Alkylation and Insertion Reactions in Dichloro Azatantalacyclopropane Complexes. X-ray Crystal Structures of [TaCpCl$_2${C(Ph)CHCMe$_2$NAr-κ^2*C*,*N*}] (Cp = η^5-C$_5$Me$_5$, η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$)[§]

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Dichloro azatantalacyclopropane complexes [TaCpCl$_2$(CMe$_2$NAr-κ^2*C*,*N*)] (Ar = 2,6-Me$_2$C$_6$H$_3$; Cp = η^5-C$_5$Me$_5$, **1**; η^5-C$_5$H$_4$SiMe$_3$, **2**) can be obtained by treating TaCpCl$_2$Me$_2$ with 1 equiv of 2,6-dimethylphenylisocyanide. Alkylation of **1** with an excess of MgCl(CH$_2$SiMe$_3$) leads to [TaCp*Cl(CH$_2$SiMe$_3$)(CMe$_2$NAr-κ^2*C*,*N*)] (Cp* = η^5-C$_5$Me$_5$; Ar = 2,6-Me$_2$C$_6$H$_3$, **3**), which in solution slowly decomposes to give [TaCp*Cl{C(Me)═CH$_2$}(NAr)] (Cp* = η^5-C$_5$Me$_5$; Ar = 2,6-Me$_2$C$_6$H$_3$, **4**) with elimination of SiMe$_4$. The same reaction with other alkylating reagents takes place with the formation of **4**, although we have not observed similar intermediate monoalkyl derivatives. The complexes **1** and **2** react with ethylene to give the dichloro azatantalacyclopentane compounds [TaCpCl$_2$(CH$_2$CH$_2$CMe$_2$NAr-κ^2*C*,*N*)] (Ar = 2,6-Me$_2$C$_6$H$_3$; Cp = η^5-C$_5$Me$_5$, **5**; η^5-C$_5$H$_4$SiMe$_3$, **6**). However, benzene-d_6 solutions of **5** and **6** decompose at room temperature to give a dichloro(imido) tantalum complex [TaCpCl$_2$(NAr)] (Ar = 2,6-Me$_2$C$_6$H$_3$, Cp = η^5-C$_5$Me$_5$, **7**;η^5-C$_5$H$_4$SiMe$_3$, **8**) with elimination of 2-methyl-2-butene (Me$_2$C═CH−Me) and 3-methyl-1-butene (H$_2$C═CH−CHMe$_2$) (decomposition of **5**) and only 2-methyl-2-butene (decomposition of **6**). The complex [TaCp*Cl$_2${CH$_2$CH(Me)CMe$_2$NAr-κ^2*C*,*N*}] (Cp* = η^5-C$_5$Me$_5$; Ar = 2,6-Me$_2$C$_6$H$_3$, **9**) was detected by NMR spectroscopy after treatment of **1** with propylene in dichloromethane-d_2. The analogous reaction of **1** or **2** with alkynes RC≡CH (R = H, Ph, SiMe$_3$) leads to the formation of the dichloro azatantalacyclopentene complexes [TaCpCl$_2$(CRCHCMe$_2$NAr-κ^2*C*,*N*)] (Ar = 2,6-Me$_2$C$_6$H$_3$; Cp = η^5-C$_5$Me$_5$, R = H, **10**; Ph, **11**; SiMe$_3$, **12**; Cp = η^5-C$_5$H$_4$SiMe$_3$, R = H, **13**; Ph, **14**; SiMe$_3$, **15**), the process being regioselective when monosubstituted alkynes RC≡CH (R = Ph, SiMe$_3$) were used. All the new compounds were studied by IR and NMR spectroscopy, and the molecular structures of complexes **11** and **14** were determined by X-ray diffraction methods.

Introduction

The transfer of alkyl groups from transition metals to coordinated isocyanides is one of the most relevant organometallic reactions because the resulting metal-iminoacyl functions are key and versatile reactive intermediates in many synthetic applications. Especially the use of transition metals as catalysts for achieving coupling reactions which involve metalated species has increased the use of heterocyclic organometallics in all kinds of organic transformations.[1] In this area, we have reported the insertion processes[2] of isocyanides into metal−methyl bonds of chloro(methyl)(pentamethylcyclopentadienyl) niobium and tantalum complexes MCp*Cl$_{4-x}$Me$_x$ (M = Nb, Ta; Cp* = η^5-C$_5$Me$_5$) in which η^2-iminoacyl (x = 1), azametalacyclopropane (x = 2, 3), and (alkenylamido)imido (x = 3, 4) derivatives were isolated.

