Synthesis and Reactivity of the Monomeric Late-Transition-Metal Parent Amido Complex [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)]

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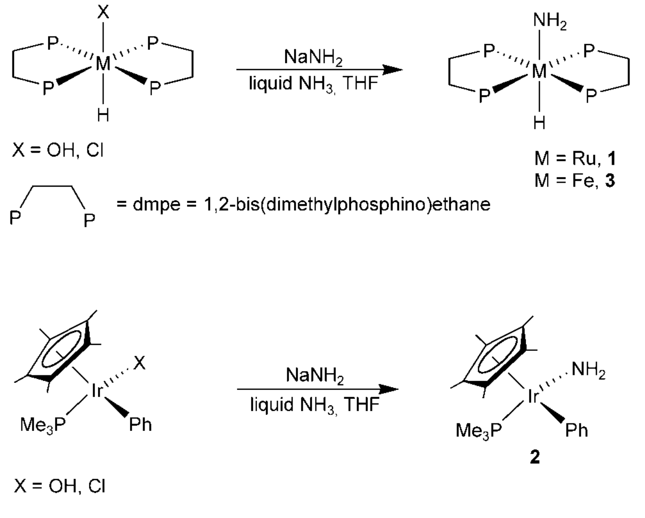
Abstract: The late-transition-metal parent amido compound [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**) has been synthesized by deprotonation of the corresponding ammine complex [Ir(Cp*)(PMe$_3$)(Ph)(NH$_3$)][OTf] (**6**) with KN(SiMe$_3$)$_2$. An X-ray structure determination has ascertained its monomeric nature. Proton-transfer studies indicate that **2** can successfully deprotonate *p*-nitrophenylacetonitrile, aniline, and phenol. Crystallographic analysis has revealed that the ion pair [Ir(Cp*)(PMe$_3$)(Ph)(NH$_3$)][OPh] (**8**) exists as a hydrogen-bonded dimer in the solid state. Reactions of **2** with isocyanates and carbodiimides lead to overall insertion of the heterocumulenes into the N−H bond of the Ir-bonded amido group, demonstrating the ability of **2** to act as an efficient nucleophile. Intriguing reactivity is observed when amide **2** reacts with CO or 2,6-dimethylphenyl isocyanide. η^4-Tetramethylfulvene complexes [Ir(η^4-C$_5$Me$_4$CH$_2$)(PMe$_3$)(Ph)(L)] (L = CO (**15**), CNC$_6$H$_3$-2,6-(CH$_3$)$_2$ (**16**)) are formed in solution through displacement of the amido group by the incoming ligand followed by deprotonation of a methyl group on the Cp* ring and liberation of ammonia. Conclusive evidence for the presence of the Ir-bonded η^4-tetramethylfulvene moiety in the solid state has been provided by an X-ray diffraction study of complex **16**.

Keywords: amides • basicity • cyclopentadienyl ligands • fulvenes • iridium

Introduction

Significant efforts have been made to develop reliable synthetic routes to late-transition-metal–amido compounds.[1,2] Their role as intermediates in important transformations such as hydroamination[4–7] and C–N coupling reactions[8–10] has called for mechanistic investigations into the chemical reactivity of metal–amido species. A more detailed understanding of the nature and chemical behavior of the nondative M–N linkage would aid elucidation of the mechanism of such transformations and thereby allow for a more rational catalyst design. However, examples of isolable late-transition-metal–amido compounds remain scarce and relevant information on their reactivity is still considerably limited.[1–3] In particular, monomeric, low-valent, parent (that is, unsubstituted) amido complexes are exceptionally rare and no general method exists for their synthesis.[11–15]

Recently, our group reported the isolation of the first structurally characterized low-valent monomeric ruthenium and iridium parent amido compounds *trans*-[Ru(dmpe)$_2$(H)(NH$_2$)] (**1**) and [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**) (Cp* = η^5-pentamethylcyclopentadienyl), synthesized from the corresponding metal chlorides or hydroxides in the presence of a NaNH$_2$/NH$_3$(l) mixture (Scheme 1).[16] The same methodolo-



Scheme 1. Synthesis of *trans*-[M(dmpe)$_2$(H)(NH$_2$)] (M = Ru (**1**); M = Fe (**3**)) and [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**) by the NaNH$_2$/NH$_3$(l) methodology.

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gy provided access to [Fe(dmpe)$_2$(H)(NH$_2$)] (**3**),[17] a rare example of a first-row parent amido species, and proved applicable to the synthesis of *cis*-[Ru(Me$_3$P)$_4$(H)(NH$_2$)] (**4**).[18] A comprehensive study of the reactivity of ruthenium amide **1** revealed its remarkable basicity, with an estimated pK_a of the corresponding ammonia complex of approximately 23–24 in THF.[19,20] Both iron complex **3** and ruthenium amide **4** were found to be somewhat less basic than **1**. However, complex **4** functioned efficiently as a nucleophile in substitution reactions with alkyl halides.[18]

The analogous investigation of the reactivity of [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**) had been prevented by difficulties in isolating the amide as a pure compound. Although quantitative formation of the complex appeared to occur in solution, attempts at isolation in the solid state led to extensive decomposition, probably induced by undetermined impurities. Furthermore, contamination of the complex with sodium halide byproducts could not be prevented. Therefore, we sought to identify an alternative, more efficient synthetic route. This paper includes details of our successful synthesis of the monomeric, sodium halide free amide [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**), its structural characterization, and results that demonstrate its significant basicity and nucleophilicity. We also describe the unusual reactivity of complex **2** toward carbon monoxide and 2,6-dimethylphenyl isocyanide, leading to the unexpected formation of η^4-tetramethylfulvene complexes [Ir(η^4-C$_5$Me$_4$CH$_2$)(PMe$_3$)(Ph)(L)] (L = CO (**15**), CNC$_6$H$_3$-2,6-(CH$_3$)$_2$ (**16**)).

Results and Discussion

Synthesis and characterization of [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (2): Synthesis of amido complex **2** had been accomplished previously, albeit in very low isolated yield, following the NaNH$_2$/NH$_3$(l) methodology employed in the synthesis of ruthenium amide **1** (Scheme 1).[16] In an effort to optimize the synthetic protocol for this compound, we pursued an alternative approach, in the hope of avoiding contamination of the amide with sodium halides or other, possibly destabilizing, impurities. Deprotonation of ammine complexes with strong bases, such as potassium hydride or organolithium reagents, is a synthetic protocol that has been successfully employed in the generation of amido species.[12,14,18] We utilized an analogous strategy for the synthesis of complex **2**.

Reaction of [Ir(Cp*)(PMe$_3$)(Ph)(OTf)][21] (OTf = trifluoromethanesulfonate) (**5**) with NH$_3$ in THF cleanly afforded ammine complex [Ir(Cp*)(PMe$_3$)(Ph)(NH$_3$)][OTf] (**6**) [Eq. (1)]. Complex **6** was isolated in 87% yield as light yellow crystals from a mixture of THF and pentane. The ^{31}P{^{1}H} NMR spectrum displayed a singlet resonance at $\delta = -37.1$ ppm, shifted upfield with respect to the starting material (**5**,[21] $\delta = -25.8$ ppm), while the protons of the Ir-bonded NH$_3$ ligand appeared in the ^{1}H NMR spectrum as a broad singlet at $\delta = 3.88$ ppm.

The structure of **6** was confirmed by an X-ray diffraction study. The ORTEP diagram and significant bond lengths and angles are shown in Figure 1. The crystallographic analysis indicated the presence of an Ir-bonded ammonia ligand with an Ir1–N1 distance (2.135(8) Å) slightly shorter than that reported for [Ir(Cp*)(PMe$_3$){CF(CF$_3$)$_2$}(NH$_3$)][BF$_4$].[22] The structure revealed the presence of a hydrogen bond between one hydrogen atom of the ammonia molecule and one of the oxygen atoms of the triflate anion, with an N1···O3 distance of 2.98 Å.

