Synthesis and Structural Characterization of Late Transition Metal Parent Amido (L_nM-NH_2) Complexes: An Acid/Conjugate Base Metathesis Approach

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Charge-neutral complexes with M−N bonds have been proposed as intermediates in many catalytic and organic functionalization reactions.[1,2] Because of this, we and others have made attempts to use simple R_2N^- or R_2NH substitution/deprotonation methods to generate such complexes so that the chemistry of the M−N bond can be studied directly.[3,4] Synthetic routes that have been used thus far, mostly for the preparation of N-aryl derivatives, include deprotonation of the corresponding amine complexes,[5] metathesis of metal chlorides with alkali amides,[6] and exchange of hydroxo or alkoxo ligands with amines.[7]

The success of these methods is erratic, and they often meet with failure. Monomeric low-valent parent L_nM-NH_2 complexes are exceptionally rare, and to our knowledge no general methods exist for their preparation.[8] We now wish to report the synthesis and structure of two unusual monomeric d^6 parent late transition metal amido complexes by using amide (NH_2^-) base in the presence of its conjugate acid, NH_3. The methodology is simple and holds promise for being general.

The first example provides a new ruthenium amido hydride. Treatment of the hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$ (**1**)[9] with 3 equiv of $NaNH_2$ in 7:5 THF/NH_3(l) for 1 day at room temperature, followed by filtration, removal of the volatile materials *in vacuo*, and crystallization from toluene or THF, gave large blocky tan crystals of $(DMPE)_2Ru(H)(NH_2)$ (*trans*-**2**) in 74% yield (eq 1). The simplicity of the NMR spectra indicate a trans disposition of the ligands about the metal center.

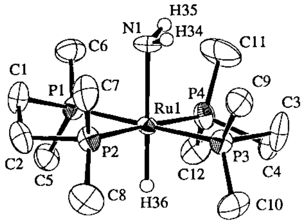
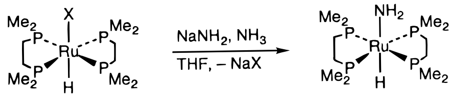


Figure 1. ORTEP diagram of $(DMPE)_2Ru(H)(NH_2)$ (*trans*-**2**).[11]



X = OH (**1**), Cl (**3**)

trans-**2**

(1)

The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ 45.6 ppm. In the ^1H NMR spectrum, the hydride is observed as a quintet at δ −16.57 ppm, and the NH_2 protons appear as a slightly broad peak at δ −3.42 ppm. The ruthenium hydride stretch appears at 1883 cm^{-1} in the IR spectrum, and an N−H stretch is observed at 3504 cm^{-1}. Amide *trans*-**2** may also be synthesized (81%) from the chloride **3**[10] under similar conditions (eq 1). The structural assignment of *trans*-**2** was confirmed by X-ray crystallography (Figure 1).[11] The structure of hydrido amide *trans*-**2** is a unique monomeric example of the formal N−H oxidative addition product of NH_3 to a metal center.[12] The Ru−N bond length (2.191(6) Å) lies between those reported for $(PMe_3)_4Ru(H)(NHPh)$[13] (2.160(6) Å) and $[CpRu(NH_2CMe_3)(PPh_3)(P(OMe)_3)]SO_3CF_3$ (2.216(2) Å).[5]

In a second example, we have prepared a monomeric parent amidoiridium complex. Treatment of $Cp^*(PMe_3)(Ph)Ir(OH)$[14] (**4**) with 2 equiv of $NaNH_2$ in 1:5 NH_3(l)/THF at room temperature for 1 day yields the corresponding amido complex $Cp^*(PMe_3)(Ph)Ir(NH_2)$ (**5**) (Scheme 1). Complex **5** is exceptionally sensitive to concentration: when filtered and placed under vacuum to remove the THF, partial decomposition occurs, even at low temperature, and **5** can be recovered in only 90% purity. However, monitoring the reaction in THF-d_8 by ^1H NMR spectroscopy reveals that clean conversion to the amido complex takes place in solution (95% yield vs internal standard). In the ^1H NMR spectrum the NH_2 protons resonate as a broad singlet at δ −1.32 ppm. The complex displays a singlet at δ −33.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. As with the ruthenium complex *trans*-**2**, amide **5** can also be prepared from the more easily

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(1) For the hydroamination of olefins, see: (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 892. (c) Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703. (d) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857.

