Acknowledgment. The mass spectrometer (CHE-850962) and the Varian Gemini NMR spectrometer (CHE-8613066) used for this work were purchased with funds from the National Science Foundation. This work was supported by the National Science Foundation through Grant No. CHE-8520276. J.B.K. acknowledges the Alfred P. Sloan Foundation for support. Thanks to Leigh Nevinger for the mass spectral determinations.

Intermolecular Tautomerization of Metallacyclic Imines to Enamines Formed from Tantalum Alkyne Complexes and Nitriles

Jamie R. Strickler and David E. Wigley*

Carl S. Marvel Laboratories of Chemistry, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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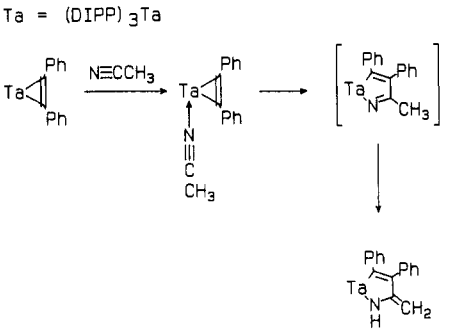
The electrophilic metal center in $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1; DIPP = 2,6-diisopropylphenoxide) coordinates a variety of nitriles to afford the η^1-nitrile adducts $(DIPP)_3(RC{\equiv}N)Ta(PhC{\equiv}CPh)$ (**2**, R = CH_3; **3**, R = CH_2CH_3; **4**, R = CMe_3; **5**, R = Ph). Those complexes of nitriles containing α-hydrogens (**2** and **3**) react further to form the metallacyclic enamine complexes $(DIPP)_3Ta(CPh{=}CPhC(=CHR)NH)$ (**6**, R = H; **7**, R = CH_3). Deuterium labeling and crossover experiments support these products as having arisen through an *inter*molecular metallacyclic imine to enamine tautomerization.

Introduction

The metal-promoted coupling of unsaturated organic substrates constitutes a powerful strategy for carbon–carbon bond formations in organic synthesis.[1] Among the reductants employed for such reactions are the middle-to low-valent early transition metals.[2-9] Of particular recent interest are the coupling reactions involving at least one nitrile, which have provided convenient routes to vicinal diamines,[10] polyfunctionalized aromatic compounds,[11] and related products derived from metallacyclic intermediates.[12] These reactions often proceed by the initial formation of a metallacyclic imine, which may subsequently rearrange[13] or dimerize.[14] Herein, we investigate the metallacyclization reactions of d^2 alkyne complexes of tantalum[15-18] with nitriles and present evidence for an *inter*molecular tautomerization of tantalacyclic imines to enamines.

Scheme I



Results

The η^1-nitrile adducts **2–5** can be isolated from the reaction of the alkyne complex $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**1**;

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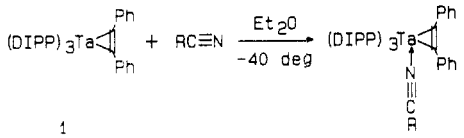
DIPP = 2,6-diisopropylphenoxide) with the free nitrile at low temperatures (eq 1). Complexes **2–5** are readily

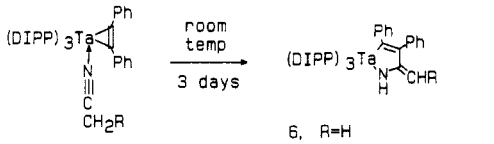


(1)

1

2, R=CH_3
2-d_3, R=CD_3
3, R=CH_2CH_3
4, R=CMe_3
5, R=Ph

identified by their medium to strong-intensity ν(C≡N) stretches in their IR spectra, which are shifted to somewhat higher energies from those of the free ligand upon coordination. Complexes of nitriles containing α-hydrogens, viz. **2** and **3**, represent kinetic products from this reaction, since they slowly react (over ca. 3 days) at ambient temperature to provide near-quantitative yields of yellow-orange complexes **6** and **7**, respectively (eq 2). Thus, the



(2)

