

kylation of 4 occurs in a rate-limiting step to give 2, which then either rapidly dissociates CO (leaving 1) or migrates methyl to ligated CO (giving 3).<sup>18</sup> Studies by Belmont and Wrighton<sup>3b</sup> have established that  $\eta^3$ - to- $\eta^5$  indenyl tautomerization can drive CO dissociation, and it is likely that the alkyl-CO migratory insertion also benefits from this indenyl transformation.

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**Registry No.** 1, 71498-19-6; 3, 96412-64-5; 4-PPN<sup>+</sup>, 106799-48-8; 4-Na<sup>+</sup>, 106799-49-9; 4-Li<sup>+</sup>, 106799-50-2; 4-PPN<sup>+</sup>-OC<sub>4</sub>H<sub>9</sub>, 106820-58-0; ( $\eta^5$ -In)Fe(CO)<sub>2</sub>-Na<sup>+</sup>, 52326-30-4.

**Supplementary Material Available:** ORTEP drawings, a unit cell diagram, and tables of bond distances, bond angles, anisotropic thermal parameters, H-atom coordinates, and fractional coordinates (12 pages). Ordering information is given on any current masthead page.

(18) Alkyl migration apparently predominates for the ruthenium analogue of 2. Reducing [In(CO)<sub>2</sub>Ru]<sub>2</sub><sup>19</sup> with Na(Hg) in THF solution (and under 1 atm of CO) affords a red-yellow solution containing a metalate that we tentatively formulate as ( $\eta^3$ -In)Ru(CO)<sub>2</sub>-Na<sup>+</sup>: IR  $\nu$ (CO) 1998, 1946 (br) cm<sup>-1</sup>. Attempts at isolating and purifying it thus far have proved unsuccessful. Treating these solutions, nevertheless, with CH<sub>3</sub>I (1 atm N<sub>2</sub>) affords ( $\eta^5$ -In)(CO)<sub>2</sub>RuCOCH<sub>3</sub><sup>20</sup> (79% isolated yield) and only a trace of the corresponding methyl compound.

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(20) For (In)(CO)<sub>2</sub>RuCOCH<sub>3</sub> (yellow crystals, decomp pt 124 °C): IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO) 2030, 1969, 1646 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.43, 7.13 (AA'BB', 4 H, In:benzo), 5.97 (d, *J* = 3.0 Hz, 2 H, H1,3), 5.53 (t, *J* = 3.0 Hz, H2), 2.44 (s, 3 H, COCH<sub>3</sub>). Anal. Calcd for C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>Ru: C, 49.56; H, 3.19. Found: C, 49.48; H, 3.32.

## Observation of a Facile Isomerization of an Early-Transition-Metal $\eta^2$ -Iminoacyl Group via a 1,2-Hydrogen Shift

Sharon M. Beshouri, Phillip E. Fanwick, and Ian P. Rothwell\*<sup>1</sup>

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

John C. Huffman

Molecular Structure Center, Indiana University  
Bloomington, Indiana 47405

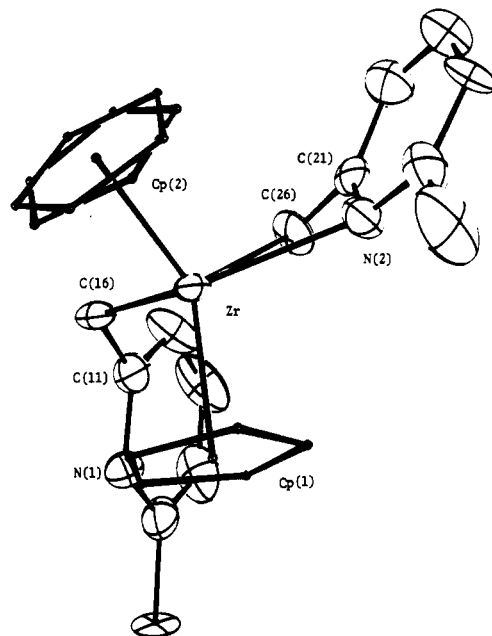
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**Summary:** The insertion of 2,6-dimethylphenyl isocyanide (ArNC) into the metal-carbon bonds of the complexes Cp<sub>2</sub>M(CH<sub>2</sub>-py-6-Me)<sub>2</sub> (M = Zr, Hf; CH<sub>2</sub>-py-6-Me = 2-(6-methylpyridyl)methyl) leads to the vinylamide complexes Cp<sub>2</sub>M(ArNCH=CH-py-6-Me)(CH<sub>2</sub>-py-6-Me) and Cp<sub>2</sub>M-(ArNCH=CH-py-6-Me)<sub>2</sub>. The vinylamide ligand is formed by a facile 1,2-hydrogen shift in intermediate  $\eta^2$ -iminoacyl complexes.

