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Rhodium and Iridium Amido Complexes Supported by Silyl Pincer Ligation: Ammonia N−H Bond Activation by a [PSiP]Ir Complex

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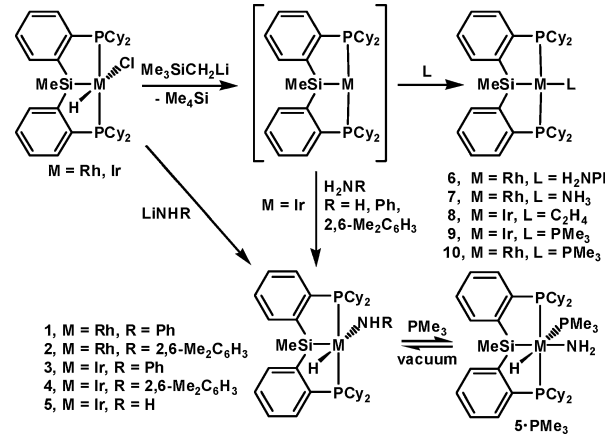
Due to the prevalence of nitrogen-containing functional groups in pharmaceuticals and other fine chemicals, significant interest exists in the development of new pathways for the functionalization of amines and, most notably, ammonia.[1] Indeed, transformations such as ammonia-arene dehydrogenative coupling and the hydroamination of olefins with ammonia have been noted among the ten greatest current challenges for catalysis.[2] Given that E−H (E = H, B, C, Si) bond oxidative addition to late metal centers underpins a number of prominent catalytic transformations,[3] the identification of late metal fragments that can insert into the N−H bonds of ammonia under mild conditions is likely to figure importantly in the emergence of new catalytic processes that utilize ammonia as a substrate. However, well-documented examples of ammonia N−H bond oxidative addition are rare.[4−6] In particular, examples of N−H activation of ammonia to form an isolable, terminal, late metal $L_nM(H)(NH_2)$ complex are limited to a single report by Zhao, Goldman, and Hartwig involving a (PCP)Ir pincer system.[4a] In the context of the reactivity challenges cited above, the identification of alternative late metal complexes capable of ammonia N−H bond activation, yet possessing divergent reactivity profiles in the ensuing $L_nM(H)(NH_2)$ species especially in the presence of alkenes or arenes, represents an important goal in the field of ammonia functionalization.

In this contribution we report that Ir complexes supported by silyl pincer ligation undergo N−H bond oxidative addition of both ammonia and anilines[7] to form isolable complexes of the type [Cy-PSiP]Ir(H)(NHR) (R = H, aryl; [Cy-PSiP] = [κ^3-(2-$Cy_2PC_6H_4)_2SiMe]^-$). Under similar reaction conditions related Rh species form simple adducts of the type [Cy-PSiP]Rh(NH_2R). Our reactivity studies reveal that, in comparison to previously reported (PCP)Ir systems, [Cy-PSiP]Ir(H)(NHR) species are significantly more resistant to N−H bond reductive elimination, even in the presence of alkene and arene substrates.

We have previously reported that complexes of the type [Cy-PSiP]Ir(H)(alkyl) rapidly eliminate alkane and in the presence of arenes undergo sp^2-C−H bond activation to generate [Cy-PSiP]Ir(H)(aryl).[8] Given that C−H and N−H bonds feature similar homolytic bond strengths, we viewed [Cy-PSiP]ML_n (M = Rh, Ir) species as attractive candidates for the study of N−H bond cleavage reactions. As complexes of the type [Cy-PSiP]M(H)(NHR) (R = H, aryl) were unknown prior to this work, we first sought to establish the viability of putative N−H bond activation products by rationally preparing and characterizing such compounds.