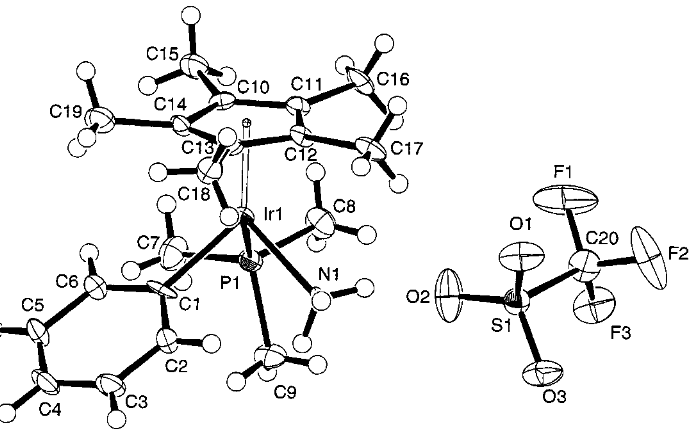
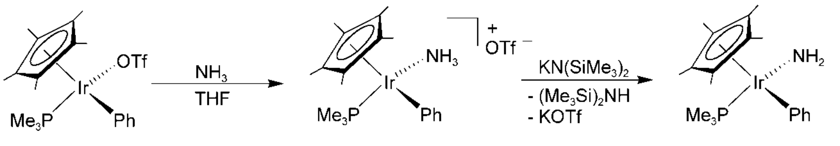


Figure 1. ORTEP diagram of **6** (thermal ellipsoids at 50% probability). Selected bond lengths [Å] and angles [°]: Ir1–N1 2.135(8), Ir1–P1, 2.284(3), Ir1–C1 2.08(1), Ir1–C10 2.216(9), Ir1–C11 2.28(1), Ir1–C12 2.257(10), Ir1–C13 2.22(1), Ir1–C14 2.184(10); P1-Ir1-N1 87.2(2), P1-Ir1-C1 89.4(3), N1-Ir1-C1 87.2(4).

Previous studies from our laboratory showed the sterically hindered base KN(SiMe$_3$)$_2$ to be an efficient deprotonating agent for the clean generation of amido species.[18] Addition of KN(SiMe$_3$)$_2$ to a solution of ammine complex **6** in THF caused an immediate color change from pale yellow to dark orange with concomitant quantitative formation of amide [Ir(Cp*)(PMe$_3$)(Ph)(NH$_2$)] (**2**), as assigned by NMR spectroscopy [Eq. (1)]. Purification of the amide from the KOTf byproduct was achieved by extraction of **2** into pentane. However, the high solubility of the complex in organic solvents limited its isolated yield, after crystallization from pentane, to 51%. In the ^{31}P{^{1}H} NMR spectrum, the singlet resonance corresponding to the PMe$_3$ ligand was observed at $\delta = -34.1$ ppm while the diagnostic high-field resonance of the NH$_2$ protons was found in the ^{1}H NMR spectrum as a broad singlet at $\delta = -1.30$ ppm. The absence of any contaminating KOTf salt was confirmed by ^{19}F NMR spectroscopy, elemental analysis, and X-ray crystallography. Single crystals suita-



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ble for crystallographic analysis could be obtained by slow concentration of a solution of **2** in pentane under reduced pressure. The ORTEP diagram and selected bond lengths and angles are reported in Figure 2. The crystal structure confirms the monomeric nature of the parent amido compound in the solid state. The hydrogen atoms were not refined, so we do not think it possible to draw definitive structural conclusions about the planarity of the $IrNH_2$ group. However, the iridium center is in the expected three-legged piano-stool coordination geometry and is singly bonded to the nitrogen atom of the $-NH_2$ group. The Ir1−N1 distance, 2.105(8) Å, is only slightly shorter than the corresponding distance found in ammine complex **6**, 2.135(8) Å. This feature, coupled with the stability of **2** as an 18-electron complex, points toward the absence of any important Ir−N π bonding. The hydrogen atoms bonded to the amido nitrogen were located on a Fourier difference map and included in the observed positions.

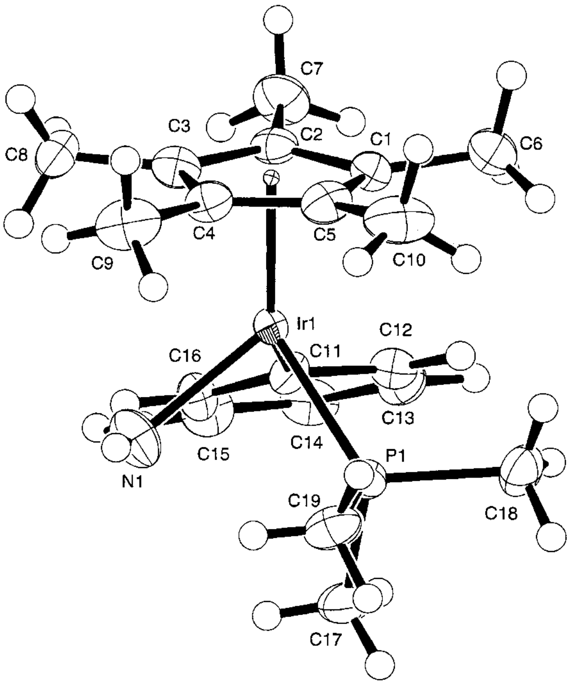


Figure 2. ORTEP diagram of **2** (thermal ellipsoids at 50% probability). Selected bond lengths [Å] and angles [°]: Ir1−N1 2.105(8), Ir1−P1 2.243(2), Ir1−C11 2.062(8), Ir1−C1 2.220(8), Ir1−C2 2.244(8), Ir1−C3 2.222(8), Ir1−C4 2.226(8), Ir1−C5 2.234(8);, N1-Ir1-P1 81.6(2), N1-Ir1-C11 88.8(3), P1-Ir1-C11 89.5(2).

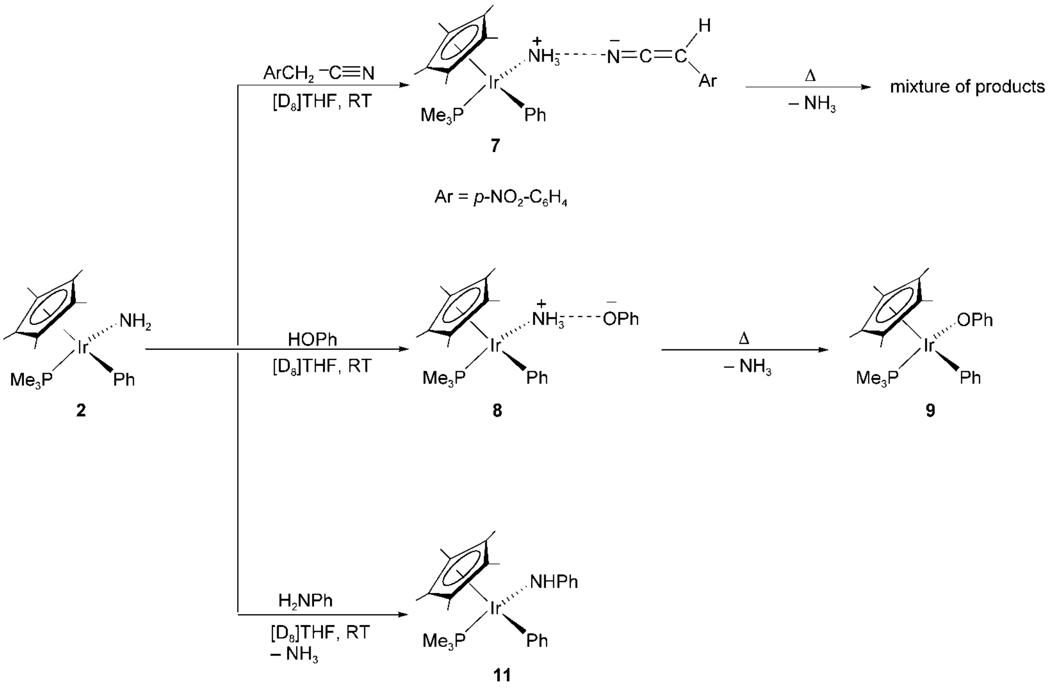
Amide **2** is extremely air-sensitive and quickly turns brown upon exposure to air. However, under an inert atmosphere it is stable in the solid state and in solution in halide-free, nonacidic solvents below 45 °C. At this temperature, it decomposes to multiple unidentified products over the course of several days.

