Directly-Observed β-Hydrogen Elimination of a Late Transition Metal Amido Complex and Unusual Fate of Imine Byproducts

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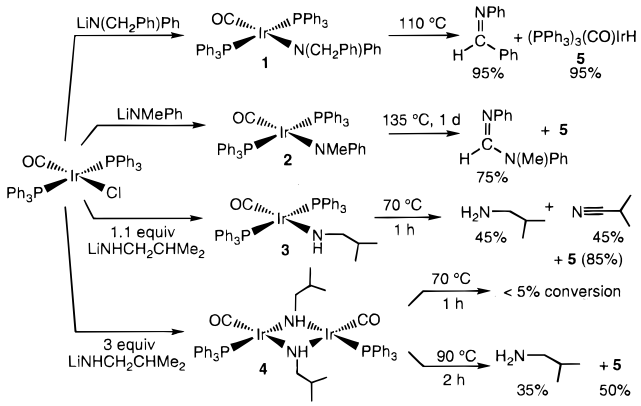
Amido complexes of low-valent platinum group metals bearing β-hydrogens are rare, particularly for simple terminal alkylamides.[1−5] It is commonly believed that β-hydrogen elimination reactions are rapid, precluding the isolation of such compounds.[6,7] However, the direct observation of β-hydrogen elimination from a monomeric amido complex has not been observed directly,[3,8−10] and its microscopic reverse—the insertion of imine into a metal hydride[3]—is rare despite its importance in imine hydrogenations.[11] We report here the synthesis and full characterization of amido compounds with β-hydrogens based on the classic Vaska's complex that undergo slow, directly-observable β-hydrogen elimination chemistry. The mechanism for this apparently fundamental, but rarely observed, reaction draws parallels to those for β-hydrogen eliminations of late metal alkyls.[12]

The chemistry we report is summarized in Scheme 1. Reaction of lithium amides with Vaska's complex provided a general route to monomeric terminal alkyl- or arylamido complexes **1**−**3** with β-hydrogens.[13] For example, reaction of Vaska's complex $[Ir(PPh_3)_2(CO)Cl]$ with an excess of LiNPhMe, $LiN(Ph)CH_2Ph$, or 1 equiv of $LiNHCH_2CHMe_2$ gave the trans terminal amido complexes **1**−**3** in isolated yields of 70%, 55%, and 65%, respectively. In the case of the *N*-alkylarylamides, exclusively monomeric materials were obtained. All three complexes were obtained in analytically pure form by removal of solvent, extraction of the solid into toluene, and cooling of the resulting solution to −35 °C after addition of pentane. In contrast to the formation of monomeric **1**−**3**, reaction of an excess of $LiNHCH_2CHMe_2$ with Vaska's complex gave the dimeric, bridging amido complex *syn*-$[Ir(PPh_3)(CO)(NHCH_2CHMe_2)]_2$ (**4**) as the only phosphine-containing metal product observed by ^{31}P NMR spectroscopy, along with PPh_3. Complex **4** was isolated in 85% yield after crystallization from pentane. The NMR and IR data for all complexes were straightforward and clearly defined their structures, except for the relative orientation of the *sec*-Bu groups in dimeric **4**. These spectroscopic data are included, along with analytical data, as supporting information. As one might expect, the ν_{CO} values for the alkylamides were lower than those for the monomeric arylamides, reflecting the more electron rich character of alkylamido complexes. The syn ligand geometry of **4** was deduced from the presence of a single phosphine resonance in the $^{31}P\{^1H\}$ NMR spectrum, but inequivalent *i*-Bu groups in the ^1H NMR spectrum.

Scheme 1



Thermal reaction of the *N*-benzylanilide complex **1** occurred cleanly in toluene solvent at 110 °C and was complete after 1−3 h depending on added phosphine concentration (*vide infra*) to form the stable *N*-phenyltoluenimine along with the iridium hydride **5**, both in yields exceeding 95% by NMR spectroscopy employing an internal standard. This reaction is a clear example of β-hydrogen elimination and constitutes the first direct observation of this transformation with a monomeric late metal amido complex.