The chemistry associated with azametalacyclopropane complexes has witnessed an important development,[3] and although some group 5 metal η^2-imine complexes have been postulated as intermediates in organometallic processes,[4] only a few have been isolated.[5] These complexes can be accessible by cyclometalation of di-

[§] This paper is dedicated to the daughter of Manuel Gómez, Maria Jesús, who was a victim of the March 11, 2004, tragedy in Madrid.

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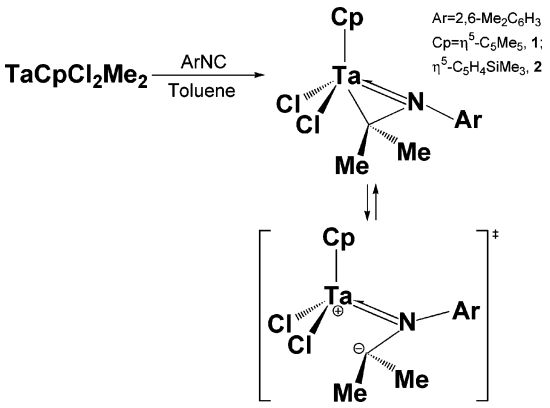
alkylamido ligands,[4b,6] by alkyl or hydride reduction of η^2-iminoacyl ligands,[3e,5e,7] by transfer of a hydrogen atom from an amine-metal complex,[5d] and also by addition of imines to low-valent metal derivatives.[3b,c,8] Such η^2-geometry has been identified in the crystal structures of some imine tantalum,[2a,c] zirconium,[7a,9] and tungsten[7b,c] derivatives and also in the analogous oxo-tantalacyclopropane complexes $TaCp^*X_2(\eta^2\text{-}OCMe_2)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; X = Cl;[4c] Me[2b]), which exhibit a bonding system through both the carbon and oxygen atoms.

On the other hand, nitrogen-containing molecules are among the most important organic compounds basically due to the biological activity[10] of amino acids and alkaloids. For the synthesis of these kinds of molecules, allylamines are considered ideal building blocks, and thus, many methods for the racemic and asymmetric syntheses of allylamines[11] have appeared in recent years. In this context, Buchwald et al. described an efficient method to prepare allylamine derivatives from simple amines.[12] This process relies on the formation of an η^2-imine zirconocene complex from an amide methyl zirconocene and its entrapment with an alkyne to give an azazirconacylopentene derivative, which affords the desired allylamine on protic workup.[13] This sequence constitutes a powerful synthetic transformation since it accomplishes both a C−H activation and a carbometalation process, reactions that are difficult to achieve with conventional reagents.

As part of a program concerned with the development of reactions involving monocylopentadienyl tantalum complexes, we wish to report in this paper the results observed when dichloro azatantalacyclopropane complexes $TaCpCl_2(CMe_2NAr\text{-}\kappa^2C,N)$ (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, **1**; η^5-$C_5H_4SiMe_3$, **2**) are treated with alkylating reagents and their behavior in olefin and acetylene insertion processes. All compounds were studied by usual spectroscopic methods and the molecular structure of some of them by X-ray diffraction.

Scheme 1. Synthesis of Dichloro Azatantalacyclopropane Complexes



Results and Discussion

Synthesis of Dichloro Azatantalacyclopropane Complexes. The azatantalacyclopropane complexes $[TaCpCl_2(CMe_2NAr\text{-}\kappa^2C,N)]$ (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, **1**; η^5-$C_5H_4SiMe_3$, **2**) were synthesized as described, by addition of 1 equiv of 2,6-$Me_2C_6H_3NC$ to a toluene solution of $TaCpCl_2Me_2$ (Cp = η^5-C_5Me_5;[14] η^5-$C_5H_4SiMe_3$[15]) via migration of both methyl groups to the isocyanide carbon atom (Scheme 1).[2a] The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data (see Experimental Section) for complex **2** are in accordance with the proposed structure and also with the previous solution isomerization studies[2a] related to this type of compounds.