Acid–base reactivity: As mentioned previously, a particularly intriguing property of ruthenium amide **1** is its remarkable basicity.[19,20] We therefore explored the basicity of $[Ir(Cp^*)(PMe_3)(Ph)(NH_2)]$ (**2**) and compared it with that of **1** by investigating the reactions of **2** with sterically encumbered weak acids with different pK_a values.

Addition of phenylacetonitrile to a solution of **2** in $[D_8]$THF led to a mixture of products. A broad triplet resonance at $\delta = 0.35$ ppm indicated the presence of noncoordinated ammonia, suggesting that protonation of the amido group by the weak acid ($pK_a = 22.6$ in THF)[23] had occurred, followed by dissociation of ammonia and formation of a neutral complex. Despite several attempts, the compound could not be isolated in pure form. However, when *p*-nitrophenylacetonitrile ($pK_a = 13.0$ in THF)[23] was used in place of phenylacetonitrile, a deep purple solution containing ion pair **7** was immediately obtained (Scheme 2). A broad singlet resonance at $\delta = 4.06$ ppm in the ^1H NMR spectrum indicated the presence of an Ir-bonded NH_3 group and a sharp singlet at $\delta = 3.92$ ppm was assigned to the methine group of the anion. Ion pair **7** proved to be remarkably stable toward ammonia dissociation. Heating at 75 °C was required to induce ammonia displacement, albeit with concomitant formation of a mixture of products (Scheme 2). Interestingly, reaction of *trans*-$[Ru(dmpe)_2(H)(NH_2)]$ (**1**) with both phenylacetonitrile and 4-(α,α,α-trifluoromethyl)phenylacetonitrile immediately led to displacement of ammonia and formation of the corresponding keteniminate complexes, without detection of the intermediate ion pairs.[19,20]

Addition of phenol ($pK_a = 18.0$ in DMSO)[24] to a solution of **2** in $[D_8]$THF led to quantitative formation of ammonia–phenoxide ion pair **8** at room temperature (Scheme 2). In the $^{31}P\{^1H\}$ NMR spectrum, a singlet resonance at $\delta = -38.1$ ppm (compare $[Ir(Cp^*)(PMe_3)(Ph)(NH_3)][OTf]$ (**6**), $\delta = -37.1$ ppm) indicated formation of the ammine complex. Accordingly, the ^1H NMR spectrum showed the coordinated NH_3 protons as a broad singlet resonance centered at $\delta = 5.41$ ppm. Crystals of **8** of quality sufficient for an X-ray diffraction study were obtained by slow diffusion of pentane into a concentrated solution of **8** in THF over the course of a week. The ORTEP diagram and relevant bond lengths are reported in Figure 3. There are two crystallographically independent complexes in the asymmetric unit, each complex consisting of an iridium–ammonia cation and a phenoxide anion. Each iridium is coordinated in a three-legged piano-stool fashion by a Cp* ligand, an NH_3 group, a trimethylphosphine, and a phenyl group. The two complexes form a hydrogen-bonded dimer about a pseudo-inversion center with the NH_3 group on each iridium cation engaging in hydrogen bonds with the oxygen on each phenoxide anion ($N1\cdots O1 = 2.73$, $N1\cdots O2 = 2.83$, $N2\cdots O1 = 2.84$, $N2\cdots O2 = 2.78$ Å). The pseudo-inversion symmetry gives rise to correlations between atoms in each molecule. This leads to unusual thermal displacement parameters in the atoms of each molecule and an overall poor refinement; therefore only the iridium and phosphorus atoms have been refined anisotropically, and the bond lengths are accurate to only two decimal places and the bond angles to one significant figure. All hydrogen atoms have been placed in calculated positions. Nevertheless, the connectivity of the complexes is reliable.[25]

In analogy to our observations on ion pair **7**, heating of **8** at elevated temperatures was required to induce dissociation of the ammonia molecule from the coordination sphere of



Scheme 2. Reactions of $[Ir(Cp^*)(PMe_3)(Ph)(NH_2)]$ (**2**) with sterically encumbered weak acids.

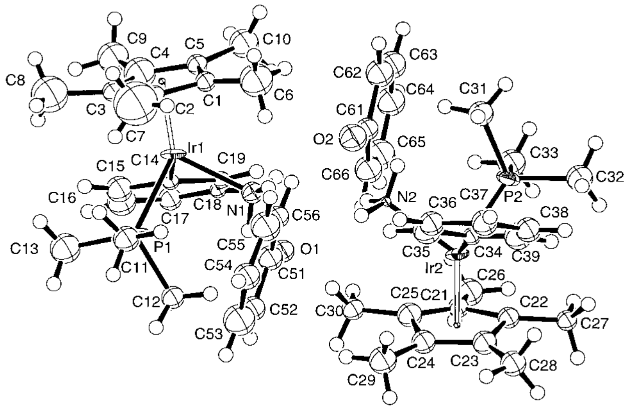


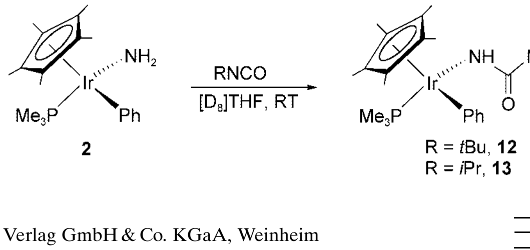
Figure 3. ORTEP diagram of **8** (thermal ellipsoids at 50 % probability). Selected bond lengths [Å]: Ir1–P1 2.28(1), Ir1–N1 2.13(3), Ir1–C1 2.25(4), Ir1–C2 2.19(3), Ir1–C3 2.21(3), Ir1–C4 2.23(4), Ir1–C5 2.27(4), Ir1–C14 2.01(3), Ir2–P2 2.29(1), Ir2–N2 2.15(2), Ir2–C21 2.20(3), Ir2–C22 2.20(4), Ir2–C23 2.27(4), Ir2–C24 2.29(4), Ir2–C25 2.23(4), Ir2–C34 1.94(3).

the iridium atom. Formation of the inner-sphere phenoxide complex $[Ir(Cp^*)(PMe_3)(Ph)(OPh)]$[21] (**9**) was accomplished upon heating a solution of **8** in $[D_8]THF$ at 75 °C for 6 h (Scheme 2). The irreversibility of this reaction contrasts with the behavior observed with the corresponding ruthenium ion pair *trans*-$[Ru(dmpe)_2(H)(NH_3)][OPh]$ (**10**), which exists in equilibrium with the corresponding inner-sphere phenoxide complex in THF at room temperature.[20] Reaction of **2** with aniline yielded the protonolysis product $[Ir(Cp^*)(PMe_3)(Ph)(NHPh)]$[21] (**11**) and NH_3, although in this case the ion-pair intermediate was not observed (Scheme 2).

Addition of cyclobutanone ($pK_a = 25.1$ in DMSO)[26] to a solution of **2** in $[D_8]THF$ at room temperature led to formation of ammonia, indicating that deprotonation of the cyclic ketone had occurred. However, a complex mixture of products was obtained that precluded the isolation of clean compounds. Surprisingly, while amide **1** quantitatively deprotonated fluorene ($pK_a = 22.9$ in THF)[27] to form the corresponding ammonia–fluorenide ion pair,[20] no reaction occurred between fluorene and amide **2**. Consistent with this observation, reaction of $[Ir(Cp^*)(PMe_3)(Ph)(NH_3)][OTf]$ (**6**) with sodium fluorenide led to quantitative formation of fluorene and iridium amide **2**, demonstrating that a low kinetic basicity of complex **2** is not the cause of its inability to deprotonate fluorene. This result clearly suggests that, despite the presence of the relatively electron-rich Cp* and PMe_3 ligands on the Ir^{III} center, amide **2** is considerably less basic than ruthenium amide **1**.