Early-transition-metal,<sup>2</sup> lanthanide,<sup>3</sup> and actinide  $\eta^2$ -acyl

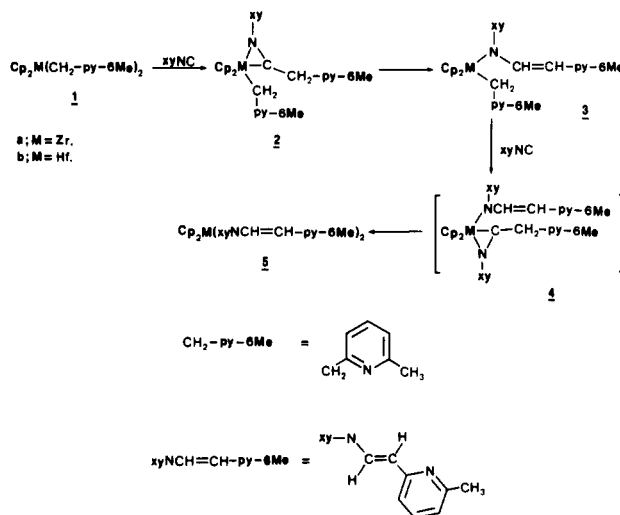
(1) (a) Camille and Henry Dreyfus Teacher-Scholar, 1985-1990. (b) Fellow of the Alfred P. Sloan Foundation, 1986-1990.

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**Figure 1.** ORTEP view of Cp<sub>2</sub>Zr(CH<sub>2</sub>-py-6-Me)<sub>2</sub> (1a) with hydrogens omitted. Some selected bond distances (Å) and angles (deg): Zr-N(2) = 2.407 (4), Zr-C(16) = 2.422 (4), Zr-C(26) = 2.406 (5), Zr-CEN(1) = 2.214 (6), Zr-CEN(2) = 2.25 (1), Zr-C(16)-py = 121.5 (3), Zr-C(26)-py = 88.5 (3), CEN(1)-Zr-CEN(2) = 128.1 (3), C(16)-Zr-C(26) = 76.2 (2).

### Scheme I

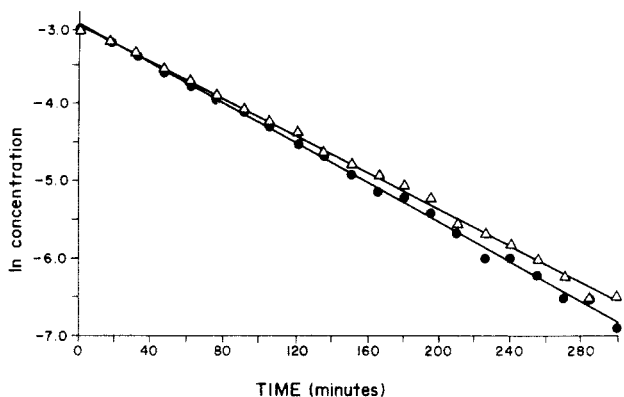


and  $\eta^2$ -iminoacyl groups have been shown to be important organometallic functionalities. Of particular synthetic interest has been their ability to undergo a range of carbon-carbon bond forming reactions.<sup>5</sup> We wish to report here our initial observations concerning a facile isomerization of a group 4 metal  $\eta^2$ -iminoacyl group into a vinylamide substituent, a reaction that essentially halts any further organometallic chemistry of this ligand.<sup>6</sup>

