Insertion of CNAr into Ta-Me Bonds of TaCp*ClnMe4-n (n = 0-3): Intramolecular Rearrangements, Dynamic Behavior, and X-ray Crystal Structure of TaCp*Cl2(NAr) (Ar = 2,6-Me2C6H3)

Mikhail V. Galakhov, Manuel Gomez, Gerardo Jimenez, Maria Angela Pellinghelli, Pascual Royo, and Antonio Tiripicchio

Organometallics, **1994**, 13 (5), 1564-1566• DOI: 10.1021/om00017a010 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

1564 *Organometallics* **1994**, *13*, 1564–1566

Insertion of CNAr into Ta–Me Bonds of $TaCp^*Cl_nMe_{4-n}$ (n = 0–3): Intramolecular Rearrangements, Dynamic Behavior, and X-ray Crystal Structure of $TaCp^*Cl_2(NAr)$ (Ar = 2,6-$Me_2C_6H_3$)

Mikhail V. Galakhov,[†] Manuel Gómez,[†] Gerardo Jiménez,[†]
Maria Angela Pellinghelli,[‡] Pascual Royo,[*,†] and Antonio Tiripicchio[‡]

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy

Received December 6, 1993[⊛]

*Summary: The dimethyltantalum complex $TaCp^*Cl_2Me_2$ (Cp^* = η^5-C_5Me_5) reacts readily with isocyanide, CNAr (Ar = 2,6-$Me_2C_6H_3$), to form the azatantalacyclopropane derivative $TaCp^*Cl_2(\eta^2$-NAr—$CMe_2)$ (**1**), which can be alkylated with 2 equiv of LiMe to give the dimethyl complex $TaCp^*Me_2(\eta^2$-NAr-$CMe_2)$ (**2**). Reaction of **1** and **2** with an additional 1 equiv of isocyanide leads to the imido complexes $TaCp^*Cl_2(NAr)$ (**3**) and $TaCp^*Me(NAr—CMe{=}CMe_2)(NAr)$ (**5**), respectively. Complex **5** is also obtained by reaction of $TaCp^*Me_4$ with 2 equiv of isocyanide, and the same reaction with $TaCp^*ClMe_3$ leads to $TaCp^*Cl(NAr—CMe{=}CMe_2)(NAr)$ (**4**). The complexes have been characterized by NMR studies (^1H, ^{13}C, and ^{13}C CP MAS), and the crystal structure of complex **3** has been determined by X-ray diffraction methods. The dynamic behavior of complexes **1**, **2**, **4**, and **5** has been studied in solution, and kinetic parameters were calculated from ^1H DNMR data.*

Migratory insertion of isocyanides into metal–alkyl bonds is an important organometallic reaction, leading to iminoacyl derivatives which are key and versatile reactive intermediates in many transition-metal-promoted transformations. These derivatives can be transformed into azaallyl complexes,[1] metallacyclic imines,[2] and aminocarbyne derivatives[3] or may participate in alkyne coupling processes[4] and double[1,5] or multiple[5] isocyanide insertion reactions. They may also be transformed into azametallacyclopropane species, which give imido complexes[6] by thermal decomposition. The behavior observed in these reactions is profoundly dependent on the metal and the nature of its substituents, particularly the number of alkyl groups bound to the metal, which can be involved in the reaction. Several studies related with early-transition-metal complexes have been reported,[7] but few are concerned with cyclopentadienyl derivatives of group 5 metals.[2b,4] We report herein the results observed by studying the insertion of $CN(2,6\text{-}Me_2C_6H_3)$ into methyltantalum bonds of (pentamethylcyclopentadienyl)chloromethyltantalum complexes of the type $TaCp^*Cl_nMe_{4-n}$ (Cp^* = η^5-C_5Me_5, n = 0–3) under different conditions and proportions.