2, R=H
3, R=CH_3

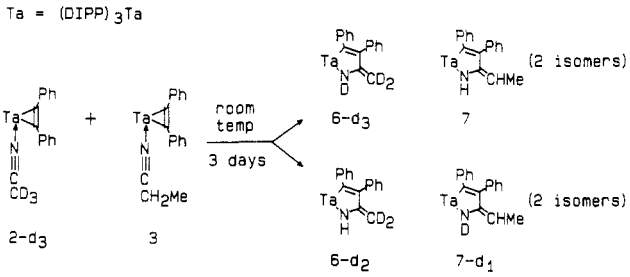
6, R=H
7, R=CH_3 (2 isomers)

intensity 3 singlet at δ 0.3 (N≡CCH_3) in the ^{1}H NMR spectrum of **2** is slowly replaced by three new singlets at δ 7.59, 4.14, and 3.95, each of intensity 1, in complex **6**. In addition, **6** displays inequivalent "alkyne" carbons in the ^{13}C NMR spectrum and a new doublet of doublets in the gated ^{13}C NMR spectrum centered at δ 94.7 ($^1J_{CH}$ = 162.4 and 162.5 Hz, =CH_2). The absence of a ν(C≡N) stretch in the IR spectrum of **6** and a new medium-intensity IR band at 3315 cm^{-1} (ν(N—H)), along with the NMR data, allow the formulation of **6** as the metallacyclic enamine complex depicted in eq **2**. Similarly, the propionitrile complex reacts at ambient temperatures to afford nearly quantitative yields of complex **7** (eq 2). Both possible geometric isomers of complex **7** form in an approximate 2:1 ratio (by ^{1}H NMR spectroscopy), although which isomer is the preferred product has not been determined. The major isomer can be crystallized selectively from pentane solutions at −40 °C.

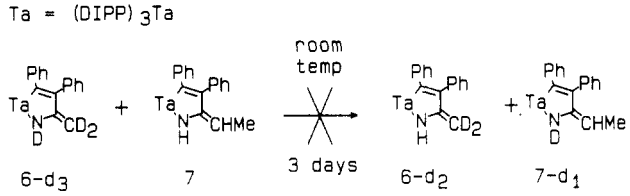
Reaction 2 most likely proceeds via an intermediate metallacyclic imine (or "azametallacyclopentadiene") complex as suggested in Scheme I. Compounds **6** and **7** can, therefore, be accounted for by an apparent 1,3-hydride shift from the alkyl group of the original nitrile fragment to the nitrogen atom of the metallacyclic imine. To unambiguously determine the origin of this transferred hydrogen, the tautomerization reaction was followed with the N≡CCD_3 adduct (DIPP)$_3$(CD_3C≡N)Ta(PhC≡CPh) (**2**-d_3). Thus, the room-temperature thermolysis of **2**-d_3 provides the new complex **6**-d_3 characterized by a ^{1}H NMR spectrum identical with that of **6**, except the resonances at δ 7.59, 4.14, and 3.95 were absent. Additionally, the ^{13}C resonance at δ 94.7 is broadened into the base line and not observed. These data, along with the shift of the ν(N—H) stretching mode at 3315 cm^{-1} in **6** to 2460 cm^{-1} upon deuteration in **6**-d_3 (ν(N—D)), require the formulation of **6**-d_3 as (DIPP)$_3$Ta(CPh=CPhC(=CD_2)ND).

A crossover experiment was contrived to discern between an inter- and an intramolecular tautomerization process, the results of which are outlined in Scheme II. An

