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Communications

Synthesis and Reactivity of Iridium(III) Dihydrido Aminocarbenes

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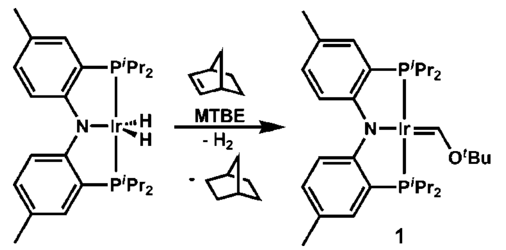
Summary: Iridium complexes supported by the PNP amidophosphine scaffold (PNP = $[N(2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]^-$) perform the selective double C−H activation of methyl amines to produce iridium(III) dihydrido aminocarbenes. The reactivity of these complexes is presented and contrasted with that observed for the previously reported iridium(I) alkoxycarbenes.

The study of metal−carbon multiple bonds has occupied a central role in the field of organometallic chemistry since seminal reports of the first Fischer- and Schrock-type carbenes.[1] A number of transformations of these moieties have been developed, and many have been implemented in catalytic processes.[2] However, the fact that most synthetically useful transition-metal carbenes are generated from high-energy precursors such as diazoalkanes, ylides, and alkyllithium reagents serves as a fundamental limitation on the types of catalytic reactions that can be developed. Nevertheless, several important reports have indicated that later transition metals can mediate the double C−H activation of ethers and amines to generate heteroatom-substituted carbene complexes.[3] Such a process would be highly desirable in the context of a potential catalytic cycle, since it directly affords an M=C_{sp^2} fragment for further elaboration but circumvents the use of high-energy carbene precursors.

Scheme 1. Dehydrogenation of *tert*-Butyl Methyl Ether at (PNP)Ir



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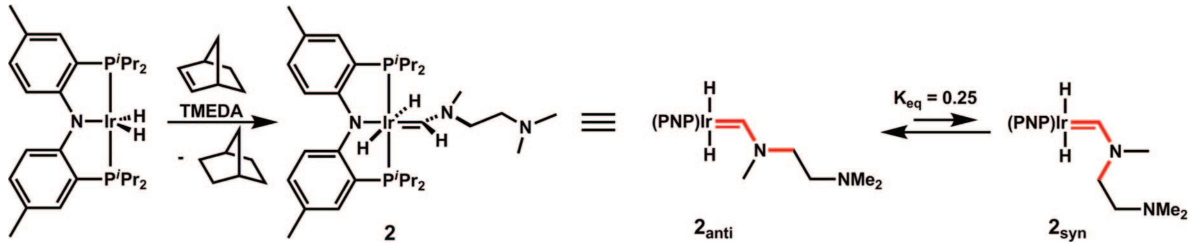
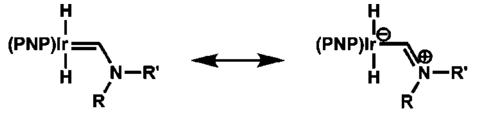
Scheme 2. Dehydrogenation of TMEDA at (PNP)Ir



Recently, we have reported that iridium complexes supported by Ozerov's PNP ligand (PNP = $[N(2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]^-$)[4] mediate the double C−H activation of *tert*-butyl methyl ether (MTBE) to afford an unusual square-planar Ir(I) alkoxycarbene (**1**) upon loss of H_2 (Scheme 1).[3f] The geometry of the low-valent complex confers nucleophilic character to the metal center, allowing access to unprecedented heterocumulene metatheses across the M═C bond.[5,6] Thus, we were interested to learn whether the multiple C−H activation processes could be generalized to substrates containing heteroatoms other than oxygen. In this contribution, we report that the (PNP)Ir framework performs the double C−H activation of methyl amines without loss of H_2, producing octahedral Ir(III) dihydrido aminocarbenes, and the structure and reactivity of these complexes are contrasted with those of the related Ir(I) alkoxycarbenes.