(2) For the amination of arenes, aryl halides, and triflates, see: (a) Diversi, P.; Ermini, L.; Ingrosso, G.; Lucherini, A.; Pinzino, C.; Sagamora, L. *J. Organomet. Chem.* **1995**, *494*, C1. (b) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 6066. (c) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (d) Hartwig, J. F. *Synlett* **1997**, 329. (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (f) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1264. (g) Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 1268. (h) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.

(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(4) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1 and references therein.

(5) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.

(6) (a) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 12800. (b) Rahim, M.; Bushweller, C. H.; Ahmed, K. J. *Organometallics* **1994**, *13*, 4952. (c) Driver, S. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708. (d) Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7010. (e) Danopoulos, A. A.; Hay-Motherwell, R. S.; Wilkinson, G.; Cafferkey, S. M.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3177.

(7) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (b) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206. (c) Glueck, D. S.; Winslow, N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.

(8) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971. (c) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1991**, *10*, 615. See also ref 1a. For the recent synthesis of a parent rhenium amide $Re(NH_2)(EtC{\equiv}CEt)_3$ by the stepwise generation of an ammonium cation followed by deprotonation with $NaNH_2$, see: (d) Tahmessabi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342. Use of this method has not been successful in either of the systems presented in this paper. No evidence for the formation of $[(DMPE)_2Ru(H)(NH_3)]^+$ has been noted to date. The cationic iridium salt $[(Cp^*)(PMe_3)(Ph)Ir(NH_3)][OTf]$ has been synthesized, but many attempts to deprotonate it have not led to clean formation of the desired amide.

(9) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.

(10) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 2605.

(11) The NH_2 group is disordered to either side of the P4 plane. N1 represents the major component (80%) and is presented in Figure 1. The hydrogen atoms on N1 were located, but the ruthenium-bound hydride was not; it was therefore placed in the idealized position based on an expected N−Ru−H angle of 180° and a Ru−H distance of 1.6 Å. See Supporting Information for full details.

(12) For a dimeric example, see: Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.

(13) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.

(14) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888.

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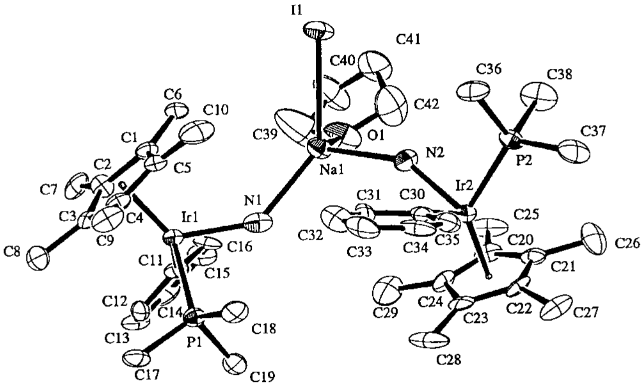
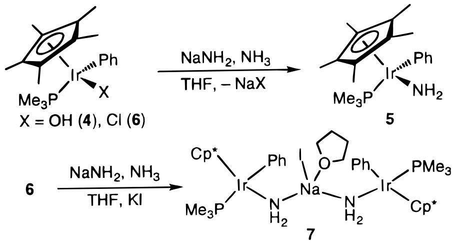


Figure 2. ORTEP diagram of $[Cp^*(PMe_3)(Ph)IrNH_2]_2NaI(THF)$ (**7**).

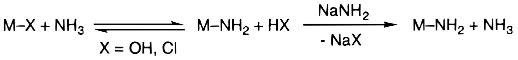
Scheme 1



accessible chloride. In this case $Cp^*(PMe_3)(Ph)Ir(Cl)$[15] (**6**) was treated with $NaNH_2$ (1.4 equiv) in 1:5 NH_3(l)/THF. Monitoring by ^1H NMR spectroscopy again indicates clean formation of the amide complex in 95% yield (vs internal standard); filtration and solvent evaporation provide amide **5** as a tan solid in 90% purity (Scheme 1).