Scheme II



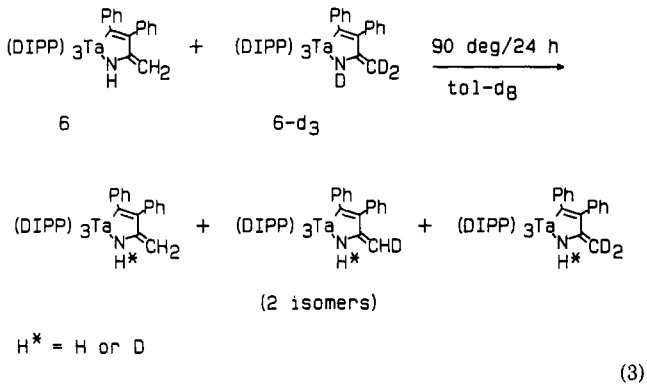
Scheme III



equimolar mixture of **2**-d_3 and **3** was allowed to react at room temperature (diethyl ether solution) for 3 days, after which time the solvent was removed in vacuo and the entire sample prepared for NMR spectroscopy. The sample consisted of an approximately equimolar mixture of four products. The expected compounds **6**-d_3 and **7** (both isomers) were present, along with the two new, partially deuterated, products **6**-d_2 and **7**-d_1 (two isomers) (Scheme II). As a control experiment, a mixture of **6**-d_3 and **7** was also prepared as an equimolar diethyl ether solution and monitored by ^{1}H NMR spectroscopy (room temperature, 3 days) as reported in Scheme III. Thus, under the same reaction conditions that led to the four products of Scheme II, no H/D exchange occurred between the two metallacyclic enamines **6**-d_3 and **7**. Two observations can be summarized from these experiments: (i) some *inter*molecular H/D exchange process is necessary to account for the formation of products **6**-d_2 and **7**-d_1 and (ii) under identical reaction conditions that lead to **6**-d_2 and **7**-d_1, H/D scrambling does not occur betweeen metallacyclic enamines *after* they have formed. Therefore, we must conclude that H/D exchange has ensued before metallacyclic enamine formation, which implicates the unobserved metallacyclic imine[13,14] (depicted in Scheme I) as the active species capable of an intermolecular H/D transfer.[19]

Evidence for a metallacyclic imine intermediate (or transition state) was obtained by considering whether the intermolecular H/D transfer might be a reversible process and therefore a metallacyclic imine might be accessible, albeit in low concentrations, at elevated temperatures. When a toluene-d_8 solution of **6** was heated to 90 °C in a NMR tube, the ^{1}H NMR signals at δ 4.08 and 3.92 (=CH_aH_b) had collapsed to one singlet at δ 4.03. The N—H resonance had broadened but not shifted significantly. When an equimolar mixture of **6** and **6**-d_3 was heated to 70 °C (toluene-d_8), slow H/D exchange could be initiated. Statistical scrambling among all three sites (NH and =CH_aH_b) was achieved by continuing heating to 90 °C for 24 h (eq 3). Thus, the δ 4.08 and 3.92 singlets (=CH_aH_b)

(19) By carefully monitoring this crossover experiment over the 3-day period required to achieve complete reaction, we observe that no H/D exchange occurs between starting materials (Scheme II), *before* coupling, to form the metallacyclic imine. Thus, no deuterium exchanges into either the methylene or the methyl resonances of the coordinated N≡CCH_2CH_3 of compound **3**, nor do any proton resonances exchange into the N≡CCD_3 ligand in compound **2**-d_3.



(3)

decreased in intensity, while new singlets appeared slightly upfield at δ 4.06 and 3.91, corresponding to the two isomers of the =CHD metallacyclic enamine, and grew in intensity until all four singlets were of near-equal intensity (Figure 1). These data, along with the concomitant broadening of the δ 7.59 singlet (NH), further implicate the reversible (although energetically unfavorable) intermolecular metallacyclic imine to enamine tautomerization. Thus, it appears to be the metallacyclic imine complex, accessible only in low concentrations and at elevated temperatures, that is active toward H/D transfer.

Finally, we note that the N≡CCMe$_3$ and N≡CPh complexes (**4** and **5**, respectively) do not metallacyclize to form isolable metallacyclic imine derivatives as one might predict. Adducts **4** and **5** are stable in solution at room temperature for extended periods of time, and thermolysis of these solutions under forcing conditions leads to unidentifiable decomposition products. Thus, although a metallacyclic imine may be reversibly formed in low concentrations, it is apparently unstable with respect to the nitrile adducts **4** and **5**.

Discussion

This intermolecular tautomerization reaction contrasts with Bercaw's titanacyclic imine complexes, e.g. (η^5-C$_5$Me$_5$)$_2$Ti(N=CMeCH$_2$CH$_2$), which reversibly tautomerize to the corresponding titanacyclic enamines as shown in eq 4.[13] Labeling and crossover experiments with ^{15}N,

(4)

^{13}C, and ^{2}H labels have clearly established reaction 4 as proceeding via an *intra*molecular 1,3-hydride shift mechanism, perhaps involving a β-hydrogen elimination (vide infra) to effect this tautomerization.[13] In another group 4 metallocene system, the zirconium benzyne complexes were shown to metallacyclize with nitriles to form metallacyclic imines and, in some cases, metallacyclic enamines, by an unidentified mechanism.[14] It is noteworthy that zirconacyclic imine complexes dimerize by coordination of the imine nitrogen to an adjacent metal center.[14]

The differences in the intermolecular process reported here and Bercaw's intramolecular system[13] may be attributed to the kinetic accessibility, via a β-hydrogen elimination, of the titanacyclic imine to enamine tautomerization, as has been proposed for the C$_5$Me$_5$-supported titanium system (Scheme IV). Since such a reaction is not possible for this tantalum system (the ring carbon β to the nitrogen is phenyl substituted), another less accessible pathway is traversed to accommodate the basicity of the metallacyclic imine nitrogen. Thus, these tantalum complexes are restricted to an *inter*molecular abstraction