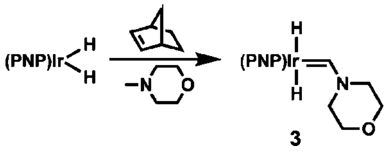
Dehydrogenation of (PNP)IrH_2[4b] with norbornene (NBE, 1 equiv) in *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) affords a mixture of two iridium(III) dihydrido aminocarbene atropisomers (**2**$_{\mathbf{syn}}$ and **2**$_{\mathbf{anti}}$, Scheme 2). Although the isomers are initially formed in equal quantities, equilibration over a period of 16 h affords a 4:1 mixture of **2**$_{\mathbf{anti}}$ and **2**$_{\mathbf{syn}}$, indicating that there is not a kinetic preference for formation of either atropisomer but the **2**$_{\mathbf{anti}}$ conformation is slightly more favorable thermodynamically. This dehydrogenative reactivity is in contrast with the dehydrogenation of methyl ethers by the same system, where H_2 is lost to give square-planar iridium(I) carbene species. The aminocarbene **2**$_{\mathbf{anti}}$, which can be isolated cleanly by crystallization,[7] exhibits a distinctive ^{1}H NMR chemical shift for the carbene proton (δ 12.4 ppm) as well as a broad hydride signal at −9.3 ppm. Decoalescence of the hydride resonance into two distinct multiplets at −8.4 and −9.8 ppm occurs at −5 °C due to slow rotation about the Ir−C bond, and activation parameters for Ir−C bond rotation were determined by variable-temperature ^{1}H NMR spectroscopy ($\Delta G^\ddagger = 4.2$ kcal mol^{-1}).[8] The isomeric complex **2**$_{\mathbf{syn}}$ exhibits similar properties.

The aminocarbene **2**$_{\mathbf{anti}}$ has been characterized by single-crystal X-ray diffraction (XRD) analysis (Figure 1). Interestingly, the plane of the carbene ligand is perpendicular to the plane defined by the C−N−C bonds of the amidophosphine ligand, preventing the synergistic push−pull effect between the π-donor arylamido and π-acceptor carbene observed for **1**.[5] The less electron-rich metal center is partially responsible for the elongated Ir−C bond (1.97 Å compared to 1.88 Å for **1**),[3f] as is increased π-donation from nitrogen compared to oxygen. A significant π component in the C27−N2 bond is supported by the X-ray crystal structure, which depicts a trigonal-planar nitrogen and a short C27−N2 bond (1.32 Å). As a result of significant N→C π-donation, rotation about the C27−N2 bond is sluggish at room temperature, resulting in the slow (24 h) reappearance of the **2**$_{\mathbf{syn}}$ atropisomer upon dissolution of crystalline **2**$_{\mathbf{anti}}$ in benzene. The combination of crystallographic and spectroscopic evidence, therefore, indicates that complex **2** is best described by two major resonance structures (eq 1), affording effective Ir−C and C−N bond orders that are between 1 and 2. Similar behavior has been previously noted for aminocarbenes, particularly those of the late transition metals.[9]



(1)

A related dihydrido aminocarbene (**3**) may be prepared from *N*-methylmorpholine (eq 2).[7] The properties of this complex generally mirror those observed for **2**, though syn and anti isomers are not obtained, due to the symmetrical nature of the amine.[10] The activation parameters for Ir−C bond rotation were determined by NMR spectroscopy ($\Delta G^\ddagger = 3.6$ kcal mol^{-1}), indicating that the "tied-back" nature of the nitrogen substituent slightly lowers the barrier to rotation. The dihydrido aminocarbene was the only complex observed to form, indicating a preference for N−CH_3 activation over O−CH_2 activation.



(2)

We have previously reported detailed studies on the reactivity of carbene **1**, and these generally support reactivity that is dominated by a nucleophilic, low-valent iridium(I) center.[5,6] The octahedral iridium(III) complexes obtained by dehydrogenation of methyl amines would not be expected to interact with electrophiles due to the lower electron density at iridium and the lack of a vacant coordination site. As predicted, **2** did not react with carbon dioxide, even under forcing thermal conditions. However, thermolysis of **2** in the presence of trimethylphosphine (20 equiv) resulted in a phosphine-induced 1,2-hydride migration to the carbene, affording complex **4** (Scheme 3). The phosphine adduct **4** was characterized by XRD analysis, revealing elongated Ir1−C27 (2.12 Å compared to 1.97 Å for aminocarbene **2**) and C27−N2 (1.48 Å compared to 1.32 Å for **2**) bonds, as well as a pyramidalized N2 atom, consistent with a loss of π-interaction between C27 and N2 (Figure 2). An analogous carbonyl complex (**5**) was obtained by thermolysis of **2** in the presence of CO (1 atm) (Scheme 3). This behavior is not surprising in light of Crabtree's observation that a similar octahedral iridium(III) aminocarbene can undergo reversible α-hydrogen elimination mediated by the presence or absence of an additional acetone ligand.[3e] Given the coordinatively saturated nature of the starting material and the isomerization of **2** that has been observed upon thermolysis (vide infra), we

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(4) (a) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326. (b) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792.

(5) Whited, M. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 5874.

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(7) Although the formation of complexes **2** and **3** was quantitative, as judged by ^{31}P and ^{1}H NMR spectroscopy, the difficulty in crystallizing pure **2**$_{\mathbf{anti}}$ and **3** to remove norbornane and residual amine resulted in low isolated yields (35% and 13%, respectively).