When $Cp^*(PMe_3)(Ph)Ir(NH_2)$ is prepared from the chloride **6** as described above, but with an added 2 equiv of KI,[16] the product in solution is less sensitive to concentration, and colorless crystals of $[Cp^*(PMe_3)(Ph)IrNH_2]_2NaI(THF)$ (**7**) are obtained at −35 °C. The isolated yield is low (7%), but the crystals were suitable for X-ray diffraction and gave satisfactory elemental analysis. X-ray crystallography confirms the presence of an Ir−N bond (Figure 2). Two amidoiridium centers are linked by a sodium ion in the unit cell. This unusual structure shows that an iodide ion and a molecule of tetrahydrofuran are also bound to Na, resulting in a tetrahedral geometry at the sodium center. The complex has Ir−N−Na angles of 139.0(6)° and 148.8(6)°. The Ir−N bond lengths in **7** (2.089(12) and 2.106(11) Å) are between those in *trans*-$Ir(CO)(NHC_6H_4Me)(PPh_3)_2$[17] (2.041(3) Å) and those in the bridging parent amidoiridium complexes reported by Casalnuovo *et al.* (2.10−2.13 Å).[18] The Ir−N bond lengths for **7** are comparable to that found for the Ir−O bond (2.115(5) Å) in the hydroxide analogue $Cp^*(PMe_3)(Ph)Ir(OH)$.[19]

Scheme 2



$$M{-}X + NH_3 \underset{X\,=\,OH,\,Cl}{\rightleftharpoons} M{-}NH_2 + HX \xrightarrow[-\,NaX]{NaNH_2} M{-}NH_2 + NH_3$$

To make sure that both NH_3 and its conjugate base are required for the efficient generation of the pure amide complexes *trans*-**2** and **5**, separate reactions were performed with the individual reagents. In the ruthenium system, simple metathesis reactions (e.g., treatment of hydroxide **1** or chloride **3** with $NaNH_2$ in THF) give no reaction at room temperature. The reaction of hydroxide **1** with NH_3 leads to a 1:1 mixture of **1** and *cis*-$(DMPE)_2Ru(H)(NH_2)$.[20] Similar results were obtained in the iridium system. The amide complex **5** can be detected (^1H NMR spectroscopy) when hydroxide **4** is treated with $NaNH_2$ in the absence of NH_3. However, the reaction is very slow (60% conversion after 19 h), and several impurities accompany the generation of the amide.[21] When **5** is treated with NH_3 (20 equiv) in THF-d_8, an equilibrium mixture of amide **5** and hydroxide **4** in a 3:1 ratio is established within 1 day. Attempts to isolate the product by evaporation of the NH_3 results in reversion to hydroxide **4** and some decomposition. These results show that clean, efficient generation of the amide complexes *trans*-**2** and **5** depends on the combined use of NH_3 and $NaNH_2$. We believe that NH_3 reacts with the metal chlorides and hydroxides to form amide complexes and $NaNH_2$ acts to remove the conjugate acid of the leaving group, generating only additional NH_3 (Scheme 2).[22,23]

In summary, after many attempts to prepare late transition metal parent amide complexes, we have found that substitution of common leaving groups by NH_2^-, in the presence of its conjugate acid NH_3, works well at both Ru and Ir centers. Studies aimed at extending this acid/conjugate base approach as well as exploration of the chemical and physical properties of M-NH_2 complexes are underway.

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Supporting Information Available: Spectroscopic and analytical data for complexes *cis*- and *trans*-**2** and **5**−**7** and structural data for *trans*-**2** and **7** (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[15] $Cp^*(PMe_3)(Ph)Ir(Cl)$ (**6**) was prepared from $[Cp^*IrCl_2]_2$ and 2 equiv of PhMgCl in THF. Spectroscopic and analytical data for **6** are included in the Supporting Information.

[16] Potassium iodide was added in an effort to increase the rate of halide exchange by substituting the chloride for the more labile iodide.

[17] Rahim, M.; White, C.; Rheingold, A. L.; Ahmed, K. J. *Organometallics* **1993**, *12*, 2401.

[18] Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.

[19] Ritter, J. C. M.; Bergman, R. G. Unpublished results.

[20] This species was observed in a mixture and was not isolated. We presume it to be the cis isomer of amide **2** due to its spectroscopic features (see Supporting Information).

[21] When chloride **6** is treated with $NaNH_2$, no reaction is observed. In the reaction of hydroxide **4** with only $NaNH_2$, it is possible that amide **5** is formed due to trace amounts of water reacting initially with the $NaNH_2$ to form NH_3.

[22] Sodium hydride may also be used to drive the equilibrium to amide, but the reaction is not as clean.

[23] Similar results have been observed in the formation of analogous iridium alkoxide complexes: Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* in press.