The *N*-methylanilide complex **2** was remarkably stable, and the organic product marked an unusual outcome for the β-hydrogen elimination chemistry. Complex **2** remained unchanged for 2 h at 110 °C, but reacted over 1.5 d at 135 °C to form the hydride **5** in 90% yield. The monomeric imine formed from β-hydrogen elimination in this case would be highly reactive and was not observed. Instead, the amidine PhN═C(H)NMePh[14,15] was formed in 85% yield. This surprising product was clearly identified by comparison of ^1H NMR spectra, GC retention times, and MS data to an authentic sample prepared by addition of MeI to Li[PhNCHNPh]. The remainder of the organic products were *N*-methylaniline, presumably from hydrolysis of **2**. Thermolysis of **2**-d_3 containing the amide $N(CD_3)Ph$ led to formation of $PhN{=}C(D)NCD_3Ph$ and to the formation of **5** containing 60−70% deuterium in the hydride position,[16] with the remaining deuterium incorporated into the phosphine ligand, by reversible orthometalation of the phosphine. These labeling results confirmed that the metal hydride was generated from the amide β-hydrogen. Methoxide complexes can be dehydrogenated to form CO;[17] the formation of amidine can be envisioned as a combination of *N*-methylaniline and phenyl isocyanide that result from formal disproportionation of unstable methylideneaniline.

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(11) For a recent review see: James, B. R. *Chem. Ind.* **1995**, *62*, 167.
(12) Cross, R. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, S. P. F. R., Ed.; John Wiley: New York, 1985; Vol. 2, p 559.
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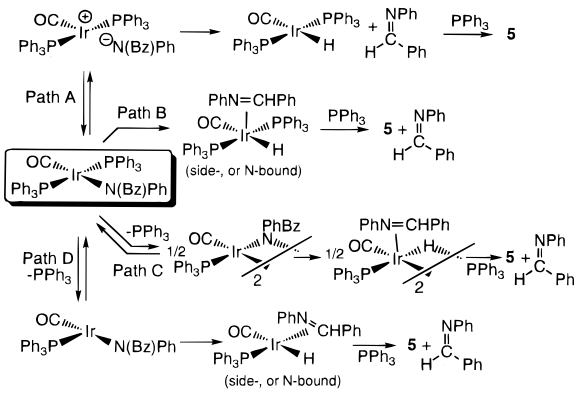
S0002-7863(96)01439-4 CCC: $12.00

Scheme 2



The isobutyl complex **3** also formed unusual organic products for β-hydrogen elimination processes. Compound **3** was less stable than the arylamido complexes, and thermal chemistry occurred cleanly at 70 °C. In this case, 0.5 equiv of isobutylamine and 0.5 equiv of isobutyronitrile were formed in a combined yield that was 90%, along with hydride **5** in 85% yield, again determined by ^{1}H NMR spectroscopy with an internal standard. The organic reaction products were identified by comparison of ^{1}H NMR spectra to those of commercial materials and reflect a formal disproportionation of the unstable isobutanimine into amine and nitrile. This transformation resembles a Cannizarro reaction in which aldehydes undergo hydroxide-induced formation of carboxylic acid and alcohol.[18] Complex **3** must not form dimeric **4** during this β-elimination chemistry. Complex **4** showed less than 5% conversion during the time that led to complete conversion of **3**, while complete conversion of **4** after 4 h at 90 °C gave only 50% yield of **5**, 35% yield of amine, and less than 5% nitrile.