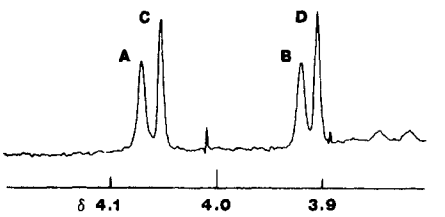
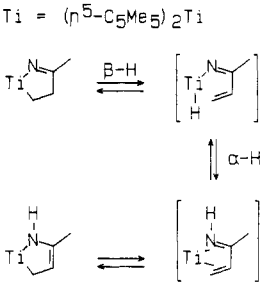
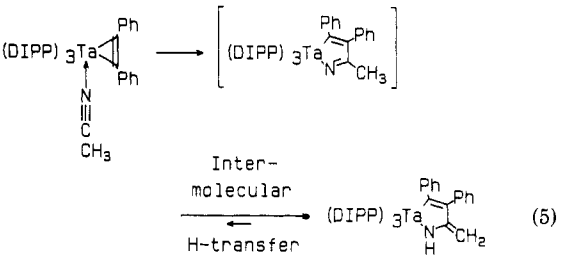


Figure 1. Partial ^{1}H NMR spectrum of the alkene proton resonances arising from reaction 3, in toluene-d_8: (A) CH_aH$_b$; (B) CH$_a$$H_b$; (C) CH$_aD_b$; (D) CD$_aH_b$.

Scheme IV



of a proton from the alkyl substituent of a neighboring conjugated metallacyclic imine, as summarized in eq 5.



(5)

Experimental Section

General Details. All experiments were performed under an atmosphere of dry nitrogen either by standard Schlenk techniques[20] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N$_2$ by standard techniques[21] and transferred to the drybox without exposure to air. The "cold" pentane used to wash the solid products was at ca. -30 °C. In all preparations, DIPP = 2,6-diisopropylphenoxide.

Starting Materials. All nitriles used in this study were obtained from Aldrich and were passed down a short (ca. 5–6 cm) column of activated alumina prior to use. (DIPP)$_3$Ta(PhC≡CPh) (**1**) was prepared as reported previously.[17]

Physical Measurements. ^{1}H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on either a Bruker WM-250 or AM-250 spectrometer in C$_6$D$_6$, CDCl$_3$, or C$_6$D$_5$CD$_3$ solvent. Chemical shifts were referenced to protio solvent impurities and solvent ^{13}C resonances and are reported in ppm downfield from Me$_4$Si. Assignments of ^{13}C resonances were assisted by attached proton tests, off-resonance decoupled or gated decoupled spectra. Infrared spectra (reported in cm^{-1}) were recorded as Nujol mulls between 4000 and 600 cm^{-1} with a Perkin-Elmer 1310 spectrometer and were not assigned, except as noted (w = weak, m = medium, s = strong (intensities); sh = shoulder, br = broad, v = very). All microanalytical samples were handled under nitrogen and were combusted with WO$_3$ (Desert Analytics, Tucson, AZ).

Preparations. (DIPP)$_3$(CH$_3$C≡N)Ta(PhC≡CPh) (2). To a -40 °C solution of 0.44 g (0.49 mmol) of (DIPP)$_3$Ta(PhC≡CPh)

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(21) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.