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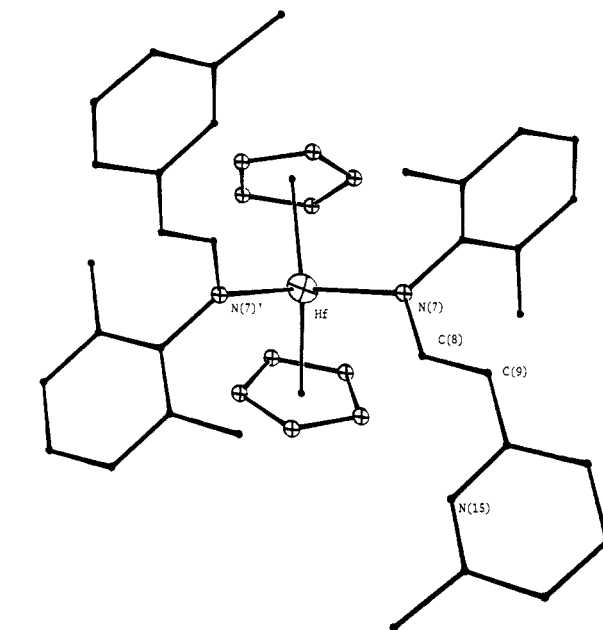
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**Figure 2.** Plots of  $\ln[\text{Cp}_2\text{M}(\eta^2\text{-xyNCCH}_2\text{-py-6-Me})(\text{CH}_2\text{-py-6-Me})]$  ( $\text{M} = \text{Zr}$  (●),  $\text{Hf}$  (Δ)) vs. time at 28 °C for the reaction  $2 \rightarrow 3$ . First-order rate constants:  $\text{M} = \text{Zr}$ ,  $12.8 (0.6) \times 10^{-5} \text{ s}^{-1}$ ;  $\text{M} = \text{Hf}$ ,  $11.9 (0.6) \times 10^{-5} \text{ s}^{-1}$ .

The addition of  $\text{LiCH}_2\text{-py-6-Me}$  ( $\text{LiCH}_2\text{-py-6-Me} = (2\text{-}(6\text{-methylpyridyl)methyl})\text{lithium}$ )<sup>7</sup> to the metallocene dihalides  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Zr, Hf}$ ) in diethyl ether results in the formation of the dialkyls **1a** and **1b** as shown (Scheme I).<sup>8</sup> An X-ray diffraction study of the zirconium compound **1a** shows the metal atom to be five-coordinate (Figure 1) with one of the pyridylmethyl ligands being C,N bound, resulting in an 18-electron complex.<sup>9</sup> The  $\text{Cp}_2\text{Zr}$  coordination is typical while the carbon and nitrogen atoms are contained in a plane bisecting the metallocene unit.<sup>10</sup> The Zr-C distances are significantly longer than typically found for  $\text{Cp}_2\text{ZrR}_2$  compounds<sup>11</sup> while the Zr-N distance of 2.407 (4) Å is comparable to that found for other Zr(IV)-pyridine derivatives.<sup>12</sup> Although the solid-state structure of **1a** shows the two pyridylmethyl ligands to be nonequivalent, Zr-C-py angles of 88.5 (3)° and 121.5 (3)°,



**Figure 3.** ORTEP view of  $\text{Cp}_2\text{Hf}(\text{xyNCH}=\text{CH-py-6-Me})_2$  (**5b**) emphasizing the coordination sphere. Some selected bond distances (Å) and angles (deg):  $\text{Hf-N}(7) = 2.182 (12)$ ,  $\text{N}(7)\text{-C}(8) = 1.376 (19)$ ,  $\text{N}(7)\text{-Hf-N}(7) = 98.5 (7)$ ,  $\text{Hf-N}(7)\text{-C}(8) = 119.7 (10)$ .

spectroscopic data do not support this idea in solution with only one set of  $\text{CH}_2\text{-py-6-Me}$  resonances being observed in the  $^1\text{H}$  NMR of both **1a** and **1b** even down to  $-75$  °C. Hence either both ligands are only carbon bound in solution or else exchange of the two types of ligand by dissociation and recoordination of nitrogen atoms may be taking place. The addition of 1 equiv of 2,6-dimethylphenyl isocyanide ( $\text{ArNC}$ ) to hydrocarbon solutions of **1** results in the rapid formation of a mono( $\eta^2$ -iminoacyl) derivative (**2**) as evidenced from spectroscopic data.<sup>13</sup> However, over a period of time at room temperature changes in the  $^1\text{H}$  NMR spectra of **2** indicate the formation of a second product (**3**). After several hours, formation of **3** is complete. Analysis of the spectra of **3** is consistent with a structure containing a trans-substituted vinylamide (Scheme I). Particularly characteristic are the doublets due to the trans vinyl hydrogens in the region  $\delta$  4.6–4.8 and 8.5–9.5,  $^3J(\text{H-H}) = 12\text{--}13$  Hz.<sup>14</sup> A kinetic study of the isomerization  $2 \rightarrow 3$  indicates the reaction to be first order in **2** with little change in the rate on going from Zr to Hf (Figure 2).