(8) Gasparro, F. P.; Kolodny, N. H. *J. Chem. Educ.* **1977**, *54*, 258.

tentatively propose that hydride migration precedes phosphine or carbonyl ligand association.

Alkoxycarbene **1**, which contains no hydride coligands, is clearly incapable of exhibiting the same reactivity patterns. Thus, we examined the reaction of **1** with strong L-type ligands with the hope of elucidating potentially divergent pathways. Exposure of **1** to an excess (>20 equiv) of PMe_3 resulted in no reaction at ambient temperature, and only decarbonylative decomposition was observed upon prolonged thermolysis.[3f] However, reaction of **1** with CO (1 atm) at ambient temperature resulted in an immediate color change from purple to gold, affording a product of ligand migration quite different from **4** or **5** (eq 3). Spectroscopic evidence (NMR and IR) indicated the presence of two bound carbonyl ligands (ν_{sym} 1981 cm^{-1}, ν_{asym} 1924 cm^{-1}), and XRD analysis confirmed the migratory insertion of the carbene into the Ir−N bond, affording a five-coordinate, trigonal-bipyramidal iridium(I) dicarbonyl (**6**, Figure 3).

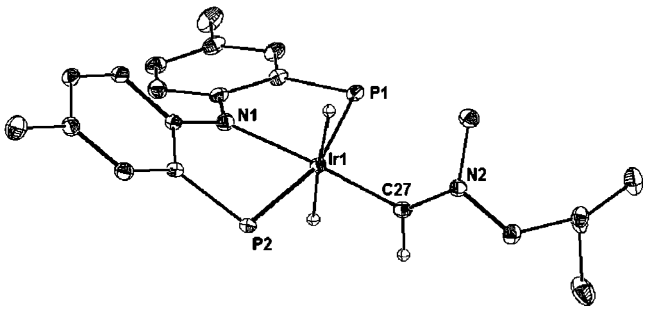


Figure 1. Displacement ellipsoid (35% probability level) representation of aminocarbene $\mathbf{2}_{anti}$ with ^{i}Pr phosphine substituents omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C27 = 1.970(2), Ir1−N1 = 2.138(2), Ir1−P1 = 2.2947(5), Ir1−P2 = 2.2903(5); N1−Ir1−C27 = 177.20(7), P1−Ir1−P2 = 160.20(2), Ir1−C27−N2 = 133.3(2).

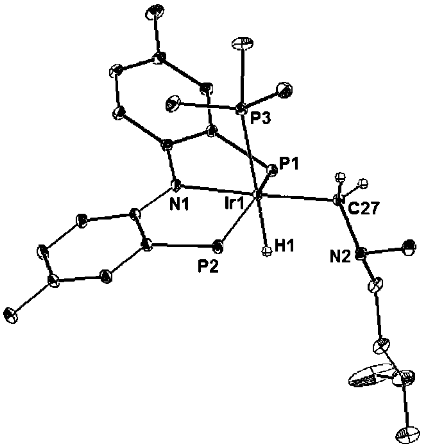
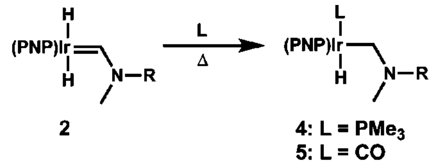


Figure 2. Displacement ellipsoid (35% probability level) representation of complex **4** with ^{i}Pr phosphine substituents omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C27 = 2.125(1), Ir1−N1 = 2.156(1), Ir1−P1 = 2.2969(3), Ir1−P2 = 2.2867(4), Ir1−P3 = 2.3813(4), Ir1−H1 = 1.578(9), C27−N2 = 1.479(2); N1−Ir1−C27 = 177.27(5), P1−Ir1−P2 = 151.67(1), P3−Ir1−H1 = 177.9(9), Ir1−C27−N2 = 119.01(9).

Scheme 3. Reaction of Aminocarbene 2 with PMe_3 and CO ($R = (CH_2)_2NMe_2$)



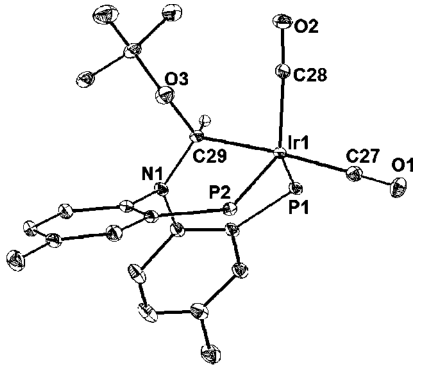
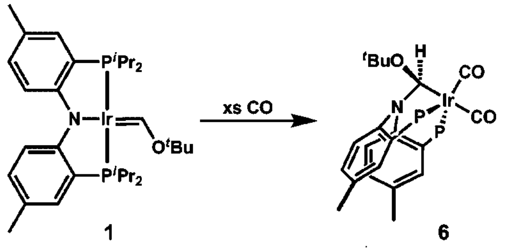