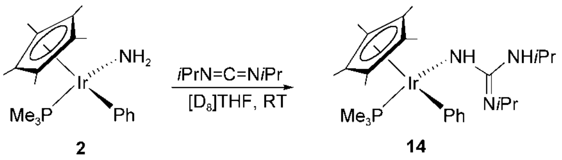
Nucleophilic reactivity: The nucleophilic properties of $[Ir(Cp^*)(PMe_3)(Ph)(NH_2)]$ (**2**) were probed by exploring its reactivity toward a representative set of organic electrophiles. Treatment of complex **2** with *tert*-butyl isocyanate (*t*BuNCO) afforded the product of isocyanate insertion into the N–H bond of the Ir-bonded NH_2 group, to yield ureate complex $[Ir(Cp^*)(PMe_3)(Ph)(NHC(O)(NHtBu))]$ (**12**) [Eq. (2)].

In the ^1H NMR spectrum, a sharp singlet resonance at $\delta = 1.88$ ppm was assigned to the Ir–N*H* proton, while the *t*Bu–



(2)

N*H* resonance was observed as a singlet at $\delta = 4.67$ ppm. An analogous reaction occurred upon addition of isopropyl isocyanate (*i*PrNCO) to amide **2** with formation of complex **13** [Eq. (2)]. Reaction of di-*p*-tolylcarbodiimide with **2** led to a mixture of unidentified products. However, treatment of **2** with diisopropylcarbodiimide cleanly afforded guanidinate complex [Ir(Cp*)(PMe$_3$)(Ph)(NHC(N*i*Pr)(NH*i*Pr))] (**14**) in 58 % yield as bright yellow crystals [Eq. (3)].



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The ^{1}H NMR spectrum of the product was characterized by the presence of two multiplet resonances for the methine protons of the two isopropyl groups ($\delta = 4.10$–4.05 and 3.21–3.15 ppm) and a single Ir–N*H* proton at $\delta = 2.85$ ppm. In the ^{31}P{^{1}H} NMR spectrum, the PMe$_3$ ligand resonated as a singlet at $\delta = -36.6$ ppm. Single crystals suitable for an X-ray diffraction study were obtained upon cooling a solution of **14** in pentane at −30 °C for 24 h. The crystallographic analysis confirmed the compound's structure. The ORTEP diagram and significant bond lengths and angles are shown in Figure 4.

Reactions with 2,6-dimethylphenyl isocyanide and CO: Iron–amido complex **3** was shown to react with CO by the unexpected insertion of carbon monoxide into the N–H rather than the Fe–N bond.[17] Mechanistic studies suggested direct nucleophilic attack of the amido nitrogen atom on the CO carbon atom as the likely reaction pathway. Intrigued by this result, we explored analogous reactions of CO and isocyanides with iridium amide **2** and observed chemical reactivity substantially different from that of the iron system. When complex **2** was subjected to 1 atm of carbon monoxide, the solution immediately changed color from amber to pale yellow. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture exhibited a new, significantly upfield-shifted, singlet resonance at $\delta = -53.8$ ppm. In the ^{1}H NMR spectrum, the presence of noncoordinated NH$_3$ was indicated by a broad triplet centered at $\delta = 0.35$ ppm. In addition, two signals at $\delta = 2.67$ and 2.57 ppm, each integrating to one proton, were observed, and the doublet resonance typical of the η^5-pentamethylcyclopentadienyl ligand was replaced by four signals, indicating the presence of nonequivalent methyl groups, at $\delta = 2.43$, 1.65, 1.62, and 1.29 ppm. These spectral data are consistent with the formation of η^4-tetramethylfulvene complex [Ir(η^4-C$_5$Me$_4$CH$_2$)(PMe$_3$)(Ph)(CO)] (**15**) (Scheme 3). Unfortunately, the instability of the complex prevented its isolation in the solid state in pure form. Indeed, **15** could be observed in solution for only a short time, after which it decomposed to several unidentified products.

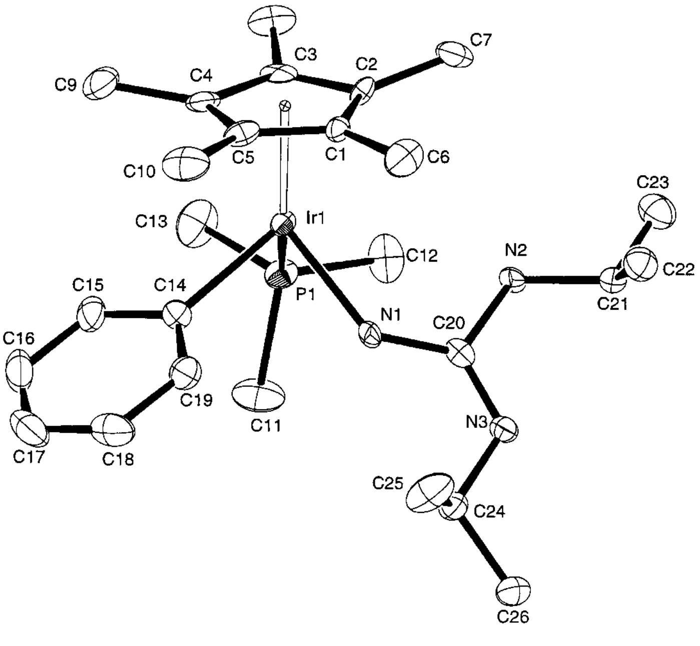
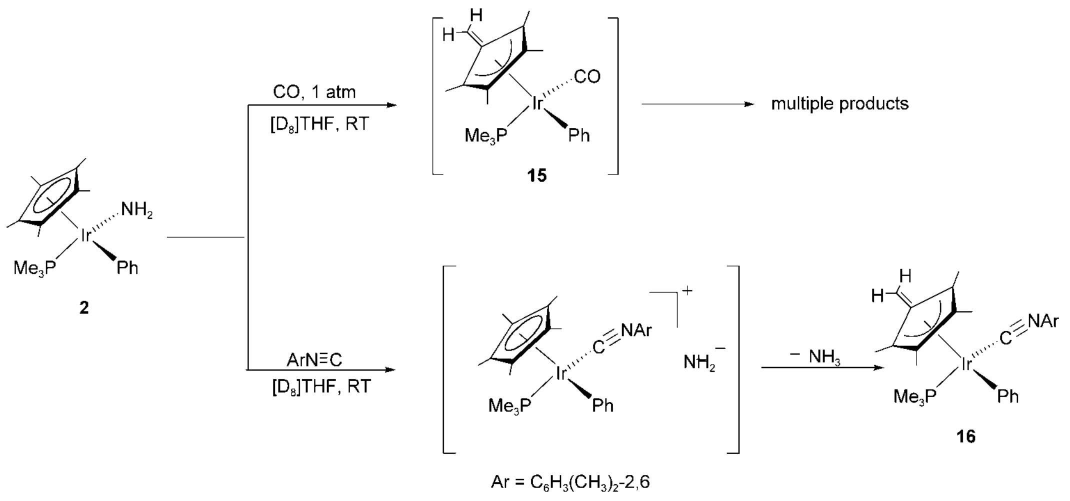


Figure 4. ORTEP diagram of **14** (thermal ellipsoids at 50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1–P1 2.256(2), Ir1–N1 2.092(5), Ir1–C14 2.085(7), Ir1–C1 2.281(6), Ir1–C2 2.278(7), Ir1–C3 2.218(7), Ir1–C4 2.174(7), Ir1–C5 2.251(7); Ir1-N1-C20 135.9(5), N1-C20-N2 114.9(6), N1-C20-N3 128.8(6), C14-Ir1-P1 90.1(2), C14-Ir1-N1 84.4(2), N1-Ir1-P1 85.1(2).