Alkylation Reactions of Dichloro Azatantalacyclopropane Complexes. Reaction of a toluene solution of the dichloro azatantalacyclopropane complex **1** at −78 °C with an excess of YCH_2SiMe_3 (Y = MgCl, Li) afforded the chloro trimethylsilylmethyl derivative $[TaCp^*Cl(CH_2SiMe_3)(CMe_2NAr\text{-}\kappa^2C,N)]$ ($Cp^* = \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **3**), which was isolated as a yellow solid and characterized by elemental analysis and NMR spectroscopy (Scheme 2). Complex **3** is thermally stable in the solid state, but its benzene-d_6 or toluene solutions slowly decompose at room temperature, leading to the imido 2-propenyl complex $[TaCp^*Cl\{C(Me)=CH_2\}(NAr)]$ ($Cp^* = \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **4**) with elimination of $SiMe_4$, as confirmed by ^1H NMR spectroscopy.

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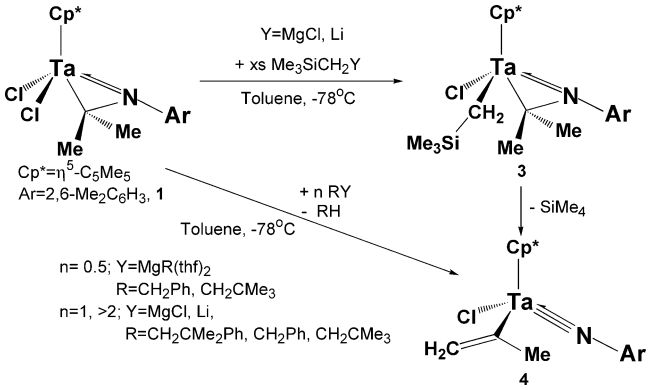
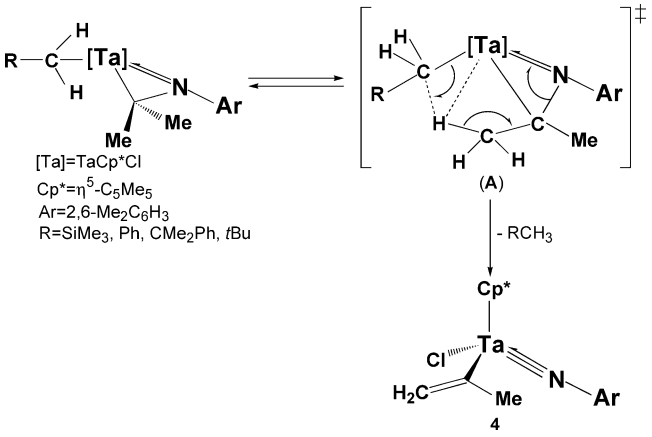
(15) Synthesis of $Ta(\eta^5\text{-}C_5H_4SiMe_3)Cl_2Me_2$. A 2 M solution of $ZnMe_2$ in toluene (1.09 mL, 2.10 mmol) was injected dropwise into a stirred suspension of $Ta(\eta^5\text{-}C_5H_4SiMe_3)Cl_4$ (1.00 g, 2.10 mmol) in toluene (25 mL). The resultant brown suspension was stirred to room temperature for 8 h. Afterwards, the brown suspension was filtered and the solvent removed in a vacuum. The residue was extracted with hexane (3 × 20 mL) and the solution concentrated to ca. 10 mL and cooled to −40 °C to give yellow crystals of $Ta(\eta^5\text{-}C_5H_4SiMe_3)Cl_2Me_2$. Yield: 0.70 g (78%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2960(m), 1631(m), 1404(m), 1251(s), 1171(m), 1048(m), 908(w), 842(vs), 759(w), 699(w), 629(w), 498-(w), 460(m), 420(w). ^1H NMR (δ ppm, in benzene-d_6): 5.99 (m, 2H), 5.59 (m, 2H, $C_5\mathbf{H}_4SiMe_3$), 1.28 (s, 6H, Ta-$\mathbf{Me}_2$), 0.135 (s, 9H, C_5H_4-Si$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 125.08 (C_i, $\mathbf{C}_5H_4SiMe_3$), 120.95 ($C_{2,5}$, $\mathbf{C}_5H_4SiMe_3$), 118.02 ($C_{3,4}$, $\mathbf{C}_5H_4SiMe_3$), 72.05 (Ta-$\mathbf{Me}_2$), 0.85 ($C_5H_4Si\mathbf{Me}_3$). Anal. Calcd for $C_{10}H_{19}Cl_2SiTa$: C, 28.65; H, 4.57. Found: C, 28.81; H, 4.45.

