text{HH}} = 8.7$ Hz, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 22.48. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 158.03 (s), 148.10 (s), 137.86 (s), 133.37 (t, $J = 6.3$ Hz), 132.64 (t, $J = 26.7$ Hz), 130.54 (s), 128.64 (t, $J = 5.0$ Hz), 124.91 (s), 123.50 (s). Anal. Calcd for $\text{C}_{41}\text{H}_{38}\text{BF}_4\text{IrN}_2\text{P}_2\cdot\text{CH}_2\text{Cl}_2$: C, 51.23; H, 4.09; N, 2.84. Found: C, 51.65; H, 3.91; N, 2.62.

Trihydrido(2-aminopyridine)bis(triphenylphosphine)iridium(III). *An Alternative Preparation from 3.* To a flame-dried Schlenk flask was added dihydrido(2-aminopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) tetrafluoroborate (93.7 mg, 0.104 mmol, 1 equiv). After purge and backfill with dinitrogen, a 1 M tetrahydrofuran solution of DBU (115 μL , 0.115 mmol, 1.1 equiv), and 3 mL of DCM were added. The flask was cooled to 0 $^\circ\text{C}$. H_2 was introduced by bubbling and the reaction was stirred for 5 min. The DCM was removed under reduced pressure and 2 mL of toluene was added. The suspension was filtered through Celite under dinitrogen. Degassed pentanes were layered on top of the filtrate and the reaction was stored at –20 $^\circ\text{C}$ overnight. The solid was dried in vacuo at 0 $^\circ\text{C}$ for 15 min. Yield 13.4 mg, 16%. The spectra of the obtained yellow-white solid were consistent with the previously reported data.¹⁵ $\text{Ir}(\text{PPh}_3)_3\text{H}_3$ is a major byproduct of this reaction and is removed in the filtration step.

Dihydrido(2-methylamidopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) (4-PPh₃). To a suspension of $\text{IrH}_5(\text{PPh}_3)_2$ (108 mg, 0.15 mmol) in 6 mL of dry C_6H_6 in a 50-mL flame-dried Schlenk flask, 2-methylaminopyridine (16 mg, 0.15 mmol) was added. The mixture was heated at 65 $^\circ\text{C}$ for 21 h. The volatiles were removed under vacuum. The resulting residue was recrystallized from a mixture of C_6H_6 /pentane (1:3) to give 4-PPh₃ as a pale yellow solid, which was dried under vacuum. Yield: 92 mg, 74%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.60–7.55 (m, 12H, Ar), 7.36–7.26 (m, 18H, Ar), 6.74 (d, $J = 4$ Hz, 1H, pyridine C–H), 6.66 (t, $J = 8$ Hz, 1H, pyridine C–H), 5.25 (m, pyridine C–H), 5.02 (d, $J = 8$ Hz, 1H, pyridine C–H), 1.80 (s, 3H, –NMe), –22.22 (td, $J_{\text{PH}} = 16$ Hz, $J_{\text{HH}} = 8$ Hz, 1H, Ir–H), –22.75 (td, $J_{\text{PH}} = 16$ Hz, $J_{\text{HH}} = 8$ Hz, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 20.84 (t, $J = 15$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 171.60 (s), 147.40 (s), 136.14 (t, $J = 25$ Hz), 133.72 (s), 129.79 (s), 128.88 (s), 128.17 (t, $J = 5$ Hz), 104.48 (s), 101.55 (s), 32.78 (s). Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{IrN}_2\text{P}_2$: C, 61.08; H, 4.76; N, 3.39. Found: C, 61.33; H, 4.89; N, 3.12.