The synthesis of the anilido hydride complexes [Cy-PSiP]M(H)(NHR) (M = Rh: R = Ph, **1**; R = 2,6-$Me_2C_6H_3$, **2**; M = Ir: R = Ph, **3**; R = 2,6-$Me_2C_6H_3$, **4**) was readily achieved by the reaction of [Cy-PSiP]M(H)Cl with 1 equiv of the corresponding lithium anilide Li(NHR) (Scheme 1). These reactions occur upon mixing to generate isolable anilido hydride complexes (80−89%). In each case, the solution ^{1}H, ^{13}C, and ^{31}P NMR spectra indicate the formation of a C_s-symmetric species and, along with ^{29}Si and ^{15}N NMR data, support the structural formulation depicted in Scheme 1. For **1**, **3**, and **4** the connectivity was confirmed by use of single crystal X-ray diffraction techniques (Figure 1 for **1** and **4**). The geometry at the metal center in each complex can be described as distorted square-based pyramidal, with Si occupying the apical coordination site.[9] These structures differ from that of the related complex [C_6H_3-2,6-($CH_2P^tBu_2)_2$]Ir(H)(NHPh),[7b] which features square pyramidal coordination geometry with the hydride occupying the apical position and, thus, oriented *cis* to the anilide ligand. The Ir−N distances in **3** (2.056(2) Å) and **4** (2.077(3) Å) are comparable to that of [C_6H_3-2,6-($CH_2P^tBu_2)_2$]Ir(H)(NHPh) (Ir−N = 2.082(2) Å),[7b] while the Rh−N distance of 2.123(5) Å in **1** is slightly longer.

Scheme 1. Synthesis and Reactivity of [Cy-PSiP]M(H)(NHR) and [Cy-PSiP]ML Complexes (M = Rh and Ir)



In an attempt to prepare parent amido complexes of the type [Cy-PSiP]M(H)(NH_2), [Cy-PSiP]Ir(H)Cl was treated with 5 equiv

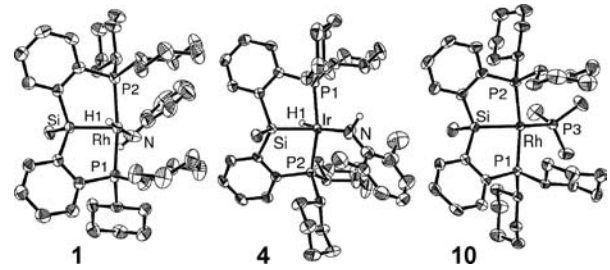


Figure 1. Crystallographically determined structures of **1**, **4**, and **10** shown with 50% ellipsoids. Selected interatomic distances (Å) and angles (deg) for: **1**, Rh−Si 2.243(1), Rh−N 2.123(5), Si−Rh−N 118.3(2); **4**, Ir−Si 2.2791(8), Ir−N 2.077(3), Si−Ir−N 129.7(1); **10**, Rh−Si 2.2872(5), Rh−P3 2.3597(5), Si−Rh−P3 147.61(2).

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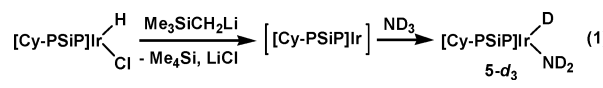
of $LiNH_2$, which led to clean formation of [Cy-PSiP]Ir(H)(NH_2) (**5**) upon heating (65 °C, 12 h). Complex **5** was isolated in 92% yield as a yellow benzene-soluble solid. Isolated **5** features NMR characteristics that are similar to those of **3** and **4**. The ^{31}P and ^{29}Si NMR spectra of **5** each contain a single resonance at 55.5 and 14.6 ppm, respectively. The ^1H NMR spectrum of **5** (benzene-d_6) features a hydride resonance at −20.13 ppm (t, $^2J_{HP}$ = 15 Hz) as well as a slightly broad triplet at 5.03 ppm ($^3J_{HP}$ = 6 Hz) corresponding to the NH_2 protons; the latter correlates to a ^{15}N NMR resonance at −309.8 ppm (referenced to $MeNO_2$) in a $^1H-^{15}N$ HMQC experiment. Attempts to prepare a Rh variant of **5** by a similar route led to complex reaction mixtures from which no pure materials could be isolated.