Scheme 2. Alkylation of Dichloro Azatantalacyclopropane Complexes



Scheme 3. Alkylation of Dichloro Azatantalacyclopropane Complexes

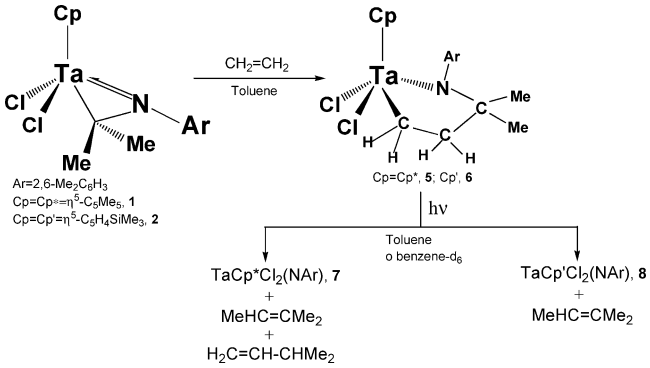


However, when complex **1** was treated with other alkylating reagents such as $MgR_2(thf)_2$ (R = CH_2Ph, CH_2CMe_3), MgClR, or LiR (R = CH_2CMe_2Ph, CH_2Ph, CH_2CMe_3) in 1:1 or 1:2 molar ratios or even in excess, complex **4** can be obtained with a similar yield, but the formation of the intermediate alkyl chloro azatantalacyclopropane could not be verified. A similar treatment of the trimethylsilylcyclopentadienyl derivative **2** led, in all cases, to mixtures of unidentified species.

As ilustrated in Scheme 3, we suggest that the formation of compound **4** takes place through a concerted transition state (A) by means of a C−H bond activation of one of the two methyl groups with the subsequent rearrangement and spontaneous elimination of the corresponding hydrocarbon. Similar ruptures of the C(Me)−N(Ar) bond have been previously observed[2a,b] in the formation of imido and alkenylamido imido tantalum compounds by reaction of $TaCp^*Cl_{4-x}Me_x$ ($Cp^* = \eta^5$-C_5Me_5; $x = 2, 3, 4$) with 2 equiv of isocyanides. The larger steric hindrance of the trimethylsilylmethyl substituent makes it difficult to reach the concerted transition state (A), and in agreement with this, we observed the alkyl chloro azatantalacyclopropane complex **3**.

The IR spectrum of complex **3** shows the characteristic absorptions due to the pentamethylcyclopentadienyl ring,[16] the trimethylsilyl substituent,[2c,17] and the Ta−C[2a,17c] bond at $\bar{\nu}$ 1049 (ν_{C-C}), 1245 [$\delta_{as}(CH_3)$], and 589 cm^{-1}, respectively, while complex **4** shows absorptions assigned to the ν C=C[4c,7b,c,18] and Ta=N[19] stretching vibrations at $\bar{\nu}$ 1585 and 1314 cm^{-1}, respectively.

Scheme 4. Synthesis of Dichloro Azatantalacyclopentane Complexes



The ^{1}H NMR spectrum of **3** shows all the expected resonances for the proposed structure with a chiral metal center. In the ^{1}H NMR spectrum of complex **4** appear two doublets of quartets at δ 5.83 (1H, ^4J = 1.5 Hz) and 4.96 (1H, ^4J = 1.2 Hz) (^2J = 0.6 Hz) and one doublet of doublets at δ 2.46 (3H), corresponding to the resonances of the 2-propenyl group bonded to the tantalum atom in agreement with the value of the carbon chemical shift δ 212.2. Moreover, the ^{1}H NMR spectra of complexes **3** and **4** show that the 2,6-dimethylphenyl ring (δ C_{ipso} = 153) of the imido susbtituent[4c,20] possesses a C_{2v} symmetry.