Dihydrido(2-phenylamidopyridine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) (5-PPh₃). To a suspension of

$\text{IrH}_5(\text{PPh}_3)_2$ (70 mg, 0.10 mmol) in 10 mL of dry C_6H_6 in a 50-mL flame-dried Schlenk flask, 2-phenylaminopyridine (34 mg, 0.20 mmol) was added. The mixture was heated at 65 $^\circ\text{C}$ for 25 h. The volatiles were removed under vacuum. The resulting residue was triturated with ether and washed with benzene and dried under vacuum to give 5-PPh₃ as a white solid. Yield: 59 mg, 66%. ^1H NMR (500 MHz, C_6D_6): δ 7.79–7.75 (m, 12H, Ar), 7.01–6.86 (m, 23H, Ar), 6.69 (t, $J = 8$ Hz, 1H, pyridine C–H), 6.36 (d, $J = 10$ Hz, 1H, pyridine C–H), 6.19 (d, $J = 10$ Hz, pyridine C–H), 5.51 (t, $J = 6$ Hz, 1H, pyridine C–H), –21.61 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 10$ Hz, 1H, Ir–H), –22.84 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 10$ Hz, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ 20.67 (t, $J = 13$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 167.38 (s), 147.81 (s), 147.68 (s), 136.63 (t, $J = 25$ Hz), 134.63 (t, $J = 6$ Hz), 129.50 (s), 128.55 (s), 122.47 (s), 121.78 (s), 118.65 (s), 108.66 (s), 106.51 (s). Anal. Calcd for $\text{C}_{47}\text{H}_{41}\text{IrN}_2\text{P}_2$: C, 63.57; H, 4.65; N, 3.15. Found: C, 63.32; H, 4.69; N, 3.10.

Dihydrido(2-phenylamidopyridine- κ^2 -N,N')bis(tricyclohexylphosphine)iridium(III) (5-PCy₃). To a suspension of $\text{IrH}_5(\text{PCy}_3)_2$ (163 mg, 0.21 mmol) in 65 mL of dry CH_2Cl_2 in a 100-mL flame-dried Schlenk flask, 2-phenylaminopyridine (37 mg, 0.21 mmol) was added. The mixture was stirred at RT for 22 h. The volatiles were removed under vacuum. The residue was dissolved in 2 mL of C_6H_6 and a precipitate formed after 10 min. After 1 h the precipitate was collected by filtration, washed with cold CH_2Cl_2 , and dried under vacuum. Yield: 89 mg, 46%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.84 (d, $J = 5$ Hz, 1H, pyridine C–H), 7.13–7.07 (m, 5H, Ar), 6.64 (t, $J = 7$ Hz, 1H, pyridine C–H), 6.59 (d, $J = 9$ Hz, 1H, pyridine C–H), 6.11 (t, $J = 7$ Hz, 1H, pyridine C–H), 1.84–1.01 (m, 66H, Cy), –24.89 (td, $J_{\text{PH}} = 17$ Hz, $J_{\text{HH}} = 8$ Hz, 1H, Ir–H), –25.32 (td, $J_{\text{PH}} = 17$ Hz, $J_{\text{HH}} = 8$ Hz, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 20.22 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): 128.70 (s), 121.90 (s), 100.88 (s), 36.94 (t, $J = 13$ Hz), 30.47 (s), 30.30 (s), 28.30 (t, $J = 6$ Hz), 27.39. (Not all carbon peaks were observed because of the low solubility). Anal. Calcd for $\text{C}_{47}\text{H}_{77}\text{IrN}_2\text{P}_2$: C, 61.07; H, 8.40; N, 3.03. Found: C, 59.94; H, 7.91; N, 2.71.