Reaction of $TaCp^*Cl_2Me_2$ with 1 equiv of the isocyanide takes place with the formation of the intermediate η^2-coordinated acylimidoyl complex, similar to that observed[8] when the same reaction is carried out with the monomethyl derivative $TaCp^*Cl_3Me$(see Scheme 1). However, a further instantaneous reaction produces the migration of the second methyl group to the electrophilic acylimidoyl carbon atom to give the azatantalacyclopropane complex **1**.[9] Compound **1** easily coordinates one additional isocyanide molecule, which is then inserted with migration of the terminal alkyl group of the azatantalacyclopropane system; the expected tantalacyclobutane complex cannot be isolated, however, because it is thermally unstable and spontaneously decomposes to give the imido derivative **3**, with elimination of the arylketenimine.[10] Formation of the intermediate azatantalacyclobutane complex is required for **3** to be formed at room temperature, because thermal decomposition of **1** gives **3** with elimination of propene only by refluxing in toluene. The structure of complex **3**, determined by X-ray diffraction methods and represented in Figure 1,[11] shows the Ta atom in a three-legged piano-stool arrangement[2a,12] with a short Ta–N distance of 1.774(5) Å, consistent with a triple bond.[13]

[†] Universidad de Alcalá.

[‡] Università di Parma.

[⊛] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) (a) Filippou, A. C.; Grünleitner, W.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *413*, 181. (b) Filippou, A. C.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *415*, 375. (c) Martín, A.; Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2117.

(2) (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203. (b) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. (c) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (d) Brunner, H.; Wachter, J.; Schmidbauer, J. *Organometallics* **1986**, *5*, 2212.

(3) Filippou, A. C.; Grünleitner, W. *J. Organomet. Chem.* **1990**, *378*, 387.

(4) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.

(5) Carmona, E.; Marín, J. M.; Palma, P.; Poveda, P. L. *J. Organomet. Chem.* **1989**, *377*, 157.

(6) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(7) (a) Kwok, W. C.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088. (b) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341.

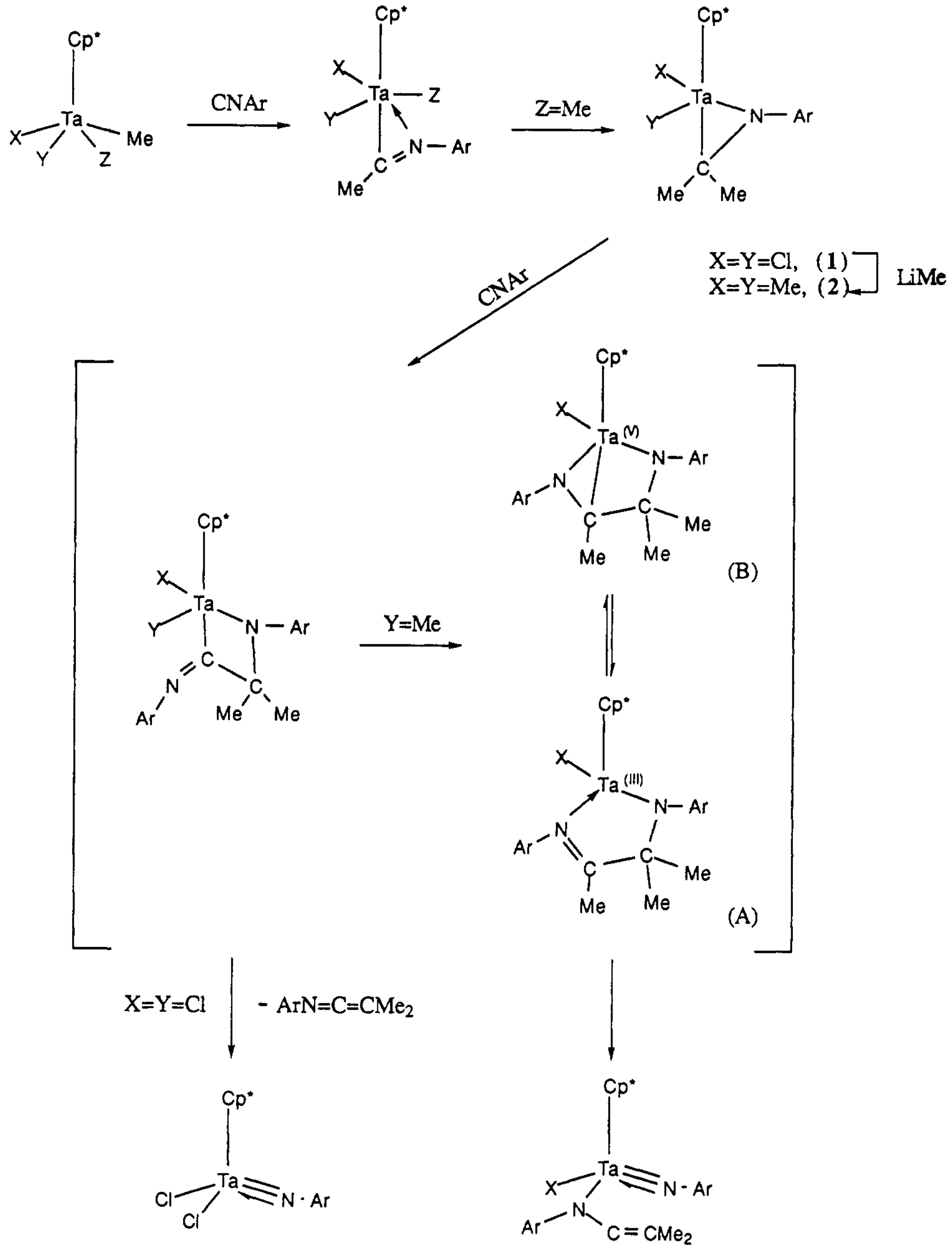
(8) ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 1.89 (s, 6H, $Me_2C_6H_3$), 2.06 (s, 15H, C_5Me_5), 2.54 (s, 3H, $MeC{=}NAr$).