Synthesis of Dichloro Azatantalacyclopentane Complexes. Complexes **1** and **2** react with ethylene (1 atm) at room temperature in toluene to give, in good yields, the azatantalacyclopentane complexes [$TaCpCl_2$-($CH_2CH_2CMe_2NAr$-κ^2C,N)] (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, **5**; η^5-$C_5H_4SiMe_3$, **6**), as result of an ethylene insertion reaction into the Ta−C bond of the starting azatantalacyclopropane derivatives (Scheme 4).

Both complexes were found to be air- and moisture-sensitive but in the solid state and under a rigorously dry inert gas atmosphere are stable for weeks. However, toluene or benzene-d_6 solutions of complexes **5** and **6** slowly and spontaneously decompose at room temperature to give dichloro(imido) tantalum compounds [$TaCpCl_2$(NAr)] (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, **7**;[2a,21] η^5-$C_5H_4SiMe_3$, **8**[22]). When these reactions were followed by ^{1}H NMR spectroscopy in extremely dry conditions, the elimination of 2-methyl-2-butene (Me_2C=CH−Me) and 3-methyl-1-butene (Me_2CH−CH=CH_2) in a 4:1 ratio (decomposition of **5**) and only 2-methyl-2-

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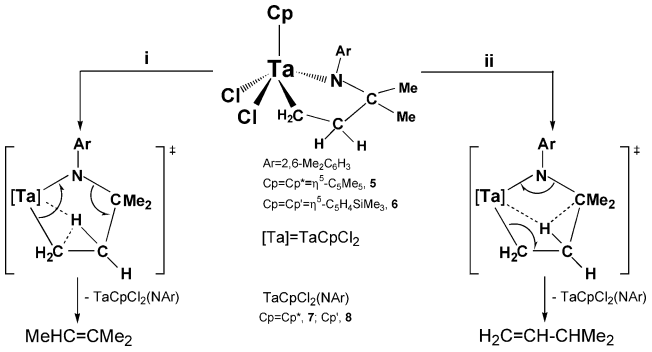
Scheme 5. Decomposition of Dichloro Azatantalacyclopentane Complexes



butene (decomposition of **6**) was detected. At room temperature, the decomposition process is very slow in the darkness but in the presence of light takes place quickly and is complete after 5 h.

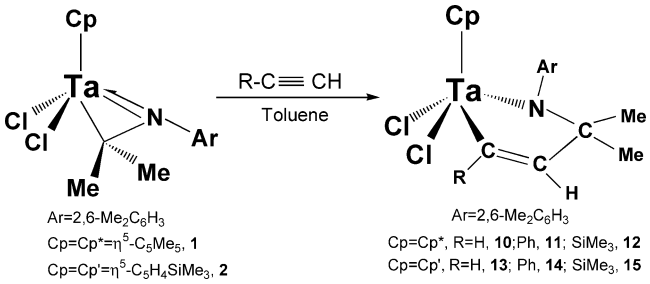
We suggest that a plausible decomposition process could consist in a β-hydrogen activation and a subsequent rupture of the Ta−C and N−C bonds into a concerted four-center transition state. So, the migration of hydrogen to the α-CH_2 carbon atom (i) leads to the internal olefin (2-methyl-2-butene), while the migration to the β-CMe_2 carbon atom (ii) produces the terminal olefin (3-methyl-1-butene) (see Scheme 5).

The analytical and spectroscopic data for complexes **5** and **6** are consistent with the expected four-legged piano-stool geometry. IR spectra show the characteristic absorptions of the pentamethylcyclopentadienyl ($\bar{\nu}_{C-C}$ = 1023 cm^{-1})[2c,16,17c] and trimethylsilylcyclopentadienyl rings ($\bar{\nu}_{C-H}$ = 839 cm^{-1})[2c,17,23] and the trimethylsilyl substituent {$\bar{\nu}$ [$\delta_{as}(CH_3)$] = 1247 cm^{-1}).[2c,17,23] Absorptions due to the C−N,[24] Ta−N,[24] and Ta−C[2c,17,23] stretching vibrations are observed at $\bar{\nu}$ 1179, 575, and 501 cm^{-1}, respectively.