Having shown that complexes of the type [Cy-PSiP]M(H)(NHR) are synthetically accessible and readily isolable, we sought to demonstrate that such compounds could be prepared via N−H bond activation starting from in situ generated [Cy-PSiP]M(H)(alkyl) and H_2NR (Scheme 1). Treatment of [Cy-PSiP]Ir(H)Cl with 1 equiv of Me_3SiCH_2Li in cyclohexane-d_{12} led to an immediate reaction in which [Cy-PSiP]Ir(H)Cl was consumed and Me_4Si was generated (^1H and ^{31}P NMR).[10] The reaction mixture was subsequently treated with 1 equiv of H_2NPh, and upon heating (65 °C, 16 h), ^1H and ^{31}P NMR analysis indicated the quantitative formation of **3**. In a preparative-scale reaction **3** was obtained in 96% isolated yield by this N−H bond activation pathway. For the sterically hindered $H_2N(2,6\text{-}Me_2C_6H_3)$, quantitative conversion (^1H and ^{31}P NMR) to **4** was attained under similar reaction conditions (65 °C, 72 h) utilizing 20 equiv of $H_2N(2,6\text{-}Me_2C_6H_3)$. Under analogous conditions in benzene solution, C−H bond activation of the solvent is competitive with aniline N−H bond activation. Thus, treatment of [Cy-PSiP]Ir(H)Cl with Me_3SiCH_2Li in benzene-d_6 solution led to the formation of [Cy-PSiP]Ir(D)(Ph-d_5) and Me_4Si (^1H and ^{31}P NMR).[8] Subsequent reaction with 1 equiv of H_2NPh led to 35% conversion (^1H and ^{31}P NMR) to **3** following heating for 72 h at 65 °C; after 168 h at 65 °C complete conversion to **3** was not observed. However, quantitative conversion to **3** was obtained when 20 equiv of H_2NPh were reacted with [Cy-PSiP]Ir(D)(Ph-d_5) in benzene-d_6 solution (65 °C, 70 h).

Remarkably, the Ir parent amido complex **5** was readily prepared via N−H bond activation of ammonia. Treatment of [Cy-PSiP]Ir(H)Cl with 1 equiv of Me_3SiCH_2Li in cyclohexane-d_{12} resulted in the consumption of [Cy-PSiP]Ir(H)Cl and formation of 1 equiv of Me_4Si (^1H and ^{31}P NMR). The reaction mixture was subsequently degassed, and an excess of anhydrous gaseous ammonia (ca. 1 atm) was introduced. While no reaction was observed at room temperature, heating at 65 °C for 14 h led to 72% conversion to **5** (^1H and ^{31}P NMR). In a preparative scale experiment, **5** was obtained in 69% isolated yield by this ammonia N−H bond activation pathway. Under analogous conditions in benzene-d_6 solution, heating at 65 °C over the course of 144 h led to 45% conversion to **5** (^1H and ^{31}P NMR), in which substantial deuterium incorporation into the Ir−*H* and P*Cy*$_2$ fragments of **5** was observed (^1H and ^2H NMR).[11] Additional heating at this temperature led to the formation of multiple unidentified products and provided no further conversion to **5**. The analogous oxidative addition of ammonia in benzene solution to form (PCP)Ir(H)(NH_2) species has yet to be demonstrated.

Attempts to form amido hydride complexes such as **1** via N−H bond activation led to the generation of Rh^I amine adducts. Treatment of [Cy-PSiP]Rh(H)Cl with 1 equiv of Me_3SiCH_2Li in cyclohexane-d_{12} led to an immediate reaction in which [Cy-PSiP]Rh(H)Cl was consumed and Me_4Si was generated (^1H and ^{31}P NMR).[12] Subsequent addition of either 20 equiv of H_2NPh or an atmosphere of anhydrous ammonia led to the quantitative generation of new Rh complexes that are tentatively assigned as adducts of the type [Cy-PSiP]Rh(NH_2R) (R = Ph, **6**; R = H, **7**; ^1H, ^{31}P, ^{29}Si NMR). For **6**, heating of the reaction mixture (65 °C, 72 h) led to 25% conversion to **1** (^1H and ^{31}P NMR); additional heating generated multiple unidentified products and afforded no further conversion to **1**. No reaction was observed upon heating of **7** (65 °C, 48 h) under an atmosphere of ammonia. Complexes **6** and **7** were stable in solution in the presence of an excess of aniline or ammonia; however the coordinated amine was readily displaced upon exposure to vacuum, precluding the isolation of these compounds.