(9) Data for **1** are as follows. Anal. Calcd for $C_{21}H_{30}Cl_2NTa$: C, 45.99; H, 5.51; N, 2.55. Found: C, 46.23; H, 5.62; N, 2.47. ^1H NMR ($CDCl_3$, 20 °C, 300 MHz): δ 2.00 (s, 15H, C_5Me_5), 2.08 (s, 6H, $Me_2C_6H_3$), 2.11 (s, 6H, Me_2CNAr), 6.90 (t, J = 7.5 Hz, 1H, p-$C_6H_3Me_2$), 7.02 (d, J = 7.5 Hz, 2H, m-$C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, 75 MHz): δ 10.8 (C_5Me_5), 20.5 ($Me_2C_6H_3$), 28.8 (Me_2CNAr), 93.5 (Me_2CNAr), 122.1 (C_5Me_5), 125.3, 128.9, 133.5, 150.5 (p, m, o, *ipso* $C_6H_3Me_2$).

(10) Data for **3** are as follows. Anal. Calcd for $C_{18}H_{24}Cl_2NTa$: C, 42.70; H, 4.78; N, 2.77. Found: C, 43.02; H, 4.91; N, 2.75. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 1.83 (s, 15H, C_5Me_5), 2.45 (s, 6H, $Me_2C_6H_3$), 6.66 (t, J = 7.5 Hz, p-$C_6H_3Me_2$), 6.96 (d, J = 7.5 Hz, m-$C_6H_3Me_2$). $^{13}C\{^1H\}$ (benzene-d_6, 20 °C, 75 MHz): δ 11.2 (C_5Me_5), 18.8 ($Me_2C_6H_3$), 121.3 (C_5Me_5), 124.1, 127.3, 135.1, 151.1 (p, m, o, *ipso* $C_6H_3Me_2$). Data for $ArN{=}C{=}CMe_2$ are as follows. IR spectrum (in benzene): $\nu(C{=}N)$ 2015 cm^{-1}. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 1.44 (s, 6H, $Me_2C_6H_3$), 2.24 (s, 6H, $Me_2C{=}$), 6.87, 6.95 (m, 3H, m, p $C_6H_3Me_2$).

0276-7333/94/2313-1564$04.50/0

Scheme 1



(3)

X=Cl (4) Me (5)

When a third methyl group is present, as for TaCp*ClMe$_3$, coordination of the first isocyanide is followed by the migration of two methyl groups to give the monomethylated derivative of **1**, which then coordinates a second isocyanide molecule. A new double migration of two alkyl groups to the electrophilic isocyanide carbon atom takes place with migration of the methyl and the terminal alkyl group of the azatantalacyclopropane system, giving a complex which cannot be isolated because it rapidly rearranges by C–C coupling and simultaneous C–N bond breaking, leading finally to the formation of the imido alkenylamido[2a,7] complex **4**.[14] We have no experimental evidence to formulate this intermediate as a tantalum(III) diazametallacyclopent-2-ene (**A**) or as a tantalum(V) metallabicyclo complex (**B**) (see Scheme 1).