The rapidity of the isomerization for these pyridylmethyl compounds contrasts markedly with the thermal robustness of the corresponding simple benzyl analogues.<sup>15</sup>

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(8)  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): **1a**,  $\delta$  5.53 (s, Cp), 2.15 (s, Zr- $\text{CH}_2$ ), 2.28 (s,  $\text{CH}_2\text{-py-6-Me}$ ), 6.0–7.4 (m, aromatics); **1b**,  $\delta$  5.71 (s, Cp), 1.90 (s, Hf- $\text{CH}_2$ ), 2.46 (s,  $\text{CH}_2\text{-py-6-Me}$ ), 6.0–7.4 (m, aromatics).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): **1a**,  $\delta$  43.6 (Zr- $\text{CH}_2\text{-py}$ ,  $^1J(^{13}\text{C-H}) = 134$  Hz), 24.0 ( $\text{CH}_2\text{-py-6-Me}$ ), 110.2 (Cp); **1b**,  $\delta$  63.6 (Hf- $\text{CH}_2\text{-py}$ ,  $^1J(^{13}\text{C-H}) = 121$  Hz), 24.8 ( $\text{CH}_2\text{-py-6-Me}$ ), 111.4 (Cp).

(9) Crystal data for  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{-py-6-Me})_2$  (**1a**) at 22 °C: space group  $P1$ ,  $a = 7.679 (3)$  Å,  $b = 11.239 (3)$  Å,  $c = 12.672 (2)$  Å,  $\alpha = 95.67 (2)^\circ$ ,  $\beta = 100.57 (2)^\circ$ ,  $\gamma = 108.37 (3)^\circ$ ,  $Z = 2$ ,  $d_{\text{calcd}} = 1.432 \text{ g cm}^{-3}$ . Of the 4587 unique intensities collected with Mo K $\alpha$  radiation,  $4^\circ \leq 2\theta \leq 55^\circ$ , the 3411 having  $F > 3\sigma(F)$  were used in the full-matrix refinement. Final residuals are  $R = 0.05$  and  $R_w = 0.065$ . One of the Cp rings was found to be disordered, the final refinement used 50% occupancy for the two conformers.

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(13)  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): **2a**,  $\delta$  5.53 (s, Cp), 2.63 (s, Zr- $\text{CH}_2\text{-py}$ ), 3.42 (s, xyNCCH $_2$ Ph), 2.28 (s), 2.44 (s,  $\text{CH}_2\text{-py-6-Me}$ ), 1.70 (s, xy-Me); **2b**,  $\delta$  5.51 (s, Cp), 2.27 (s, Hf- $\text{CH}_2\text{-py}$ ), 3.49 (s, xyNCCH $_2$ Ph), 1.91 (s, xy-Me).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 28 °C): **2a**,  $\delta$  246.7 (xyNCCH $_2\text{-py-6-Me}$ ); **2b**,  $\delta$  254.4 (xyNCCH $_2\text{-py-6-Me}$ ).

(14)  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): **3a**,  $\delta$  2.40, 2.53 (s, py-6-Me), 2.77 (s, Zr- $\text{CH}_2\text{-py}$ ), 5.76 (s, Cp), 2.11 (s, Zr-N-xy-Me), 4.78 (d), 8.76 (d, xyNCH=CH-py-6-Me,  $^3J(\text{H-H}) = 12$  Hz); **3b**,  $\delta$  2.40, 2.52 (s, py-6-Me), 2.54 (s, Hf- $\text{CH}_2\text{-py}$ ), 5.73 (s, Cp), 2.14 (s, Hf-N-xy-Me), 4.77 (d), 8.63 (d, xyNCH=CH-py-6-Me,  $^3J(\text{H-H}) = 13$  Hz).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): **3a**,  $\delta$  113.0 (Cp), 55.5 (Zr- $\text{CH}_2\text{-py}$ ,  $^1J(^{13}\text{C-H}) = 123$  Hz), 99.1 (xyNCH=CH-py-6-Me,  $^1J(^{13}\text{C-H}) = 154$  Hz), 146.7 (xyNCH=CH-py-6-Me,  $^1J(^{13}\text{C-H}) = 164$  Hz); **3b**,  $\delta$  112.1 (Cp), 57.2 (Hf- $\text{CH}_2\text{-py}$ ,  $^1J(^{13}\text{C-H}) = 121$  Hz), 100.3 (xyNCH=CH-py-6-Me,  $^1J(^{13}\text{C-H}) = 177$  Hz), 147.8 (xyNCH=CH-py-6-Me,  $^1J(^{13}\text{C-H}) = 165$  Hz).