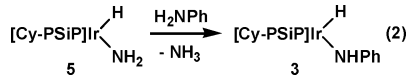
In a preliminary investigation into the mechanism of Ir-mediated ammonia activation, we studied the reactivity of in situ generated [Cy-PSiP]Ir(H)(alkyl) (which undergoes rapid loss of alkane, *vide supra*) with an atmosphere of ammonia-d_3. In cyclohexane-d_{12}, the formation of **5-d_3** was observed (^1H and ^{31}P NMR) after heating (65 °C, 20 h; eq 1). ^2H NMR analysis of the reaction mixture (in C_6H_6) indicated deuterium incorporation solely at the hydride and amide positions, with no evidence for deuteration of the ligand P*Cy*$_2$ groups. This observation is in accord with the possible intermediacy of a [Cy-PSiP]Ir^I 14 e^- species,[13] or a reactive equivalent (e.g., an agostic species), en route to N−H bond oxidative addition and is in keeping with our previous studies of room temperature sp^2-C−H bond activation by [Cy-PSiP]Ir, where reaction with benzene-d_6 cleanly afforded [Cy-PSiP]Ir(D)(Ph-d_5).[8]



(1)

We also undertook trapping experiments to gain further support for the intermediacy of [Cy-PSiP]M^I species in the observed E−H (E = C, N) bond activation chemistry. For M = Rh, [Cy-PSiP]Rh(NH_2R) complexes (**6**, **7**) were directly observed when [Cy-PSiP]Rh was generated in the presence of excess NH_2R. However, these complexes were not isolable (*vide supra*), and for M = Ir intermediates of this type could not be unequivocally identified en route to **3** and **5**. Trapping experiments conducted with donor ligands such as PMe_3 and ethylene did, however, lead to the formation of isolable [Cy-PSiP]ML complexes (M = Ir: L = C_2H_4, **8**; L = PMe_3, **9**; M = Rh: L = PMe_3, **10**), confirming for the first time the viability of isolable Rh^I and Ir^I species supported by [Cy-PSiP] ligation (Scheme 1). Surprisingly, the geometry at Rh in the crystal structure of **10** (Figure 1) is significantly distorted from square planarity, as indicated by the P3−Rh−Si bond angle of 147.61(2)°.

The reaction of **5** with an atmosphere of ammonia-d_3 was carried out to assess if **5** undergoes exchange with free ammonia. Upon standing for 14 h in cyclohexane-d_{12} (25 °C), evidence for ^2H incorporation was observed only at the IrNH_2 position (^1H and ^2H NMR). The observed ^2H incorporation in **5** suggests that this transformation does not proceed via simple reductive elimination of NH_3 followed by oxidative addition of ND_3; mechanistic examinations of this transformation are ongoing. Treatment of **5** with 1 equiv of H_2NPh at room temperature in cyclohexane-d_{12} solution resulted in an immediate and quantitative reaction to form **3** as well as free ammonia (^1H and ^{31}P NMR; eq 2). In light of the greater acidity of aniline relative to ammonia, the latter result is not surprising.[14] However, this result stands in contrast to the observation that [CH($CH_2CH_2P^tBu_2$)$_2$]Ir(H)(NH{3,5-$Me_2C_6H_3$}) reacts with ammonia to generate [CH($CH_2CH_2P^tBu_2$)$_2$]Ir(H)(NH_2) and the free aniline.[4a]