Indirect support for the proposed structure of **15** was obtained from the analogous reaction of **2** with 2,6-dimethylphenyl isocyanide. Upon addition of the isonitrile, a bright yellow solution containing η^4-tetramethylfulvene complex [Ir(η^4-C$_5$Me$_4$CH$_2$)(PMe$_3$)(Ph)(CNC$_6$H$_3$-2,6-(CH$_3$)$_2$)] (**16**) was immediately obtained (Scheme 3). The compound was sufficiently stable to be isolated in the solid state as bright yellow crystals in 34 % yield, after crystallization from pentane at −30 °C. However, it was found to decompose slowly in solution at room temperature to give a mixture of three unidentified products, over the course of several days. The ^{1}H NMR spectral data for the tetramethylfulvene portion of **16** were similar to those of **15**. Interestingly, unusually large long-range ^{1}H–^{31}P couplings were observed in the ^{1}H NMR spectrum (as ascertained by ^{31}P-filtered 1D HMQC NMR experiments). The two C=C*H*$_2$ protons gave rise to two doublets at $\delta = 2.54$ and 2.47 ppm (J(H,P) = 5.0 Hz), while the protons for two of the four methyl groups appeared as two doublets at $\delta = 2.39$ and 1.59 ppm (J(H,P) = 3.5 and 5.5 Hz, respectively). The resonances for the remaining two methyl groups were observed as singlets at $\delta = 1.57$ and 1.22 ppm.

The identity of complex **16**, as predicted by NMR spectroscopy, was confirmed by X-ray crystallography. The ORTEP diagram and significant bond lengths are shown in Figure 5. The structural analysis showed the presence of a fulvene moiety bound in an η^4 fashion to the iridium center through its planar 1,3-diene system. The C–C bonds within the diene part range from 1.42(1) to 1.44(1) Å long and are shorter than the C2–C3 and C3–C4 bonds (1.46(1) and 1.49(1) Å, respectively). Examination of the mean plane of the cyclopentadiene moiety reveals that C3 deviates from the plane formed by C1, C2, C4, and C5 by 0.38 Å. The distance of the metal from the four Ir-bonded carbon atoms on



Scheme 3. Synthesis of η^4-tetramethylfulvene complexes [Ir(η^4-$C_5Me_4CH_2$)(PMe_3)(Ph)(L)] (L = CO (**15**), CNC_6H_3-2,6-$(CH_3)_2$ (**16**)).

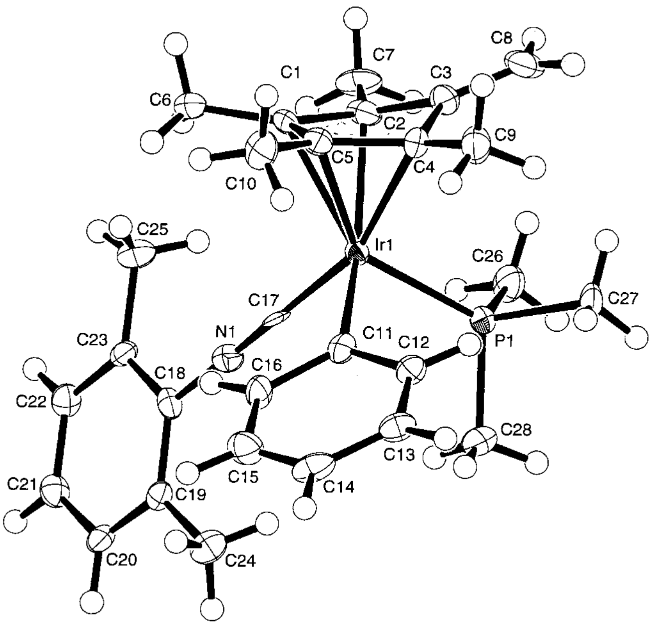


Figure 5. ORTEP diagram of **16** (thermal ellipsoids at 50 % probability). Selected bond lengths [Å]: Ir1–P1 2.285(2), Ir1–C11 2.106(8), Ir1–C17 1.907(9), Ir1–C1 2.204(8), Ir1–C2 2.260(8), Ir1–C4 2.221(8), Ir1–C5 2.164(8), C1–C2 1.43(1), C2–C3 1.46(1), C3–C4 1.49(1), C4–C5 1.44(1), C5–C1 1.42(1), C3–C8 1.33(1).

the ring ranges from 2.164(8) to 2.260(8) Å, while the exocyclic C3–C8 length (1.33(1) Å) indicates an ethylenic bond.

Amide decomposition by deprotonation of the Cp* ligand has rarely been observed.[28] The reactivity toward CO and isocyanides displayed by amide **2** finds a relevant precedent in the reaction of anilido complex [Ir(Cp*)(PPh_3)(Me)(NHPh)] (**17**) with 1,2-bis(diphenylphosphino)ethane (DPPE) to yield [Ir(η^4-$C_5Me_4CH_2$)(dppe)(Me)] (**18**) and aniline.[29] The proposed mechanism for this transformation involves displacement of the anilido group as an anion from **17** by the incoming ligand and subsequent deprotonation of one of the methyl groups on the Cp* ring to form the fulvene moiety and ammonia. Although the formation of **16** from **2** has not been studied mechanistically, the similarities between the starting materials **2** and **17** suggest that a similar mechanism might operate (Scheme 3).

Summary and Conclusions

An improved synthetic route to the monomeric, parent iridium–amido compound [Ir(Cp*)(PMe_3)(Ph)(NH_2)] (**2**) has been developed. Isolation of the amide in pure form is possible by the new methodology, without contamination with alkali metal halides. Although proton transfer studies suggest that **2** is moderately less basic than the ruthenium amide *trans*-[(Rudmpe)$_2$(H)(NH_2)] (**1**), its reactions with heterocumulenes demonstrate its ability to act as an efficient nucleophile. Unusual reactivity is observed upon addition of CO and 2,6-dimethylphenyl isocyanide, leading to formation of the η^4-tetramethylfulvene complexes [Ir(η^4-$C_5Me_4CH_2$)(PMe_3)(Ph)(L)] (L = CO (**15**), CNC_6H_3-2,6-$(CH_3)_2$ (**16**)). The presence of the Ir-bonded η^4-fulvene moiety in solution has been reliably deduced on the basis of NMR data; an X-ray diffraction study on complex **16** has provided conclusive evidence of the same connectivity being retained in the solid state.

Experimental Section

General: All manipulations were performed under an inert atmosphere in a nitrogen-filled glovebox or by using standard Schlenk and vacuum-line techniques unless noted otherwise. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker 400 MHz Fourier Transform spectrometer with a commercial Bruker AM series interface or on a Bruker 500 MHz Fourier Transform spectrometer with a commercial Bruker DRX series interface.

[Ir(Cp*)(PMe_3)(Ph)(OTf)] (**5**) was prepared according to literature methods.[21] All other reagents were purchased from commercial vendors, checked for purity, and used without further purification unless otherwise noted. Liquids were degassed using three freeze–pump–thaw cycles and dried over 4 Å activated molecular sieves. Solids were stored in an inert atmosphere glovebox. Pentane (UV grade, alkene-free) was passed through a column of activated alumina (A1, 12 × 32, Purifry Co.) under nitrogen pressure and sparged with nitrogen before use.[30] Tetrahydrofuran and diethyl ether were distilled from purple sodium/benzophenone ketyl under nitrogen. $[D_8]$THF was vacuum-transferred from sodium/benzophenone ketyl and stored under an inert atmosphere.