Dihydrido(2-amidopyrimidine- κ^2 -N,N')bis(triphenylphosphine)iridium(III) (6-PPh₃). To a suspension of $\text{IrH}_5(\text{PPh}_3)_2$ (117 mg, 0.16 mmol) in 10 mL of dry C_6H_6 in a 50-mL flame-dried Schlenk flask, 2-aminopyrimidine (19 mg, 0.20 mmol) was added. The mixture was heated at 70 $^\circ\text{C}$ for 20 h. The volatiles were removed under vacuum for 4 h. The resulting residue was redissolved in ~1 mL of benzene and 1 mL of pentane was added. The resulting precipitate was decanted off the solution and washed with pentane and dried under vacuum to give 6-PPh₃ as an off-white solid. Yield: 92 mg, 70%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.62–7.58 (m, 12H, PPh₃), 7.36–7.28 (m, 18H, PPh₃), 7.42 (m, 1H, pyrimidine C–H), 7.06 (m, 1H, pyrimidine C–H), 6.72 (m, pyrimidine C–H), 3.89 (s, 1H, –NH), –22.21 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 10$ Hz, 1H, Ir–H), –22.84 (m, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 19.31 (t, $J = 14$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 171.17 (s), 155.24 (s), 155.08 (s), 135.11 (t, $J = 25$ Hz), 134.03 (t, $J = 6$ Hz), 129.40 (s), 128.25 (s), 127.64 (t, $J = 5$ Hz), 102.09 (s). Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{IrN}_3\text{P}_2$: C, 59.10; H, 4.46; N, 5.17. Found: C, 60.12; H, 4.54; N, 4.85.

Trihydrido(pyridine)bis(triphenylphosphine)iridium(III) (8-PPh₃). To a suspension of $\text{IrH}_5(\text{PPh}_3)_2$ (70 mg, 0.10 mmol) in 10 mL of dry C_6H_6 in a 50-mL flame-dried Schlenk flask, pyridine (25 μL , 0.20 mmol) was added. The mixture was heated at 45 $^\circ\text{C}$ for 19 h. The volatiles were removed under vacuum for 4 h. The resulting residue was dissolved in ~1 mL of benzene and 1 mL of pentane was added. The resulting precipitate was decanted off the solution and washed with pentane and dried under vacuum to give 8-PPh₃ as pale yellow solid. Yield: 51 mg, 63%. This compound has previously been prepared using an alternative method.²⁸ The IR spectrum of our sample matched that previously reported. The NMR data for 8-PPh₃ is reported here for future reference. ^1H NMR (500 MHz, C_6D_6): δ 8.36 (d, $J = 6$ Hz, 2H, pyridine C–H), 8.12–8.09 (m, 12H, PPh₃), 7.02–6.94 (m, 18H, PPh₃), 6.32 (m, 1H, pyridine C–H), 5.59 (dd, $J = 7$, 6 Hz, 2H, pyridine C–H), –8.73 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 5$ Hz, 2H, Ir–H), –21.98 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 5$ Hz, 1H, Ir–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ 33.50 (d, $J = 16$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz,

C_6D_6): δ 160.77 (s), 138.50 (t, $J = 25$ Hz), 135.07 (t, $J = 6$ Hz), 128.83 (s), 128.59 (s), 127.57 (t, $J = 4$ Hz), 123.70 (s).

Dihydrido(*N*-(2-pyridyl)carbamato- κ^2 -*N'*,*O*)bis-(triphenylphosphine)iridium(III) (10-PPh₃). To a 25-mL round-bottomed flask was added trihydrido(2-aminopyridine)bis-(triphenylphosphine)iridium(III) (45.0 mg, 0.055 mmol) and DCM (3 mL). The flask was purged with CO₂ gas, which was bubbled through the solution for 10 min (alternatively the solution could be degassed using three freeze–pump–thaw cycles and then placed under a static atmosphere of CO₂). The reaction was allowed to stir for 24 h, during which time a white crystalline solid began to precipitate. The solid was filtered off under air, washed with DCM, cooled to 0 °C, and dried under vacuum. The precipitated crystals were suitable for X-ray diffraction. Yield 33.1 mg, 70%. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.59 (m, 12H), 7.36 (d, $J = 6.0$ Hz, 1H), 7.27 (m, 18H), 6.93 (t, $J = 7.8$ Hz, 1H), 5.87 (d, $J = 8.3$ Hz, 1H), 5.68 (t, $J = 6.0$ Hz, 1H), δ –20.67 (td, $J = 16.8, 7.1$ Hz, 1H), –26.41 (td, $J = 17.1, 7.4$ Hz, 1H). ¹³C{¹H} NMR: The full carbon spectrum of this compound could not be recorded due to its insolubility in all common solvents. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 21.30 (d, $J = 15.3$ Hz). IR (nujol, cm^{–1}): 1667.5 ($\nu_{\text{C=O}}$), 1329.1 ($\nu_{\text{C=O}}$). Anal. Calcd for C₄₂H₃₇IrN₂O₂P₂: C, 58.94; H, 4.36; N, 3.27. Found: C, 58.89; H, 4.31; N, 3.28.