The mechanism of the simple β-hydrogen elimination from *N*-benzylanilide **1** to form *N*-phenyltoluenimine and hydride **5** was probed by kinetic methods. Reaction rates were measured at 110 °C by monitoring the decay of the benzylic resonance in the ^{1}H NMR spectra. Four possible mechanisms for the β-hydrogen elimination are shown in Scheme 2. Reaction by pathway A would be first order in **1** and zero order in phosphine concentration. This mechanism would also be expected to show a pronounced solvent effect. Pathway B would, again, provide reactions that would be first order in iridium amide and zero order in phosphine concentration, but would be unlikely to provide a significant solvent effect. Reaction by pathway C would exhibit inverse second-order behavior in phosphine concentration and second-order behavior in amide **1**. Reaction by pathway D would be first order in **1** and inverse first order in phosphine concentration.

Observed rate constants were measured with concentrations of added phosphine (PPh_3-d_{15}) that ranged from 2.3 to 9.5 mM. Linear first-order plots for the decay of *N*-benzylanilide **1** were obtained, indicating first-order behavior in **1**. Observed rate constants varied by less than 5% for reactions involving initial concentrations of **1** that varied by a factor of 3, confirming the first-order behavior in **1**. The kinetic behavior in added phosphine was clearly inverse first order and the reaction followed one major pathway. A plot of ln k_{obs} vs ln [PPh_3-d_{15}] gave a slope of -1.1 ± 0.1, and a plot of $1/k_{obs}$ vs [PPh_3-d_{15}] was linear with a *y* intercept within experimental error of zero. Although determined qualitatively by ^{31}P NMR spectroscopy, reaction rates in C_6D_6 and THF were essentially identical.

These results are consistent with only pathway D, involving a 14-electron intermediate that undergoes β-hydrogen elimination to presumably form an imine complex before final displacement of the imine with 2 equiv of PPh_3. The most common pathway for β-hydrogen elimination of late metal alkyl complexes involves a similar formation of an unsaturated intermediate that provides a binding site for the resulting alkene.[12,19] The lack of solvent effect suggests that the presence of the nitrogen heteroatom does not lead to a transition state with significant charge buildup.

The β-hydrogen elimination chemistry of **2** was inhibited by added phosphine, although the effect was not measured quantitatively as for **1**, and may not be a simple inverse first-order dependence. In contrast, the rate of thermal reaction of **3** was independent of the concentration of added phosphine. Conversions of **3** to **1** at various reaction times were identical for reactions conducted in the presence of a 5-fold difference of added [PPh_3]. It is not necessary to invoke a mechanism for the initial stages of the reaction of **3** that is different from the one deduced for **1**. Rate-determining dissociation of PPh_3 or reversible β-hydrogen elimination followed by associative imine displacement is consistent with the reaction orders.

It was surprising that such high temperatures were necessary for the β-hydrogen elimination processes to occur, particularly the slow reaction of **1** that forms an unusually stable imine. The analogous alkyl complex [$Ir(PPh_3)_2(CO)(octyl)$] generated *in situ* from Vaska's complex and octyllithium produces octene at room temperature.[20,21] Thus, β-hydrogen elimination of late metal amides can be much slower than elimination of the corresponding alkyl complexes.

We have shown previously that β-hydrogen elimination reactions of palladium(II) amides can be more facile than those directly observed with these Ir(I) compounds and are important in the catalytic selectivity of late transition metal amides.[8] β-Hydrogen elimination can be minimized by the use of bulky phosphine ligands, as in catalytic amination of aryl halides.[22−27] Alternatively, chelating ligands would minimize β-hydrogen elimination of late metal amides by reducing the equilibrium for phosphine dissociation. In addition to amination chemistry, these results are relevant to imine hydrogenation, as noted in the introduction. Since the β-hydrogen elimination chemistry of these Vaska-type systems is more rapid from monomers, imine insertion clearly can involve a single metal center, despite the fact that some of the best catalysts for asymmetric imine hydrogenation are dimeric,[28] and the only directly observed imine insertion involves a bridging hydride to form a bridging amido product.[3]

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Supporting Information Available: Spectroscopic and analytical data for **1**−**4**, along with representative plots of kinetic data (5 pages). See any current masthead page for ordering and Internet access instructions.

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