The observation that in the [Cy-PSiP]Ir system both aniline and ammonia N−H bond activation products are formed in benzene solution suggests that the thermodynamics of N−H bond activation are more favorable than those of arene C−H bond activation. Interestingly, unlike related (PCP)Ir(H)(NHR′) (R′ = aryl) complexes that at room temperature in arene solvents exhibit an equilibrium between N−H and arene sp^2-C−H bond activation products (the balance of which depends on the Ir fragment and the amine involved),[7b,c] the [Cy-PSiP]M(H)(NHR′) complexes **1**−**4** reported herein are stable at room temperature in benzene or toluene, with no spectroscopic evidence of an equilibrium between N−H and C−H bond activation products. Similarly, no evidence for N−H bond reductive elimination was observed at room temperature or at 65 °C (72 h) when [Cy-PSiP]Ir(H)(NH_2) (**5**) was dissolved in arene solvents; only under forcing conditions (100 °C, 48 h, benzene-d_6) was NH_3 reductive elimination observed to cleanly generate [Cy-PSiP]Ir(D)(Ph-d_5). Notably, only two comparator systems of the type (PCP)Ir(H)(NH_2) exist: [C_6H_3-2,6-($CH_2P^tBu_2$)$_2$]Ir(H)(NH_2)[7b] and [$CH(CH_2CH_2P^tBu_2)_2$]Ir(H)(NH_2).[4a] While the former was generated in situ via dehydrohalogenation of [C_6H_3-2,6-($CH_2P^tBu_2$)$_2$]Ir(H)(Cl)(NH_3) and was observed to undergo N−H reductive elimination above −10 °C in THF solution, the latter isolable complex is stable in alkane and ethereal solvents at room temperature. In benzene-d_6 solution [$CH(CH_2CH_2P^tBu_2)_2$]Ir(H)(NH_2) undergoes deuterium incorporation into the backbone methine position of the pincer ligand, possibly via a mechanism involving N−H reductive elimination.[15] Furthermore, while a mixture of [$CH(CH_2CH_2P^tBu_2)_2$]Ir(H)(NH_2) and [$CH(CH_2CH_2P^tBu_2)_2$]Ir(1-pentene) was formed upon treatment of the latter with excess 1-pentene (Et_2O-d_{10} or benzene-d_6),[4a,15] no reaction was observed at room temperature upon exposure of a benzene-d_6 solution of **5** to an atmosphere of ethylene.[16] As well, whereas treatment of **5** with 1 equiv of PMe_3 led to the quantitative formation of **5**·PMe_3 (^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR), upon exposure to vacuum the loss of PMe_3 to reform **5** was observed in the absence of N−H reductive elimination (Scheme 1).[16] Collectively, these observations confirm that, in addition to supporting reactive Ir species that are able to undergo N−H bond activation reactions, [Cy-PSiP] ligation provides a means of stabilizing amido hydride complexes from N−H reductive elimination in a manner that has not been demonstrated in previously reported (PCP)Ir systems. Such ancillary ligand effects may prove important in the development of novel catalytic chemistry involving amine N−H bond activation.

In conclusion, we have demonstrated that Ir complexes supported by [Cy-PSiP] ligation undergo N−H bond oxidative addition of anilines and ammonia under mild conditions to form isolable [Cy-PSiP]Ir(H)(NHR) complexes. In comparison to previously reported (PCP)Ir systems, [Cy-PSiP]Ir(H)(NHR) species are significantly more resistant to N−H bond reductive elimination, even in the presence of alkene and arene substrates. Such an example of ammonia N−H bond activation is exceedingly rare and may provide inroads to new atom-economical chemical transformations that incorporate N−H bond oxidative addition steps in the functionalization of this abundant feedstock.

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Supporting Information Available: Experimental details and characterization data, including crystallographic data for **1**, **3**·OEt_2, **4**, and **10** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Alternatively, given that these complexes feature acute Si−M−H1 angles (**1**, 67.8°; **4**, 68.8°) that are similar to those previously observed for [Cy-PSiP]M(H)Cl (M = Rh, 65.8°; M = Ir, 68.7°), they can also be described as "Y-shaped".[8]

(10) The Ir product of this reaction, which gives rise to a very broad ^{31}P NMR resonance at 56.2 ppm, has previously been observed and shown to react with arenes to form [Cy-PSiP]Ir(H)(aryl).[8]

(11) Control experiments in which [Cy-PSiP]Ir(D)(Ph-d_5) was heated at 65 °C for 48 h also revealed substantial deuterium incorporation into the PCy_2 fragments.

(12) The Rh-containing product of this reaction, which gives rise to a broad ^{31}P NMR resonance at 62.9 ppm ($^1J_{RhP}$ = 162 Hz), has previously been documented.[8]

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(16) The viability of the ethylene and PMe_3 Ir(I) adducts **8** and **9** that could result from reductive elimination of ammonia was confirmed via independent synthesis.

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