An isotopologue of 10-PPh₃ with the carbon of the carbamato group ¹³C-labeled was prepared by exposing a degassed solution of 10-PPh₃ in DCM to ¹³C-labeled CO₂. Exchange occurred over a period of 24 h at RT. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): 154.28 (¹³C=O).

Dihydrido(*N*-(2-pyridyl)carbamato- κ^2 -*N'*,*O*)bis-(tricyclohexylphosphine)iridium(III) (10-PCy₃). Excess CO₂ at 1 atm was added via a dual-manifold Schlenk line to a degassed and shaken solution of 2-PCy₃ (6 mg, 0.007 mmol) in 0.8 mL of CD₂Cl₂ in a J. Young tube at RT. After 0.5 h the mixture was evaporated to dryness to give 10-PCy₃ as a white solid. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ at –35 °C. Yield: 5.8 mg, 92%. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.42 (d, $J = 5$ Hz, 1H, pyridine C–H), 7.50 (br s, 1H, –NH), 7.43 (m, 1H, pyridine C–H), 6.46 (m, 2H, pyridine C–H), 1.96–1.05 (m, 66H, Cy), –23.64 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 10$ Hz, 1H, Ir–H), –28.83 (td, $J_{\text{PH}} = 20$ Hz, $J_{\text{HH}} = 10$ Hz, 1H, Ir–H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 22.38. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 30.00 (s), 29.07 (s), 27.68 (br s), 26.80 (s), 26.30 (s). The full carbon spectrum of this compound could not be recorded due to its insolubility in all common solvents. IR (cm^{–1}) 1662 ($\nu_{\text{C=O}}$), 1311 ($\nu_{\text{C=O}}$). Anal. Calcd for C₄₂H₇₃IrN₂O₂P₂·CH₂Cl₂: C, 52.85; H, 7.74; N, 2.87. Found: C, 52.44; H, 7.28; N, 2.84.

Dihydrido(*N*-(2-methylpyridyl)carbamato- κ^2 -*N'*,*O*)bis-(triphenylphosphine)iridium(III) (11-PPh₃). Excess CO₂ at 1 atm was added via a dual-manifold Schlenk line to a degassed and shaken solution of 4-PPh₃ (8.4 mg, 0.01 mmol) in 0.5 mL of CD₂Cl₂ in a J. Young tube at RT. After 0.5 h ¹H and ³¹P spectra of the solution showed that it was a mixture containing 91% 10-PPh₃ and 9% 4-PPh₃. The mixture was dried under vacuum for 2 h. ¹H and ³¹P spectra of the resulting residue in CD₂Cl₂ showed that it was a mixture containing 27% 10-PPh₃ and 73% 4-PPh₃. As a result no pure 10-PPh₃ was isolated. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/pentane under CO₂ at –35 °C. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.69 (d, $J = 5$ Hz, 1H, pyridine C–H), 7.55–7.51 (m, 12H, Ar), 7.32–7.25 (m overlapping with 4-PPh₃, 18H, Ar), 7.13 (m, 1H, pyridine C–H), 6.28 (d, $J = 10$ Hz, 1H, pyridine C–H), 5.83 (m, 1H, pyridine C–H), 2.38 (s, 3H, –NMe), –20.69 (m, 1H, Ir–H), –26.55 (m, 1H, Ir–H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 20.22 (m).