(1) in 15 mL of diethyl ether was added 0.08 mL (1.5 mmol) of acetonitrile. After this reaction mixture was maintained at −40 °C for 30 min, the solvent was removed in vacuo to provide the product as a pale yellow solid. Cold pentane was added, and the insoluble product (0.40 g, 0.43 mmol, 87% yield) was filtered off, washed with a small portion of cold pentane, and dried in vacuo. Analytically pure samples were obtained by recrystallization from Et_2O/pentane at −40 °C. ^1H NMR (C_6D_6): δ 7.47–7.44 and 7.12–6.89 (m, 19 H, H_{aryl} (DIPP) and C_6H_5), 3.66 (spt, 6 H, C*H*Me$_2$), 1.16 (d, 36 H, CH*Me*$_2$), 0.34 (s, 3 H, N≡CC*H*$_3$). ^{13}C NMR (C_6D_6): δ 201.1 (C_{alkyne}), 158.6 (C_{ipso}, DIPP), 141.8 (C_{ipso}, C_6H_5), 138.1 (C_o, DIPP), 129.3 and 128.3 (C_o and C_m, C_6H_5), 127.5 (C_p, C_6H_5), 123.3 (C_m, DIPP), 121.8 (C_p, DIPP), 27.1 (*C*HMe$_2$), 24.1 (CH*Me*$_2$), −0.1 (N≡*C*CH$_3$); N≡*C*CH$_3$ was not observed. IR: 2303 w, 2275 w, 1651 br w, 1585 w, 1428 s, 1324 s, 1250 s, 1194 s, 1110 m, 1089 m, 1066 w, 1040 m, 930 w, 891 m, 859 m, 789 w, 765 m, 755 m, 749 m, 742 m, 692 m cm^{-1}. Anal. Calcd for $C_{52}H_{64}NO_3Ta$: C, 67.01; H, 6.92; N, 1.50. Found: C, 66.71; H, 7.21; N, 0.67. Nitrogen consistently gave a low reanalysis due to the volatility of the coordinated acetonitrile.

(DIPP)$_3$(CD$_3$C≡N)Ta(PhC≡CPh) (2-*d*$_3$). The reaction of (DIPP)$_3$Ta(PhC≡CPh) (1) (0.53 g, 0.59 mmol) with acetonitrile-d_3 (0.09 g, 2.0 mmol), by the procedure used to prepare **2**, provided 0.46 g (0.49 mmol, 83%) of fluffy, pale yellow product. ^1H NMR (C_6D_6): all resonances are identical with those for **2** except for the singlet at δ 0.34, which was absent.

(DIPP)$_3$(CH$_3$CH$_2$C≡N)Ta(PhC≡CPh) (3). To a −40 °C solution of 0.47 g (0.52 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 15 mL of diethyl ether was added 0.08 mL (1.1 mmol) of propionitrile. After the mixture was reacted at −40 °C for 1 h, the solvent was removed in vacuo to afford the product as a yellow solid. Cold pentane was added, and the insoluble solid (0.38 g, 0.40 mmol, 78% yield) was filtered off, washed with additional cold pentane, and dried in vacuo. Analytically pure samples were obtained by recrystallization from Et_2O/pentane at −40 °C. ^1H NMR (C_6D_6): δ 7.49–7.46 and 7.12–6.88 (m, 19 H, H_{aryl} (DIPP) and C_6H_5), 3.68 (spt, 6 H, C*H*Me$_2$), 1.17 (d, 36 H, CH*Me*$_2$), 0.93 (q, 2 H, N≡CC*H*$_2$CH$_3$), 0.07 (t, 3 H, N≡CCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 199.8 (C_{alkyne}), 158.6 (C_{ipso}, DIPP), 141.8 (C_{ipso}, C_6H_5), 138.2 (C_o, DIPP), 129.3 and 128.2 (C_o and C_m, C_6H_5), 127.5 (C_p, C_6H_5), 123.3 (C_m, DIPP), 121.7 (C_p, DIPP), 27.1 (*C*HMe$_2$), 24.1 (CH*Me*$_2$), 10.3 (N≡*C*CH$_2$CH$_3$), 8.8 (N≡CCH$_2$*C*H$_3$); N≡*C*CH$_2$CH$_3$ was not observed. IR: 2272 m, 1657 br m, 1560 w, 1320 br s, 1248 br s, 1190 br s, 1150 w, 1105 m, 1085 m, 1065 w, 1038 m, 1020 w, 929 m, 903 m, 889 s, 861 s, 788 m, 766 w, 744 s, 690 br m cm^{-1}. Anal. Calcd for $C_{53}H_{66}NO_3Ta$: C, 67.29; H, 7.03; N, 1.48. Found: C, 67.03; H, 7.09; N, 1.38.