$[Ir(Cp^*)(PMe_3)(Ph)(NH_3)][OTf]$ (6): Complex **5** (194 mg, 0.31 mmol) and THF (3 mL) were added to a heavy-walled glass vessel with a fused Teflon stopcock. On a vacuum line, the solution was degassed with three freeze–pump–thaw cycles. The vessel was cooled with liquid nitrogen and NH_3 was added so that when the vessel was allowed to warm to 25 °C the total solution volume was 4 mL. The reaction mixture was stirred at 25 °C for 30 min, after which the NH_3 was allowed to evaporate under N_2 and the remaining volatile materials were removed in vacuo. The tan-colored solid was crystallized from THF/pentane to give analytically pure **6** (174 mg, 87 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.14$ (d, $J = 7.2$ Hz, 2H; o-C_6H_5), 6.96 (t, $J = 7.2$ Hz, 2H; m-C_6H_5), 6.86 (t, $J = 7.6$ Hz, 1H; p-C_6H_5), 3.88 (brs, 3H; NH_3), 1.69 (d, $J(H,P) = 2.0$ Hz, 15H; C_5Me_5), 1.52 ppm (d, $J(H,P) = 10.4$ Hz, 9H; PMe_3); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): $\delta = 137.8$ (d, $J(C,P) = 3.7$ Hz, o-C_6H_5), 137.4 (d, $J(C,P) = 12.5$ Hz, i-C_6H_5), 127.7 (s, m-C_6H_5), 122.2 (s, p-C_6H_5), 92.8 (d, $J(C,P) = 3.0$ Hz, C_5Me_5), 13.3 (d, $J(C,P) = 37.4$ Hz, PMe_3), 7.9 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -37.1$ ppm (s); IR (Nujol): $\tilde{\nu} = 3355$, 3301 cm^{-1} (N–H); elemental analysis calcd (%) for $C_{20}H_{32}NF_3IrO_3PS$: C 37.14, H 4.95, N 2.17; found: C 36.84, H 4.93, N 2.23.

$[Ir(Cp^*)(PMe_3)(Ph)(NH_2)]$ (2): A solution of $KN(SiMe_3)_2$ (228 mg, 1.15 mmol) in THF (1 mL) was added to a stirred solution of **6** (742 mg, 1.15 mmol) in THF (3 mL). The dark red-brown mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the brown residue was treated with pentane (3 × 5 mL). The yellow solution was filtered through glass fiber filter paper and the filtrate evaporated under reduced pressure to give **2** as pale yellow crystals (292 mg, 51 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.24$ (d, $J = 6.8$ Hz, 2H; o-C_6H_5), 6.79 (t, $J = 7.2$ Hz, 2H; m-C_6H_5), 6.71 (t, $J = 7.2$ Hz, 1H; p-C_6H_5), 1.59 (d, $J(H,P) = 1.6$ Hz, 15H; C_5Me_5), 1.31 (d, $J(H,P) = 10.0$ Hz, 9H; PMe_3), −1.30 ppm (s, 2H; NH_2); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): $\delta = 141.6$ (d, $J(C,P) = 14.1$ Hz, i-C_6H_5), 138.3 (br s, o-C_6H_5), 126.4 (s, m-C_6H_5), 120.5 (s, p-C_6H_5), 91.0 (d, $J(C,P) = 4.0$ Hz, C_5Me_5), 12.6 (d, $J(C,P) = 37.4$ Hz, PMe_3), 7.9 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -34.1$ ppm (s); IR (KBr): $\tilde{\nu} = 3237$ cm^{-1} (m, vbr, N–H); elemental analysis calcd (%) for $C_{19}H_{31}NIrP$: C 45.95, H 6.29, N 2.82; found: C 46.22, H 6.34, N 2.85.

$[Ir(Cp^*)(PMe_3)(Ph)(NH_3)][p\text{-}NO_2C_6H_4CHCN]$ (7): A solution of p-nitrophenylacetonitrile (16 mg, 0.096 mmol) in THF (1 mL) was added to a stirred solution of **2** (48 mg, 0.096 mmol) in THF (1 mL). The deep purple mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the purple residue was treated with pentane (2 × 3 mL) and diethyl ether (2 × 1 mL) to yield ion pair **7** as a purple powder (42 mg, 66 %). ^{1}H NMR (500 MHz, $[D_8]$THF): $\delta = 7.50$ (d, $J = 9.5$ Hz, 1H; p-NO_2-C_6H_4CHCN), 7.38 (dd, $J = 9.5$, 2.0 Hz, 1H; p-NO_2-C_6H_4CHCN), 7.16 (d, $J = 7.0$ Hz, 2H; o-C_6H_5), 6.98 (t, $J = 7.5$ Hz, 2H; m-C_6H_5), 6.88 (t, $J = 7.0$ Hz, 1H; p-C_6H_5), 6.47 (dd, $J = 8.5$, 2.0 Hz, 1H; p-NO_2-C_6H_4CHCN), 6.12 (dd, $J = 9.5$, 2.0 Hz, 1H; p-NO_2-C_6H_4CHCN), 4.06 (brs, 3H; NH_3), 3.92 (s, 1H; p-NO_2-C_6H_4CHCN), 1.69 (d, $J(H,P) = 1.5$ Hz, 15H; C_5Me_5), 1.52 ppm (d, $J(H,P) = 10.0$ Hz, 9H; PMe_3); $^{13}C\{^1H\}$ NMR (126 MHz, $[D_8]$THF): $\delta = 152.8$ (s), 137.8 (d, $J(C,P) = 3.8$ Hz, o-C_6H_5), 137.6 (d, $J(C,P) = 12.6$ Hz, i-C_6H_5), 128.5 (s), 127.9 (s, m-C_6H_5), 125.6 (s, CH), 125.0 (s, CH), 123.5 (s, CH), 122.4 (s, p-C_6H_5), 117.6 (s, CH), 115.9 (s, CH), 92.9 (d, $J(C,P) = 3.8$ Hz, C_5Me_5), 65.0 (s, p-$NO_2C_6H_4$CHCN), 13.4 (d, $J(C,P) = 36.5$ Hz, PMe_3), 8.1 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (203 MHz, $[D_8]$THF): $\delta = -37.8$ ppm (s); IR (Nujol): $\tilde{\nu} = 3152$ cm^{-1} (vbr, N–H), 2149 cm^{-1} (vs, CN); elemental analysis calcd (%) for $C_{27}H_{37}N_3IrO_2P$: C 49.18, H 5.62, N 6.38; found: C 49.45, H 5.76, N 5.93.

$[Ir(Cp^*)(PMe_3)(Ph)(NH_3)][OPh]$ (8). A solution of phenol (13 mg, 0.14 mmol) in THF (1 mL) was added to a stirred solution of **2** (70 mg, 0.14 mmol) in THF (1 mL). The amber mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the brown residue was treated with pentane (2 × 3 mL) to yield ion pair **8** as a tan-colored powder (40 mg, 48 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.21$ (d, $J = 7.2$ Hz, 2H; C_6H_5), 6.86–6.75 (m, 5H; C_6H_5, OC_6H_5), 6.37 (d, $J = 8.4$ Hz, 2H; C_6H_5), 6.04 (t, $J = 7.2$ Hz, 1H; C_6H_5), 5.41 (brs, 3H; NH_3) 1.67 (d, $J(H,P) = 2.0$ Hz, 15H; C_5Me_5), 1.37 ppm (d, $J(H,P) = 19.6$ Hz, 9H; PMe_3); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): $\delta = 170.3$ (s, i-OC_6H_5), 138.5–138.4 (m, o-C_6H_5, i-C_6H_5), 128.3 (s, m-C_6H_5), 127.5 (s, p-C_6H_5), 121.6 (s, o-OC_6H_5), 119.7 (s, m-OC_6H_5), 108.7 (s, p-OC_6H_5) , 92.3 (d, $J(C,P) = 3.0$ Hz, C_5Me_5), 13.2 (d, $J(C,P) = 36.4$ Hz, PMe_3), 8.2 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -38.1$ ppm (s); IR (Nujol): $\tilde{\nu} = 3335$, 3289 cm^{-1} (vbr, N–H); elemental analysis calcd (%) for $C_{25}H_{37}NIrOP$: C 50.78, H 6.27, N 2.37; found: C 50.77, H 6.47, N 2.46.