Hence the related  $\eta^2$ -iminoacyls  $Cp_2M(\eta^2-ArNCCH_2Ph)(CH_2Ph)$  ( $M = Zr, Hf$ ) were found to be stable for months at 100 °C in toluene. Only after 15 days at 120 °C was any reactivity detected for  $M = Zr$ , but the spectra obtained indicated a number of products being formed. Attempts to induce the 1,2-hydrogen shifts in these benzyl compounds by adding pyridine (2–10 equiv) to  $^1H$  NMR samples followed by thermolysis failed. After days at 120 °C, essentially no decrease in the  $\eta^2$ -iminoacyl concentration had occurred.

The formally 16-electron derivatives **3** will undergo further reaction with a second equivalent of  $ArNC$ . However, the reaction is much slower than the first insertion and leads to the bis(amido) compounds **5**, presumably via the intermediate  $\eta^2$ -iminoacyl **4** (Scheme I).<sup>16</sup> A single-crystal X-ray diffraction study of the hafnium compound **5b**<sup>17</sup> confirmed both the presence of the vinylamide function as well as the trans stereochemistry about the double bond (Figure 3). The Hf–N distance of 2.182 (12) Å is longer than typically found for simple Hf(IV) amido compounds<sup>18</sup> and probably reflects a decrease in nitrogen p to metal d  $\pi$ -bonding, possibly a consequence of the metal electron configuration and the vinyl substituent on the nitrogen atom.

Mechanistic aspects of this isomerization, whether the pyridyl ring accelerates an existing pathway or introduces a new one, are presently being studied.

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**Supplementary Material Available:** Analytical data for new compounds and tables of additional crystal structure data, atomic and thermal parameters, H atom positions, bond distances, and bond angles (24 pages); a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

(15) The compounds  $Cp_2M(\eta^2-xyNCCH_2Ph)(CH_2Ph)$  ( $M = Zr, Hf$ ) were formed in essentially quantitative yield by reacting the corresponding dibenzyls<sup>2a</sup> with  $xyNC$ .  $^1H$  NMR ( $C_6D_6$ , 25 °C):  $M = Zr$ ,  $\delta$  2.60 (s,  $Zr-CH_2Ph$ ), 3.49 (s,  $xyNCCH_2Ph$ ), 5.52 (s, Cp);  $M = Hf$ ,  $\delta$  2.24 (s,  $Hf-CH_2Ph$ ), 3.38 (s,  $xyNCCH_2Ph$ ), 5.32 (s, Cp).  $^{13}C$  NMR ( $C_6D_6$ , 25 °C):  $M = Zr$ ,  $\delta$  246.5 ( $xyNCCH_2Ph$ );  $M = Hf$ ,  $\delta$  254.1 ( $xyNCCH_2Ph$ ).

(16)  $^1H$  NMR ( $C_6D_6$ , 25 °C): **5a**,  $\delta$  2.10 (s,  $CH-py-6-Me$ ), 2.45 (s,  $N-xy-Me$ ), 5.89 (s, Cp), 4.76 (d), 9.24 (d,  $xyNCH=CH-py-6-Me$ ,  $^1J(^1H-^1H) = 13$  Hz); **5b**,  $\delta$  2.15 (s,  $CH-py-6-Me$ ), 2.50 (s,  $N-xy-Me$ ), 5.90 (s, Cp), 4.79 (d), 9.19 (d,  $xyNCH=CH-py-6-Me$ ,  $^3J(^1H-^1H) = 12$  Hz).  $^{13}C$  NMR ( $C_6D_6$ , 25 °C): **5a**,  $\delta$  114.3 (Cp), 98.3 ( $xyNCH=CH-py-6-Me$ ,  $^1J(^{13}C-^1H) = 154$  Hz), 135.9 ( $xyNCH=CH-py-6-Me$ ,  $^1J(^{13}C-^1H) = 157$  Hz); **5b**,  $\delta$  113.2 (Cp), 99.6 ( $xyNCH=CH-py-6-Me$ ,  $^1J(^{13}C-^1H) = 154$  Hz), 149.2 ( $xyNCH=CH-py-6-Me$ ,  $^1J(^{13}C-^1H) = 166$  Hz).