When the tetramethyl derivative TaCp*Me$_4$ is used as the starting compound, addition of 1 equiv of isocyanide leads to a mixture of a small amount of the expected dimethyltantalacyclopropane complex **2** (dimethylated **1**)

---

(11) Crystal data for $C_{18}H_{24}Cl_2NTa$ (**3**) at 22 °C: monoclinic, space group $P2_1/n$, $a = 13.275(4)$ Å, $b = 16.646(5)$ Å, $c = 8.511(3)$ Å, $\beta = 97.10(2)°$, $Z = 4$, $\rho_{calcd} = 1.802$ g cm^{-3}, μ(Mo Kα) = 61.07 cm^{-1}; diffractometer, Siemens AED; radiation, niobium-filtered Mo Kα ($\lambda = 0.710\ 73$ Å). A total of 4082 reflections were collected in the range $3 < \theta < 27°$ ($\pm h,k,l$). Of these, 2910 having $I > 2\sigma(I)$ were used in the structure solution. $R = 0.0297$, $R_w = 0.0415$, and $w = 0.737/[\sigma^2(F_o) + 0.0051F_o^2]$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the methyl groups of the N(Ar) ligand were localized in the final ΔF map and refined isotropically; the others were placed at their calculated positions and refined "riding" on the corresponding carbon atoms. Details of the crystallographic study will be reported in a future paper to be submitted to *Organometallics*.

(12) (a) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; Chota Vuru, G. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1069. (b) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. N. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

(13) Glueck, D. S.; Green, J. C.; Michelman, R. I.; Wright, I. N. *Organometallics* **1992**, *11*, 4221.

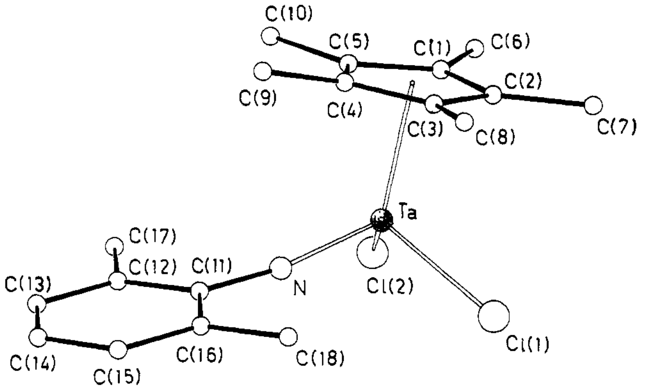


Figure 1. View of the molecular structure of the complex $TaCp^*Cl_2(NAr)$ (**3**). Important bond distances (Å) and angles (deg): Ta–Cl(1) = 2.331 (2), Ta–Cl(2) = 2.326(2), Ta–N = 1.774(5), Ta–CE = 2.115(6), N–C(11) = 1.395(8); CE–Ta–Cl(1) = 111.8(2), CE–Ta–Cl(2) = 112.4(2), CE–Ta–N = 119.8(2), Cl(1)–Ta–Cl(2) = 105.0(1), Cl(1)–Ta–N = 103.0(2), Cl(2)–Ta–N = 103.4(2), Ta–N–C(11) = 169.9(5). CE is the centroid of the C(1)···C(5) ring.

and the new complex **5** (methylated **4**) as the major product, along with an excess of the unreacted starting product. This result confirms that insertion of a second isocyanide is more favorable for **2** than for the starting tetramethyl complex. Pure **2**[15] can be obtained in higher yields by methylation of **1** with 2 equiv of LiMe.