$[Ir(Cp^*)(PMe_3)(Ph)(OPh)]$ (9): Complex **5** (21 mg, 0.036 mmol) was dissolved in $[D_8]$THF and transferred to an NMR tube. The tube was then flame-sealed under vacuum and heated at 75 °C for 5 h. The volatile materials were removed in vacuo and the remaining off-white solid was recrystallized from pentane (1 mL) at −30 °C for 48 h to yield **9** as a yellow-white solid (12 mg, 58 %). The spectroscopic features of this complex matched those reported in the literature.[21]

$[Ir(Cp^*)(PMe_3)(Ph)(NHPh)]$ (11): Complex **2** (25 mg, 0.049 mmol) and aniline were dissolved in $[D_8]$THF (2 mL) to give a bright yellow solution. The mixture was kept at 25 °C for 30 min, after which analysis of the reaction mixture by NMR spectroscopy revealed complete conversion of the starting materials to anilido complex **9**. The volatile materials were removed in vacuo and the yellow residue recrystallized from pentane (1 mL) at −30 °C for 24 h to yield **11** as bright yellow crystals (11 mg, 38 %). The spectroscopic features of this complex matched those reported in the literature.[21]

$[Ir(Cp^*)(PMe_3)(Ph)(NHC(O)(NHt\mathrm{Bu}))]$ (12): A solution of tBuNCO (8 mg, 0.076 mmol) in THF (1 mL) was added to a stirred solution of **2** (37 mg, 0.076 mmol) in THF (1 mL). The amber mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the light brown residue was recrystallized from pentane at −30 °C for 24 h to yield **12** as a tan powdery solid (19 mg, 44 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.23$ (d, $J = 6.8$ Hz, 2H; o-C_6H_5), 6.84 (t, $J = 7.2$ Hz, 2H; m-C_6H_5), 6.77 (t, $J = 7.2$ Hz, 1H; p-C_6H_5), 4.67 (s, 1H; tBu–NH), 1.88 (s, 1H; Ir–NH), 1.65 (d, $J(H,P) = 2.0$ Hz, 15H; C_5Me_5), 1.42 (d, $J(H,P) = 10.8$ Hz, 9H; PMe_3), 1.24 ppm (s, 9H; tBu); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): $\delta = 163.6$ (s, NHC(O)(NHtBu)), 139.0 (d, $J(C,P) = 12.5$ Hz, i-C_6H_5), 138.6 (d, $J(C,P) = 3.0$ Hz, o-C_6H_5), 126.5 (s, m-C_6H_5), 121.0 (s, p-C_6H_5), 92.1 (d, $J(C,P) = 3.0$ Hz, C_5Me_5), 49.0 (s, $(CH_3)_3C$), 29.3 (s, $(CH_3)_3C$), 14.2 (d, $J(C,P) = 36.4$ Hz, PMe_3), 8.5 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -34.5$ ppm (s); IR (KBr): $\tilde{\nu} = 3414$, 3368 cm^{-1} (N–H), 1629 cm^{-1} (C=O). Despite several attempts, satisfactory elemental analysis or HR-MS for this compound could not be obtained.

$[Ir(Cp^*)(PMe_3)(Ph)(NHC(O)(NHi\mathrm{Pr}))]$ (13). A solution of iPrNCO (13 mg, 0.15 mmol) in THF (1 mL) was added to a stirred solution of **2** (73 mg, 0.15 mmol) in THF (1 mL). The amber mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the light brown residue was recrystallized from pentane at −30 °C for 24 h to yield **13** as a tan powdery solid (58 mg, 66 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.24$ (d, $J = 7.2$ Hz, 2H; o-C_6H_5), 6.86 (t, $J = 7.6$ Hz, 2H; m-C_6H_5), 6.80 (t, $J = 6.8$ Hz, 1H; p-C_6H_5), 4.58 (d, $J = 8.0$ Hz, 1H; $(CH_3)_2$CH–NH), 3.82–3.62 (m, 1H; $(CH_3)_2CH$), 1.88 (s, 1H; Ir–NH), 1.65 (d, $J(H,P) = 2.0$ Hz, 15H; C_5Me_5), 1.42 (d, $J(H,P) = 10.4$ Hz, 9H; PMe_3), 1.03 (d, $J = 6.8$ Hz, 3H; $(CH_3)_2$CH), 0.99 ppm (d, $J = 6.4$ Hz, 3H; $(CH_3)_2$CH); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): $\delta = 161.7$ (s, NHC(O)(NHiPr)), 137.6 (d, $J(C,P) = 12.1$ Hz, i-C_6H_5), 136.8 (d, $J(C,P) = 3.1$ Hz, o-C_6H_5), 124.9 (s, m-C_6H_5), 119.3 (s, p-C_6H_5), 90.4 (d, $J(C,P) = 4.0$ Hz, C_5Me_5), 40.5 (s, $(CH_3)_2CH$), 21.7 (s, $(CH_3)_2$CH), 21.4 (s, $(CH_3)_2CH$), 12.4 (d, $J(C,P) = 37.4$ Hz, PMe_3), 6.8 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -34.2$ (s); IR (KBr): $\tilde{\nu} = 3357$, 3320 cm^{-1} (mbr, N–H), 1607 cm^{-1} (s, C=O); elemental analysis calcd (%) for $C_{23}H_{38}N_2IrOP$: C 47.44, H 6.53, N 4.81; found: C 47.66, H 6.76, N 4.77.

$[Ir(Cp^*)(PMe_3)(Ph)(NHC(Ni\mathrm{Pr})(NHi\mathrm{Pr}))]$ (14): A solution of diisopropylcarbodiimide (15 mg, 0.11 mmol) in THF (1 mL) was added to a stirred solution of **2** (57 mg, 0.11 mmol) in THF (1 mL). The amber mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the light brown residue was recrystallized from pentane at −30 °C for 24 h to yield **14** as bright yellow crystals (36 mg, 58 %). ^{1}H NMR (400 MHz, $[D_8]$THF): $\delta = 7.30$ (d, $J = 6.8$ Hz, 2H; o-C_6H_5), 6.95 (t, $J = 7.6$ Hz, 2H; m-C_6H_5), 6.85 (t, $J = 7.2$ Hz, 1H; p-C_6H_5), 4.10–4.05 (m, 1H; $(CH_3)_2CH$), 3.21–3.15 (m, 1H; $(CH_3)_2CH$), 2.85 (d, $J = 8.4$ Hz, 1H; $(CH_3)_2CH{-}NH$), 1.64 (d, J(H,P) = 2.0 Hz, 15H; C_5Me_5), 1.46 (d, J(H,P) = 9.2 Hz, 9H; PMe_3), 1.13 (d, J = 6.4 Hz, 3H; $(CH_3)_2CH$), 1.10 (d, J = 6.4 Hz, 3H; $(CH_3)_2CH$), 1.04 (d, J = 6.0 Hz, 3H; $(CH_3)_2CH$), 0.90 ppm (d, J = 6.0 Hz, 3H; $(CH_3)_2CH$); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF): δ = 159.6 (s, NH*C*(N*i*Pr)(NH*i*Pr)), 138.8 (d, J(C,P) = 12.1 Hz, *i*-C_6H_5), 138.2 (d, J(C,P) = 3.0 Hz, *o*-C_6H_5), 127.1 (s, *m*-C_6H_5), 121.8 (s, *p*-C_6H_5), 92.2 (d, J(C,P) = 3.0 Hz, C_5Me_5), 46.1 (s, $(CH_3)_2CH$), 41.8 (s, $(CH_3)_2CH$), 25.9 (s, $(CH_3)_2CH$), 22.9 (s, $(CH_3)_2CH$), 22.8 (s, $(CH_3)_2CH$), 14.5 (d, J(C,P) = 37.4 Hz, PMe_3), 8.6 ppm (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -36.6$ ppm (s); IR (KBr): $\tilde{\nu}$ = 3397 (s, N–H), 1605 cm^{-1} (s, C=N); elemental analysis calcd (%) for $C_{26}H_{45}N_3IrP$: C 50.14, H 7.28, N 6.74; found: C 50.32, H 7.38, N 6.70.