(DIPP)$_3$(Me$_3$CC≡N)Ta(PhC≡CPh) (4). Neat trimethylacetonitrile (0.08 mL, 0.72 mmol) was added to a stirred solution of 0.39 g (0.44 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 15 mL of diethyl ether. The solution color changed from a pale to a bright yellow immediately upon nitrile addition. After the mixture was reacted at room temperature overnight (ca. 16 h), the solvent was removed under reduced pressure to provide a yellow oil. The oil was dissolved in pentane and cooled to −40 °C, whereupon bright yellow crystals of product formed. The crystals (0.34 g, 0.35 mmol, 81%) were collected, washed with cold pentane, and dried in vacuo. This product was analytically pure but could be recrystallized from Et_2O/pentane solutions at −40 °C. ^1H NMR (C_6D_6): δ 7.24–6.80 (m, 19 H, H_{aryl} (DIPP) and C_6H_5), 3.39 (spt, 6 H, C*H*Me$_2$), 0.99 (d, 36 H, CH*Me*$_2$), 0.93 (s, 9 H, N≡CCMe$_3$). ^{13}C NMR (C_6D_6): δ 198.6 (C_{alkyne}), 158.3 (C_{ipso}, DIPP), 141.3 (C_{ipso}, C_6H_5), 137.8 (C_o, DIPP), 132.3 (N≡*C*CMe$_3$), 128.8, 127.7 (C_o and C_m, C_6H_5), 126.8 (C_p, C_6H_5), 122.7 (C_m, DIPP), 120.7 (C_p, DIPP), 28.8 (CMe$_3$), 27.2 (*C*HMe$_2$), 26.6 (CH*Me*$_2$), 23.7 (*C*Me$_3$). IR: 2265 m, 1659 m, 1582 m, 1426 s, 1355 m, 1332 m, 1320 s, 1250 br s, 1190 br s, 1106 m, 1089 m, 1064 w, 1039 m, 1020 w, 929 m, 915 m, 887 s, 865 s, 786 m, 767 m, 754 m, 745 s, 700 m, 686 m cm^{-1}. Anal. Calcd for $C_{55}H_{70}NO_3Ta$: C, 67.82; H, 7.24; N, 1.44. Found: C, 67.74; H, 7.40; N, 1.44.

(DIPP)$_3$(PhC≡N)Ta(PhC≡CPh) (5). To a −40 °C solution of 0.40 g (0.45 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 15 mL of diethyl ether was added 0.09 mL (0.88 mmol) of benzonitrile (neat). After the reaction mixture was maintained at −40 °C for 15 min, the solvent was removed in vacuo to afford the product as a yellow solid. When this product was dissolved in ca. 4 mL of an Et_2O/pentane solution (ca. 1:1) and the solution was cooled to −40 °C, a pale yellow solid formed (0.33 g, 0.33 mmol, 73%), was filtered off, was washed with minimal cold pentane, and was dried in vacuo. Analytically pure samples were obtained by recrystallization from Et_2O/pentane at −40 °C. ^1H NMR (C_6D_6): δ 7.57–7.53 and 7.12–6.53 (m, 24 H, H_{aryl} (DIPP), C_6H_5, and N≡CC$_6$H$_5$), 3.77 (spt, 6 H, C*H*Me$_2$), 1.18 (d, 36 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 200.1 (C_{alkyne}), 158.7 (C_{ipso}, DIPP), 141.8 (C_{ipso}, $C_2(C_6H_5)_2$), 138.4 (C_o, DIPP), 134.0, 132.4, 129.4, 129.1, 128.3, and 127.5 (C_o, C_m, and C_p, N≡C*C*$_6$H$_5$ and $C_2(C_6H_5)_2$), 125.4 (N≡*C*-C$_6$H$_5$), 123.4 (C_m, DIPP), 121.7 (C_p, DIPP), 109.3 (C_{ipso}, N≡*C*C$_6$H$_5$), 27.2 (*C*HMe$_2$), 24.1 (CH*Me*$_2$). IR: 2245 m, 1650 br w, 1585 br w, 1322 s, 1271 m, 1251 s, 1197 s, 1110 m, 1100 m, 1090 m, 1040 w, 929 w, 910 m, 892 s, 864 m, 790 m, 765 m, 746 s, 695 m, 677 w cm^{-1}. Anal. Calcd for $C_{57}H_{66}NO_3Ta$: C, 68.87; H, 6.69; N, 1.41. Found: C, 68.59; H, 6.78; N, 1.26.