According to the ^1H and ^{13}C NMR spectra, the structures of both complexes **1** and **2**[16] show the tantalacycle plane to be a symmetry plane perpendicular to the cyclopentadienyl ring, making the two pairs of methyl groups magnetically equivalent. The ^{13}C CP MAS NMR spectra[17] of **1** and **2** show the presence of only one isomer, whereas a fluxional behavior is observed in solution, on the ^1H and ^{13}C NMR time scale. At low temperatures down to 203 K, NMR spectra indicate the existence of two stereoisomers with the two N and C azatantalacyclopropane atoms interchanging their mutual positions, the ratios of population being 7/1 (**1**) and 3/1 (**2**), respectively, with the most abundant isomer always being coincidental with that observed in the solid. According to the kinetic parameters calculated[18] by using DNMR data, the transition state for this isomerization implies the existence of an enimine ligand, as a highly polar group, in agreement with the observed negative entropy value. Complex **5** was characterized by ^1H and ^{13}C NMR spectroscopy,[19] and its molecular structure[20] was elucidated by an X-ray diffraction study. Complexes **4** and **5** show the rotation of the CMe_2 group around the C═C double bond on the NMR time scale, according to the kinetic parameters calculated[21] for this process.

Acknowledgment. We thank the CICYT (Project No. PB92-0178) and Consiglio Nazionale delle Ricerche (Rome) for financial support.

Supplementary Material Available: Atomic coordinates, thermal parameters, and all bond distances and angles (Tables SI–IV) for complex **3** (4 pages). Ordering information is given on any current masthead page.

OM930821V

---

(14) Data for **4** are as follows. Anal. Calcd for $C_{31}H_{42}ClN_2Ta$: C, 56.49; H, 6.42; N, 4.25. Found: C, 55.98; H, 6.50; N, 4.13. ^1H NMR ($CDCl_3$, 20 °C, 300 MHz): δ 1.30 (br, 3H, $\mathit{Me}_2C{=}$), 1.60 (br, 3H, $\mathit{Me}_2C{=}$), 1.80 (sept, J = 1.0 Hz, 3H, $\mathit{Me}C{=}$), 1.85 (s, 15H, $C_5\mathit{Me}_5$), 2.20 (s, 6H, $\mathit{Me}_2C_6H_3$, amido), 2.25 (s, 3H, $\mathit{Me}_2C_6H_3$, imido), 2.58 (s, 3H, $\mathit{Me}_2C_6H_3$, imido), 6.75 (m, 6H, $C_6\mathit{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, 75 MHz): δ 11.60 ($C_5\mathit{Me}_5$), 19.40, 20.00 ($\mathit{Me}_2C_6H_3$, imido), 20.30 ($\mathit{Me}_2C_6H_3$, amido), 21.00 (very br, $\mathit{Me}_2C{=}$), 23.10 ($\mathit{Me}C{=}$), 112.40 ($Me_2\mathit{C}{=}$), 119.3 ($\mathit{C}_5\mathit{Me}_5$), 122.10, 124.20 ($p$-$\mathit{C}_6H_3$), 127.10, 135.20 ($m, o$ C_6H_3, amido), 135.00 ($Me\mathit{C}{=}$), 127.50, 128.60, 132.90, 135.10 (m, m, o, o C_6H_3, imido), 151.20, 154.50 (*ipso* C_6H_3).

(15) Data for **2** are as follows. Anal. Calcd for $C_{23}H_{36}NTa$: C, 54.43; H, 7.15; N, 2.76. Found: C, 54.13; H, 7.22; N, 2.80. ^1H NMR ($CDCl_3$, 20 °C, 300 MHz): δ 0.17 (s, 6H, Me_2Ta), 1.72 (s, 15H, $C_5\mathit{Me}_5$), 1.98 (s, 6H, Me_2CNAr), 2.31 (s, 6H, $\mathit{Me}_2C_6H_3$), 7.05 (t, J = 7.5 Hz, 1H, p $C_6\mathit{H}_3Me_2$), 7.21 (d, J = 7.5 Hz, 2H, m-$C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, 75 MHz): δ 10.6 ($C_5\mathit{Me}_5$), 20.4 ($\mathit{Me}_2C_6H_3$), 27.6 (Me_2CNAr), 52.9 (Me_2Ta), 82.9 ($Me_2\mathit{C}NAr$), 115.5 (C_5Me_5), 123.4, 128.4, 134.4, 152.3 ($p, m, o,$ *ipso* $\mathit{C}_6H_3Me_2$).

(16) The X-ray crystal structure of **2** has also been determined, and details of the crystallographic study will be reported in a future paper to be submitted to *Organometallics*.