The NMR spectra (^{1}H, ^{13}C{^{1}H}, tocsy1d, gHMQC) of both complexes **5** and **6** (see Experimental Section) show all the expected resonances for 2,6-dimethylphenyl and cyclopentadienyl rings and an ABCD spin system for the methylene groups of the Ta−*CH_2*−*CH_2*−CMe_2− moiety at δ 2.7, 2.08 (δ ^{13}C = 79.3) and 3.3, 2.16 (δ ^{13}C = 43.73) (**5**), with typical values of the proton−proton coupling constants. Moreover, the spectrum of complex **5** presents two signals for the methyl groups −C*Me_2*− that are in a very slow spin exchange process in accordance with the ^{1}H EXSY (noesy1d; mix time = 500 ms) spectrum, while in complex **6** the rate of the spin exchange is higher, in agreement with the observation of only one broad resonance at δ 0.89 (δ ^{13}C = 27.47).

On the other hand, **1** reacts with propylene (1 atm) at room temperature in benzene-d_6 or toluene to give

Scheme 6. Synthesis of Dichloro Azatantalacyclopentene Complexes



an unresolved mixture of different species, from which only the dichloro(imido)tantalum complex **7**[2a,21] was characterized. However, when the reaction of **1** with propylene in dichloromethane-d_2 was monitored by ^{1}H NMR spectroscopy, the formation of the dichloro azatantalacyclopentane complex [TaCp*Cl_2{CH_2CH(Me)-CMe_2NAr-κ^2*C*,*N*}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **9**) was proposed, in accord with the observation in the *tocsy1d* spectrum of the resonances at δ −0.28 (dd, 1H, ^2J = 3.9 Hz, ^3J = 5.4 Hz), 0.27 (dd, 1H, ^2J = 3.9 Hz, ^3J = 8.44 Hz), 0.43 (ddq, 1H, ^3J = 5.4 Hz, ^3J = 8.44 Hz, ^3J = 6.03 Hz), and 0.93 (d, 3H, ^3J = 6.03 Hz) for the Ta−*CH_2*−*$CHMe$*−CMe_2− moiety, respectively.

An unidentified mixture of several compounds was obtained by treatment of the dichloro azatantalacyclopropane complex **2** with propylene. Attempts to synthesize new azatantalacyclopentane complexes using 2-butene, styrene, *p*-metoxiphenylethylene, and 1-methoxy-2-phenylethylene were unsuccessful.

Synthesis of Dichloro Azatantalacyclopentene Complexes. Dichloro azatantalacyclopropane complexes **1** and **2** react quickly with alkynes RC≡CH (R = H, Ph, $SiMe_3$) at room temperature in toluene, leading to the dichloro azatantalacyclopentene complexes [$TaCpCl_2$(CRCHCMe_2NAr-κ^2*C*,*N*)] (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, R = H, **10**; Ph, **11**; $SiMe_3$, **12**; Cp = η^5-$C_5H_4SiMe_3$, R = H, **13**; Ph, **14**; $SiMe_3$, **15**), as result of the insertion of the alkyne into the Ta−C bond of the starting product (Scheme 6). All the complexes **10**−**15** are soluble in most organic solvents including saturated hydrocarbons. They are extremely air- and moisture-sensitive, so rigorously dried solvents and handling under dry inert atmosphere were found to be imperative for successful preparations. All of them were isolated as microcrystalline solids in good yields and are stable under argon atmosphere over a period of several weeks. Further, complexes **10**−**15** are more stable than the azatantalacyclopentane derivatives **5** and **6** proceeding from the olefin insertion, probably due to their higher electronic density delocalization.

The spectroscopic and analytical data for the complexes **10**−**15** are in agreement with the proposed structures. The NMR spectra show the disappearance of the signals for free acetylenes, a very large deshielding of the proton ($\Delta\delta$ > 5) and carbon ($\Delta\delta$ > 100)

(22) NMR spectroscopic data for [Ta(η^5-$C_5H_4SiMe_3$)Cl_2{N(C_6H_3-Me_2)}], **8**. ^{1}H NMR (δ ppm, in benzene-d_6): 6.96 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 6.63 [t, 2H, $^3J_{H-H}$ = 7.5 Hz, Ta=N(2,6-Me_2C_6**H**$_3$)], 6.14 (m, 2H), 5.9 (m, 2H, C_5**H**$_4$$SiMe_3$), 2.47 [s, 6H, Ta=N(2,6-**Me**$_2C_6H_3$)], 0.15 (s, 9H, C_5H_4Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 153 (C_i), 135.4 (C_o), 127.3 (C_p), 124.9 [C_m, Ta=N(2,6-Me_2**C**$_6H_3$)], 124.5 (C_i), 121.5 ($C_{2,5}$), 112.9 ($C_{3,4}$,**C**$_5H_4SiMe_3$), 19.1 [Ta=N(2,6-**Me**$_2C_6H_3$)], −0.75 (C_5H_4-Si**Me**$_3$).