Figure 3. Displacement ellipsoid representation of complex **6** with ^{i}Pr phosphine substituents omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C29 = 2.142(4), Ir1−C27 = 1.907(4), Ir1−C28 = 1.903(4), Ir1−P1 = 2.320(1), Ir1−P2 = 2.327(1); C29−Ir1−C27 = 175.2(2), P1−Ir1−P2 = 119.82(3), C29−Ir1−C28 = 86.4(2), P1−Ir1−C28 = 120.9(1).



(3)

(^{i}Pr omitted for clarity)

Perhaps most interesting is that thermolysis of this complex results in the formation of (PNP)Ir−CO,[5] presumably by loss of *tert*-butoxyketene, though organic products have not been definitively identified. Although insertion reactions of metal-bound carbenes are relatively common,[11] this reaction represents, to the best of our knowledge, the first example of such an insertion into a metal−amide bond.[12] Moreover, reversible migratory insertions of carbenes such as this are quite rare,[13,14] and we believe the "masked carbene" observed for complex **6** may presage a new strategy for the formation of C=C bonds via migratory deinsertion from a heteroatom-substituted metal alkyl.

In light of the previously reported decarbonylative degradation of alkoxycarbene **1**,[3f] we were interested in the thermal reactivity of iridium(III) aminocarbenes. Thermolysis of **2** results in the partial isomerization from the *trans*-dihydrido aminocarbene to the *cis*-dihydrido aminocarbene (*cis*-**2**, eq 4), and both *cis*-$\mathbf{2}_{syn}$ and *cis*-$\mathbf{2}_{anti}$ isomers are observed to form. Since prolonged thermolysis of *cis*-**2** does not result in loss of H_2, even in the presence of norbornene, it is clear that the retention of hydride ligands in **2** is not simply a kinetic preference. Instead, we find it most probable that the increased N→C π-donation associated with the aminocarbenes confers increased basicity to the iridium center, making it reluctant to reductively eliminate H_2. This picture is consistent with the resonance structure depicted

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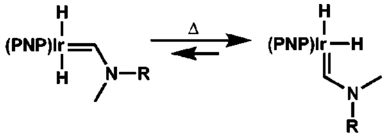
(9) (a) Busetto, L.; Palazzi, A.; Crociani, B.; Belluco, U.; Badley, E. M.; Kilby, B. J. L.; Richards, R. L. *J. Chem. Soc. Dalton Trans.* **1972**, 1800. (b) Albéniz, A. C.; Espinet, P.; Manrique, R.; Pérez-Mateo, A. *Chem. Eur. J.* **2005**, *11*, 1565. (c) Meana, I.; Albéniz, A. C.; Espinet, P. *Organometallics* **2008**, *27*, 4193.

(10) Slow N−C bond rotation in complex **3** was confirmed by the presence of four distinct ^{1}H NMR chemical shifts for the methylene protons on the morpholine ring.

for these aminocarbenes (eq 1), where a partial negative charge is imparted to iridium by virtue of strong N→C π-donation.



(4)

2 ***cis*-2**

In summary, we have reported the synthesis of iridium-supported dihydrido aminocarbenes by a double C−H activation protocol as well as preliminary reactivity studies on the resulting complexes. This dehydrogenative reactivity is fundamentally different from what has been previously observed at pincer-supported iridium. Goldman and colleagues have reported that a (PCP)Ir complex is competent to generate enamines by the catalytic transfer dehydrogenation of tertiary amines.[15] However, the (PCP)Ir system does not target methyl substituents and in all cases either α,β-dehydrogenation or no reaction was observed. Thus, it is clear that the PNP ligand examined in this report confers a selectivity pattern that is distinct from the related PCP pincer ligands. This unusual reactivity suggests that a wealth of double C−H activation chemistry may be accessed at low-valent iridium centers by judicious ligand design and substrate selection, affording new routes to $M{=}C_{sp^2}$ species for further elaboration and catalytic functionalization.

Acknowledgment. We gratefully acknowledge the Moore Foundation (fellowship to M.T.W.) and BP (MC^2 program) for financial support. Larry Henling provided crystallographic assistance.

Supporting Information Available: Text giving detailed experimental procedures and characterization data and CIF files giving crystallographic details for compounds $\mathbf{2}_{\mathbf{anti}}$, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.

(14) The related reversible insertion of CO into M−X bonds has been reported: (a) Saruyama, T.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 546. (b) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959. (c) Reference 12a.

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