(17) Data for **1** are as follows. ^{13}C CP MAS: δ 11.9 ($C_5\mathit{Me}_5$), 21.5, 22.0 ($\mathit{Me}_2C_6H_3$), 27.1, 29.6 (Me_2CNAr), 95.6 ($Me_2\mathit{C}NAr$), 123.0 (C_5Me_5), 123.0, 129.1, 133.2, 134.1, 150.4 ($J_{Q^{14}N}$ = 50 Hz) ($p, m, o, o,$ *ipso* $\mathit{C}_6H_3Me_2$). Data for **2** are as follows. ^{13}C CP MAS: δ 11.5 ($C_5\mathit{Me}_5$), 21.5, 22.4 ($\mathit{Me}_2C_6H_3$), 27.6, 29.2 (Me_2CNAr), 53.5 (br, Me_2Ta), 86.7 (br, $Me_2\mathit{C}NAr$), 115.7 (C_5Me_5), 125.6, 129.4, 129.7, 134.4, 135.2, 153.1 ($J_{Q^{14}N}$ = 68 Hz) ($p, m, m, o, o,$ *ipso* $\mathit{C}_6H_3Me_2$).

(18) Data for **1** are as follows: E_a = 9.2 kcal mol^{-1}; log A = 11.3; ΔH^* = 7.6 kcal mol^{-1}; ΔS^* = −13.2 eu; $\Delta G^*_{298\ K}$ = 11.5 kcal mol^{-1}. Data for **2** are as follows: E_a = 7.6 kcal mol^{-1}, log A = 11.5, ΔH^* = 7.1 kcal mol^{-1}; ΔS^* = −15.1 eu; $\Delta G^*_{298\ K}$ = 11.6 kcal mol^{-1}.

(19) Data for **5** are as follows. Anal. Calcd for $C_{32}H_{45}N_2Ta$: C, 60.18; H, 7.10; N, 4.39. Found: C, 60.42; H, 6.95; N, 4.37. ^1H NMR ($CDCl_3$, 20 °C, 300 MHz): δ 0.60 (s, 3H, $\mathit{Me}Ta$), 1.50 (very br, 6H, $\mathit{Me}_2C{=}$), 1.70 (sept, J = 0.95 Hz, $\mathit{Me}C{=}$), 2.00 (s, 15H, $C_5\mathit{Me}_5$), 2.06 (s, 6H, $\mathit{Me}_2C_6H_3$, imido), 2.28, 2.36 (s, s, 3H, 3H, $\mathit{Me}_2C_6H_3$, amido), 6.50 (d, J = 7.5 Hz, 1H, p $C_6\mathit{H}_3$, amido), 6.71 (t, 2H, m $C_6\mathit{H}_3$ amido), 6.70 (ABC syst, p, m $C_6\mathit{H}_3$, imido). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, 75 MHz): δ 11.30 ($C_5\mathit{Me}_5$), 19.40 ($\mathit{Me}_2C_6H_3$, imido), 20.40, 20.50 ($\mathit{Me}_2C_6H_3$, amido), 21.4 ($\mathit{Me}C{=}$), 21.6 (br, $\mathit{Me}_2C{=}$), 33.40 ($\mathit{Me}Ta$), 111.30 ($Me_2\mathit{C}{=}$), 116.20 (C_5Me_5), 120.50, 123.80 (p C_6H_3), 126.30 (o C_6H_3, imido), 127.50, 128.30 (o C_6H_3, amido), 134.20 (o C_6H_3, imido), 152.70, 153.40 (*ipso* C_6H_3).

(20) Details of the X-ray crystallographic study will be reported in a future paper to be submitted to *Organometallics*.

(21) Data for **4** are as follows: E_a = 10.0 kcal mol^{-1}; log A = 11.4; ΔH^* = 9.5 kcal mol^{-1}; ΔS^* = −15.8 eu; $\Delta G^*_{298\ K}$ = 14.2 kcal mol^{-1}. Data for **5** are as follows: E_a = 8.0 kcal mol^{-1}; log A = 11.1, ΔH^* = 7.5 kcal mol^{-1}; ΔS^* = −16.3 eu; $\Delta G^*_{298\ K}$ = 12.2 kcal mol^{-1}.