[Ir(η⁴-$C_5Me_4CH_2$)(PMe_3)(Ph)(CO)] (15): A solution of **2** (50 mg, 0.096 mmol) in $[D_8]$THF (0.5 mL) was charged to a Young NMR tube and subjected to 1 atm of carbon monoxide. The color changed from amber to pale yellow. Immediate monitoring of the reaction by NMR analysis indicated the presence of a 1:1 mixture of **2** and **15**. Available NMR data of **15**: ^1H NMR (400 MHz, $[D_8]$THF): δ = 2.67 (d, J(H,P) = 4.8 Hz, 1H; $C{=}CH_2$), 2.57 (d, J(H,P) = 4.8 Hz, 1H; $C{=}CH_2$), 2.43 (d, J(H,P) = 3.2 Hz, 3H; $C_5Me_4CH_2$), 1.65 (d, J(H,P) = 5.2 Hz, 3H; $C_5Me_4CH_2$), 1.62 (s, 3H; $C_5Me_4CH_2$), 1.42 (d, J(H,P) = 10.0 Hz, 9H; PMe_3), 1.29 ppm (s, 3H; $C_5Me_4CH_2$); the resonances of the protons of the phenyl group could not be assigned because they overlapped those of **2**; $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -53.8$ ppm (s). Attempts at acquiring $^{13}C\{^1H\}$ NMR data of **15** were hampered by the instability of the complex in solution and its decomposition to several unidentified products during the course of the experiments. Attempts at isolation of **15** in the solid state at early stages of the reaction always led to extensive decomposition of the product.

[Ir(η⁴-$C_5Me_4CH_2$)(PMe_3)(Ph)(CNC_6H_3-2,6-$(CH_3)_2$)] (16). A solution of 2,6-dimethylphenyl isocyanide (39 mg, 0.079 mmol) in THF (1 mL) was added to a stirred solution of **2** (10 mg, 0.079 mmol) in THF (1 mL). The solution immediately turned bright yellow. The mixture was stirred at 25 °C for 30 min. The volatile materials were then removed in vacuo and the yellow residue was recrystallized from pentane at −30 °C for 12 h to yield **16** as bright yellow crystals (17 mg, 34%). ^1H NMR (500 MHz, $[D_8]$THF): δ = 7.35 (d, J = 7.0 Hz, 2H; *o*-C_6H_5), 7.10 (m, 3H; $C_6H_3(CH_3)_2$), 6.75–6.70 (m, 3H; *m*-C_6H_5 + *p*-C_6H_5), 2.54 (d, J(H,P) = 5.0 Hz, 1H; $C{=}CH_2$), 2.47 (d, J(H,P) = 5.0 Hz, 1H; $C{=}CH_2$), 2.39 (d, J(H,P) = 3.5 Hz, 3H; $C_5Me_4CH_2$), 2.38 (s, 6H; $C_6H_3(CH_3)_2$), 1.59 (d, J(H,P) = 5.5 Hz, 3H; $C_5Me_4CH_2$), 1.57 (s, 3H; $C_5Me_4CH_2$), 1.44 (d, J(H,P) = 9.5 Hz, 9H; PMe_3), 1.22 ppm (s, 3H; $C_5Me_4CH_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $[D_8]$THF): δ = 158.8 ($C{=}CH_2$), 141.7 (*i*-C_6H_5), 141.6 (*o*-C_6H_5), 133.6 (*o*-$C_6H_3(CH_3)_2$), 129.9 (*i*-$C_6H_3(CH_3)_2$), 127.6 (*m*-$C_6H_3(CH_3)_2$), 126.3 (*m*-C_6H_5), 126.1 (*p*-$C_6H_3(CH_3)_2$), 120.9 (*p*-C_6H_5), 99.4 ($C_5Me_4CH_2$), 90.2 ($C_5Me_4CH_2$), 65.5 ($C{=}CH_2$), 59.0 ($C_5Me_4CH_2$), 57.0 ($C_5Me_4CH_2$), 18.4 (s, $C_6H_3(CH_3)_2$), 11.2 (d, J(C,P) = 37.4 Hz, PMe_3), 10.7 ($C_5Me_4CH_2$), 9.9 ($C_5Me_4CH_2$), 8.9 ($C_5Me_4CH_2$), 8.5 ppm ($C_5Me_4CH_2$); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF): $\delta = -52.9$ ppm (s); IR (Nujol): $\tilde{\nu}$ = 2126 (s, CN), 2044 cm^{-1} (s); elemental analysis calcd (%) for $C_{28}H_{37}NIrP$: C 55.06, H 6.06, N 2.29; found: C 55.15, H 6.18, N 2.41.

X-ray structure determinations of 2, 6, 8, 14, and 16:

General procedure: Crystal data and details of structure refinement of compounds **2**, **6**, **8**, **14**, and **16** are given in Table 1. Crystals were mounted on a glass fiber using Paratone N hydrocarbon oil and were cooled by a nitrogen-flow low-temperature apparatus. All measurements were made on a Siemens SMART (Siemens Industrial Automation, Inc.) diffractometer with a CCD area detector using graphite monochromated $Mo_{K\alpha}$ radiation and an exposure time of 10 s per frame. The raw data were integrated by the program SAINT (SAX Area-Detector Integration Program) and were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible adsorption using XPREP.[31] Empirical adsorption corrections were based on comparison of redundant and equivalent reflections as applied using XPREP or SADABS.[32] The structures were solved by direct methods and expanded using Fourier techniques. Except as noted, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed contributions but not refined. The function minimized in the full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections.

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Table 1. Crystal data and details of structure refinement of **2**, **6**, **8**, **14**, and **16**.[a]

	2	**6**	**8**	**14**	**16**
formula	$C_{19}H_{31}NIrP$	$C_{30}H_{32}NF_3IrO_3PS$	$C_{25}H_{37}NIrOP$	$C_{26}H_{45}N_3IrP$	$C_{28}H_{35}NIrP$
M_w	496.65	646.73	590.77	622.86	608.78
color	yellow	yellow	pale yellow	yellow	yellow
crystal size [mm^3]	0.05 × 0.10 × 0.18	0.12 × 0.08 × 0.05	0.13 × 0.11 × 0.03	0.24 × 0.18 × 0.08	0.17 × 0.10 × 0.06
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$(#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
a [Å]	9.1240(7)	8.6094(7)	8.763(2)	9.0192(5)	8.5312(7)
b [Å]	11.2738(9)	10.2174(8)	12.962(4)	22.445(1)	9.5754(7)
c [Å]	18.773(1)	14.028(1)	22.282(6)	13.6340(8)	16.566(1)
α [°]		88.814(1)	83.827(4)		87.588(1)
β [°]	92.110(1)	77.254(1)	79.056(4)	97.312(1)	78.611(1)
γ [°]		86.691(1)	83.349(5)		76.502(1)
V [Å^3]	1929.7(3)	1201.5(2)	2458(1)	2737.6(3)	1290.0(2)
Z	4	2	4	4	2
ρ_{calcd} [$g\,cm^{-3}$]	1.709	1.787	1.596	1.511	1.567
μ [cm^{-1}]	70.19	57.69	55.26	49.66	55.66
$F(000)$	976	636	1176	1256	604
$2\theta_{max}$ [°]	49.4	49.4	47	49.4	49.5
unique data	3383	3751	3008	4744	4303
obsd. data	2354	2900	3109	3336	3467
parameters	211	271	253	280	280
R[b]	0.033	0.041	0.08	0.032	0.039
Rw[c]	0.037	0.047	0.076	0.036	0.045
residual ρ [e Å^{-3}]	+0.90/−1.90	+1.32/−2.32	+3.46/−4.02	+1.91/−2.50	+1.57/−2.63

[a] CCDC 230915 (**2**), CCDC 230916 (**6**), CCDC 230917 (**8**), CCDC 230918 (**14**), and CCDC 230919 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $Rw = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$.

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