Dihydrido(*N*-(2-pyrimidyl)carbamato- κ^2 -*N'*,*O*)bis-(triphenylphosphine)iridium(III) (12-PPh₃). Excess CO₂ at 1 atm was added via a dual-manifold Schlenk line to a degassed and shaken solution of 6-PPh₃ (28 mg, 0.034 mmol) in 1 mL of CH₂Cl₂ in a J. Young tube at RT. After 3 h the mixture was evaporated to dryness to give crude product. Pure 12-PPh₃ was obtained by recrystallization from CH₂Cl₂/pentane as a pale yellow solid. Yield: 19 mg, 65%. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.89 (dd, $J = 5, 2$ Hz, 1H, pyrimidine C–H), 7.66–7.61 (m, 12H, PPh₃), 7.45–7.30 (m, 18H, PPh₃), 6.74 (s, 1H, pyrimidine C–H), 5.65 (m, pyrimidine C–H), –20.56 (td, $J_{\text{PH}} = 16$ Hz, $J_{\text{HH}} = 8$ Hz, 1H, Ir–H), –26.44 (td, $J_{\text{PH}} = 16$ Hz, $J_{\text{HH}} = 8$ Hz,

1H, Ir–H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 21.93(m). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 165.03 (s), 158.35 (s), 157.31 (s), 153.68 (s), 134.46 (t, $J = 6$ Hz), 134.96(s), 133.96(s), 130.36, 128.85 (s), 128.58 (t, $J = 5$ Hz), 125.41(s), 113.43 (s). IR (cm^{–1}) 1674 ($\nu_{\text{C=O}}$), 1293 ($\nu_{\text{C=O}}$). Anal. Calcd for C₄₁H₃₆IrN₃O₂P₂: C, 57.47; H, 4.23; N, 4.90. Found: C, 56.10; H, 4.32; N, 4.85.

X-ray Crystallography. Crystal samples were mounted in MiTeGen polyimide loops with immersion oil. The diffraction experiments were carried out on a Rigaku SCXmini CCD detector using filtered MoK α radiation ($\lambda = 0.71075$ Å) at a temperature of –50 °C. The data frames were processed using Rigaku CrystalClear²⁹ and corrected for Lorentz and polarization effects. The structures were solved by direct methods³⁰ or Patterson methods³¹ and expanded using Fourier techniques.³² Non-hydrogen atoms were refined anisotropically and hydrogen atoms were typically treated as idealized contributions. Further details of the refinement are given in Table 2 and the Supporting Information.

Computational Details. All calculations were performed with the Gaussian09 package³³ of programs with the hybrid B3LYP functional.³⁴ The basis set was the ECP-adapted SDDALL³⁵ with a set of polarization functions for Ir³⁶ and P,³⁶ the all-electron 6-31G(d,p)³⁷ for N, H, C, and the 6-31+G(d,p)³⁸ for O of CO₂.³⁹ Full optimization of geometry was performed without any symmetry constraints, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or transition states. Each transition state was relaxed toward reactant and product using the vibrational data to confirm its nature. The zero-point, thermal, and entropy corrections were evaluated to compute enthalpies and Gibbs free energies ($T = 298$ K, $P = 1$ atm). The effect of DCM solvent ($\epsilon = 8.93$) was included by using the continuum SMD model⁴⁰ with single point 6-311+G** calculations.⁴¹

■ ASSOCIATED CONTENT

● Supporting Information

Selected ¹H and ³¹P NMR spectra, X-ray information for 1-PPh₃, 2-PPh₃, 3-PPh₃, 7-PPh₃, 10-PPh₃, 10-PCy₃, and 11-PPh₃, the computed energy profile for the direct reaction of CO₂ with 1-PH₃, the computed energy profile for the reaction between CO₂ and 2-PPh₃, and Cartesian coordinates and energies for optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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