(DIPP)$_3$Ta(CPh=CPhC(=CH$_2$)NH) (6). To a stirred solution of (DIPP)$_3$Ta(PhC≡CPh) (1; 0.51 g, 0.57 mmol) in diethyl ether (15 mL) was added an excess of acetonitrile (0.06 mL, 1.2 mmol). The reaction mixture was maintained at room temperature overnight (ca. 16 h), after which time the solvent was removed in vacuo to afford a yellow-orange oil. When the oil was reconstituted in pentane, yellow-orange crystals began to form. This mixture was then cooled to −40 °C to allow more complete crystallization of the product. The crystals were collected, washed with cold pentane, and dried in vacuo; yield 0.39 g (0.42 mmol, 74%). Recrystallization of this product from Et_2O/pentane at −40 °C provided analytically pure samples. ^1H NMR ($CDCl_3$): δ 7.59 (s, 1 H, N*H*), 7.16–6.73 and 7.09–6.60 (m, 19 H, H_{aryl} (DIPP) and C_6H_5), 4.14, 3.95 (s, 1 H each, =C*H*$_2$), 3.39 (spt, 6 H, C*H*Me$_2$), 1.10 (d, 36 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 206.7 (s, C_α), 163.0 (s, C_β or C_β'), 155.5 (s, C_{ipso}, DIPP), 149.8 (s, C_β or C_β'), 144.6 and 138.9 (s, C_{ipso}, C_6H_5), 138.5 (s, C_o, DIPP), 130.3 and 128.0 (d, $^1J_{CH}$ = 144 and 143 Hz, C_o, C_6H_5), 127.4, 126.4, and 124.7 (d, $^1J_{CH}$ = 159, 160, and 160 Hz, C_m and C_p, C_6H_5) 123.5 (d, $^1J_{CH}$ = 162 Hz, C_p, DIPP), 123.3 (d, $^1J_{CH}$ = 160 Hz, C_m, DIPP), 94.7 (d of d, $^1J_{CH}$ = 162.4 and 162.5 Hz, =CH$_2$), 27.0 (d, $^1J_{CH}$ = 128 Hz, *C*HMe$_2$), 23.7 (q, $^1J_{CH}$ = 126 Hz, CH*Me*$_2$); one resonance from C_m or C_p (C_6H_5) was not located. IR: 3315 m, 1580 m, 1540 m, 1320 s, 1248 br s, 1220 m, 1180 br m, 1105 m, 1091 m, 1069 w, 1052 w, 1038 m, 1022 w, 1005 m, 980 w, 909 w, 900 s, 890 s, 870 m, 860 m, 800 m, 787 m, 750 m, 740 s, 695 s, 618 m cm^{-1}. Anal. Calcd for $C_{52}H_{64}NO_3Ta$: C, 67.01; H, 6.92; N, 1.50. Found: C, 66.88; H, 6.96; N, 1.57.

(DIPP)$_3$Ta(CPh=CPhC(=CD$_2$)ND) (6-*d*$_3$). The reaction of (DIPP)$_3$Ta(PhC≡CPh) (1) (0.53 g, 0.59 mmol) with acetonitrile-d_3 (0.09 g, 2.0 mmol) by the procedure used to prepare **6** provided 0.31 g (0.33 mmol, 55%) of **6**-d_3 as a yellow-orange solid. Spectra data were identical with those of **6** except for the following. ^1H NMR (C_6D_6): the resonances at δ 7.59, 4.14, and 3.95 were not observed. ^{13}C NMR (C_6D_6): the resonance at 94.7 was sufficiently broadened to not be observed. IR: the ν(N—H) mode at 3315 cm^{-1} in **6** was absent and a new band of medium intensity at 2460 cm^{-1} for ν(N—D) was present.

(DIPP)$_3$Ta(CPh=CPhC(=CHMe)NH) (7, Major Isomer). Excess propionitrile (0.13 mL, 1.8 mmol) was added neat to a stirred solution of 0.60 g (0.67 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 15 mL of diethyl ether. After 24 h, the solvent was removed under reduced pressure to afford a yellow-orange oil. When the oil was reconstituted in pentane, yellow-orange solid began to precipitate. This mixture was then cooled to −40 °C to allow more complete crystallization of the product. The solid (0.44 g, 0.46 mmol, 69% yield) was collected, washed with cold pentane, and dried in vacuo. Recrystallization of this compound from Et_2O/pentane at −40 °C provided analytically pure samples. ^1H NMR (C_6D_6): δ 7.91 (s, 1 H, NH), 7.33–7.30 and 7.13–6.61 (m, 19 H, H_{aryl} (DIPP) and C_6H_5), 4.50 (q, 1 H, =C*H*Me), 3.63 (spt, 6 H, C*H*Me$_2$), 1.49 (d, 3 H, =CH*Me*), 1.21 (d, 36 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 205.8 (C_α), 157.7 (C_β or C_β'), 156.0 (C_{ipso}, DIPP), 151.8 (C_β or C_β'), 145.4 and 139.3 (C_{ipso}, C_6H_5), 138.8 (C_o, DIPP), 130.9, 128.6, and 127.9 (C_o and C_m, C_6H_5), 126.8 and 125.2 (C_p, C_6H_5), 124.1 (C_p, DIPP), 123.8 (C_m, DIPP), 106.0 (=*C*HMe), 27.3 (*C*HMe$_2$), 24.0 (CH*Me*$_2$), 11.6 (=CH*Me*); one C_o or C_m (C_6H_5) resonance has not been located. IR: 3320 m, 1585 w, 1537 w, 1428