(17) Attempts to obtain crystals of **5b** suitable for X-ray diffraction work were frustrating. However, a few reasonably well formed samples were eventually obtained from hexane–toluene mixtures. Crystal data for  $Cp_2Hf(xyNCH=CH-py-6-Me)_2$  (**5b**) at –155 °C: space group  $I2_1$ ,  $a = 14.490$  (7) Å,  $b = 8.925$  (4) Å,  $c = 15.943$  (9) Å,  $\beta = 91.03$  (3)°,  $Z = 2$ ,  $d_{calc} = 1.262$  g  $cm^{-3}$ . Of the 1464 unique intensities collected with Mo  $K\alpha$  radiation,  $6^\circ \leq 2\theta \leq 45^\circ$ , the 1378 having  $F > 3\sigma(F)$  were used in the full-matrix refinement. There was considerable difficulty in locating several of the carbon atoms, but once located they were "well behaved". An apparent solvent molecule, toluene, was also visible in difference Fouriers and was included as a partial occupancy disordered fragment. Final residuals are  $R = 0.054$  and  $R_w = 0.049$ .

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## A High Yield Route to Rhenium(VII) Bis(imido) Neopentylidene Complexes

A. D. Horton, R. R. Schrock,\* and J. H. Freudenberger

Department of Chemistry, 6-331  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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**Summary:** The reaction between  $ReO_3(OSiMe_3)$  and  $ArNCO$  ( $Ar = 2,6$ -diisopropylphenyl) yields what is believed to be a mixture of  $Re_2O_x(NAr)_{7-x}$  complexes, one of which,  $Re_2O_2(NAr)_5$  (**1**), can be isolated in  $\sim 30\%$  yield. Pure **1**, or the crude mixture, when treated with 3 equiv of  $py\cdot HCl$  ( $py =$  pyridine) yields  $Re(NAr)_2(py)Cl_3$  (**2**) in 70–80% isolated yield vs.  $ReO_3(OSiMe_3)$ . Addition of 0.65 equiv of  $Zn(CH_2-t-Bu)_2$  to **2** yields  $Re(NAr)_2(CH_2-t-Bu)Cl_2$  (**3**) in 75% isolated yield. Dehydrohalogenation of **3** with DBU yields  $Re(NAr)_2(CH-t-Bu)Cl$  (**4**) virtually quantitatively, which can be treated with  $LiOR$  ( $OR = OCH(C-F_3)_2$  or  $O-2,6-C_6H_3-i-Pr_2$ ) to give relatives of the type  $Re(NAr)_2(CH-t-Bu)(OR)$  (**5**). Compounds **4** and **5** are very soluble, presumably monomeric, 18-electron complexes that do not react with *cis*-2-pentene or norbornene.

Rhenium is one of three metals (the others being Mo and W) that readily exhibits activity for the metathesis of olefins.<sup>1</sup> Although nothing is known about the type of active site in Re-based (all heterogeneous) metathesis catalyst systems, we propose that the metal is in its highest oxidation state (Re(VII) viewing the alkylidene ligand as a dianion) by analogy with now well-characterized homogeneous tungsten-based catalysts.<sup>2</sup> Since rhenium-based catalysts are the best so far for the metathesis of functionalized olefins,<sup>3</sup> the preparation of well-characterized homogeneous rhenium catalysts ultimately should prove to be of considerable practical importance, in addition to filling an important void in the chemistry of high oxidation state alkylidene and alkylidyne complexes. In view of the success we have had with tungsten complexes of the type  $W(CH-t-Bu)(NAr)(OR)_2$ ,<sup>2a</sup> we felt that a rhenium complex of the type  $Re(CH-t-Bu)(NAr)_2(OR)$  was a logical target, in spite of the fact that related Re(VII) bis(*tert*-butylimido) complexes (e.g.,  $Re(N-t-Bu)_2(CH-t-Bu)(CH_2-t-Bu)$ ) were shown to be unreactive toward olefins.<sup>4</sup>

The reaction between  $ReO_3(OSiMe_3)$ <sup>5</sup> and 3 equiv of  $ArNCO$ <sup>6</sup> in refluxing toluene for 5 h yields a mixture of at least three products, one of which can be obtained directly from the reaction in crystalline form in  $\sim 30\%$  yield. On the basis of elemental analysis and an  $^1H$  NMR spectrum that shows a 3:2 ratio of Ar groups, only the pair

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