s, 1355 m, 1319 s, 1260 m, 1242 m, 1180 br s, 1110 m, 1100 m, 1090 m, 1062 w, 1035 m, 1020 m, 960 w, 930 w, 900 s, 885 m, 874 w, 862 m, 848 w, 796 m, 786 m, 750 m, 741 s, 707 m, 693 m, 618 m cm^{-1}. Anal. Calcd for $C_{53}H_{66}NO_3Ta$: C, 67.29; H, 7.03; N, 1.48. Found: C, 67.36; H, 7.16; N, 1.53.

Labeling Studies. Crossover Experiments (Schemes II and III). A 45-mg (0.048-mmol) amount of **2**-d_3 ((DIPP)$_3$(CD$_3$C≡N)Ta(PhC≡CPh)) and 41 mg (0.043 mmol) of **3** ((DIPP)$_3$(CH$_3$CH$_2$C≡N)Ta(PhC≡CPh)) were dissolved in 5 mL of Et_2O and allowed to react at room temperature (Scheme II). Similarly, a control reaction was prepared by dissolving 39 mg (0.042 mmol) of **6**-d_3 ((DIPP)$_3$Ta(CPh=CPhC(=CD$_2$)ND)) and 41 mg (0.043 mmol) of **7** ((DIPP)$_3$Ta(CPh=CPhC(=CHMe)-NH)) in 5 mL of Et_2O at room temperature (Scheme III). After 3 days, the reaction mixtures were pumped to dryness to provide oily solids. In both cases, an NMR sample was prepared in C_6D_6 of the entire reaction sample. The presence of protons in N—H and =CH$_2$ sites in generic **6**-d_n compounds was monitored from the three resonances at δ 7.74, 4.12, and 3.90, respectively. Likewise, the proton populations at N—H and =C*H*CH$_3$ sites in **7**-d_n compounds were followed for both isomers by their ^{1}H NMR spectra as follows: major isomer δ 7.91 (s), 4.50 (q); minor isomer, δ 7.59 (s), 4.33 (q). The theoretical ratio of (**7** + **7**-d_1):**6**-d_2 predicted if the intermediate metallacyclic enamines *form and tautomerize* at equivalent rates, weighted according to the mole fractions of **2**-d_3 (0.53) and **3** (0.47) initially present, is calculated to be 1.9. This value assumes no selectivity in the intermolecular tautomerization. The observed ratio of (**7** + **7**-d_1):**6**-d_2 is 2.3. The control reaction in Scheme III showed no proton exchange into the N—D or =CD$_2$ sites of **6**-d_3 under identical conditions; i.e., no **6**-d_2 or **7**-d_1 formed under these conditions.

Variable-Temperature ^{1}H NMR Spectroscopy. When a toluene-d_8 sample of **6** ((DIPP)$_3$Ta(CPh=CPhC(=CH$_2$)NH)) was heated to 90 °C, the collapse of the two singlets a δ 4.08 and 3.92 (=CH$_a$H$_b$, 16 °C) to a new sharp singlet at δ 4.03 (intensity 2) was observed. The N—H proton resonance remained at ca. δ 7.69; however, it broadened significantly upon heating. A mixture of 38 mg (0.041 mmol) of **6** and 43 mg (0.046 mmol) of **6**-d_3 ((DIPP)$_3$Ta(CPh=CPhC(=CD$_2$)ND)) was dissolved in toluene-d_8, and when it was warmed to 70 °C, two new singlets at δ 4.06 and 3.91 appeared just upfield of the original =CH$_a$H$_b$ resonances, which were simultaneously decreasing in intensity. After it was heated over 24 h at 90 °C, the sample was cooled and a room-temperature spectrum was taken. The four proton resonances that correspond to =CH$_a$H$_b$ and =CHD (two isomers) were all of equal intensity as predicted from an H/D exchange leading to statistical site deuteration, viz. =CH$_2$, =CH$_a$D$_b$, =CD$_a$H$_b$, and =CD$_2$ in equimolar ratios (Figure 1).

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