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Table 1. Selected ^{1}H and ^{13}C Chemical Shifts for Complexes 10−15

R	Cp[a]	C_1−H	C_2−H
H	Cp*, **10**	205/8.25	147.3/7.36
	Cp′, **13**	198.75/8.37	147.1/7.35
Ph	Cp*, **11**	213.5/−	155.5/7.31
	Cp′, **14**	210/−	150.3/7.02
$SiMe_3$	Cp*, **12**	222.6/−	159.1/8.32
	Cp′, **15**	216.3/−	161.2/8.25

[a] Cp* = η^5-C_5Me_5. Cp′ = η^5-$C_5H_4SiMe_3$.

resonances, and a decrease of the direct carbon−proton coupling constant ($\Delta J \approx 100$ Hz) values, in accord with the hybridization change[25] of the carbon atoms from sp to sp^2 due to the alkyne insertion reaction into the Ta−C bond of the starting azatantalacyclopropane complexes.

The resonances due to C_1−H and C_2−H protons in complexes **10** and **13** were assigned on the basis of their correlations with corresponding carbon signals and by a NOESY experiment. In the NMR spectra of complexes **11**, **14** (R = Ph) and **12**, **15** (R = $SiMe_3$) we observed only one set of the signals indicating the regioselectivity of the insertion processes. The analysis of the proton and carbon chemical shifts for the Ta−*CR*═*CH*−CMe_2− moiety did not allow the assignment of the $SiMe_3$ position in complexes **12** and **15**, since the experimental values of δ (see Table 1) obtained from gHMQC and gHMBC data indicate different positions. However, the results of the noesy1d experiment show that the phenyl (**11**, **14**) and trimethylsilyl (**12**, **15**) groups fill the closest position to the cyclopentadienyl ring.

This result reflects the pure electronic control, not steric, in the insertion process of polarized unsaturated molecules into the Ta−C bond of **1** and **2**, which probably takes place in the transition state of the isomerization process in the starting azatantalacyclopropane complexes, as we have earlier proposed.[2a]

Unfortunately, the insertion of diphenylacetylene, 2-butyne, and tertbutylacetylene does not occur.

At room temperature, the ^{1}H NMR spectra show some very broad ($\Delta\nu_{1/2} > 50$ Hz) for **13**−**15** and slightly broad ($\Delta\Delta\nu_{1/2} \approx 2$ Hz) for **11**, **12** resonances due to mutual spin exchange between the −C*Me*$_2$−, −N−C_6H_3*Me*$_2$, and C_5*H*$_4$$SiMe_3$ resonances. This spectral behavior consists in an interconversion process of two four-legged piano-stool enantiomeric species with a trigonal bipyramidal transition state with C_s symmetry (see Scheme 7). The collapse point for −CMe_2− resonances was found for complexes **13** ($\Delta G^{\#236.2K}_{col} = 50.6$ kJ·mol^{-1}) and **15** ($\Delta G^{\#307K}_{col} = 63.5$ kJ·mol^{-1}). The same process was observed for complexes **5** and **6**.

The molecular structures of compounds **11** and **14** were determined by X-ray diffraction methods and are shown in the Figures 1 and 2, while selected bond distances and angles are presented in Tables 2 and 3, respectively. In the crystals of these compounds, one molecule of benzene (**11**) and toluene (**14**) solvate is present for each complex molecule.

Both complexes **11** and **14** can be described as monomers with a typical four-legged piano-stool environment for the tantalum atom, with a cyclopentadienyl ring in the cap position and the legs defined by two chlorine, the nitrogen, and one carbon atom included in an azatantalacyclopentene unit TaC_3N, in which the bonding corresponds to a diene with a double bond

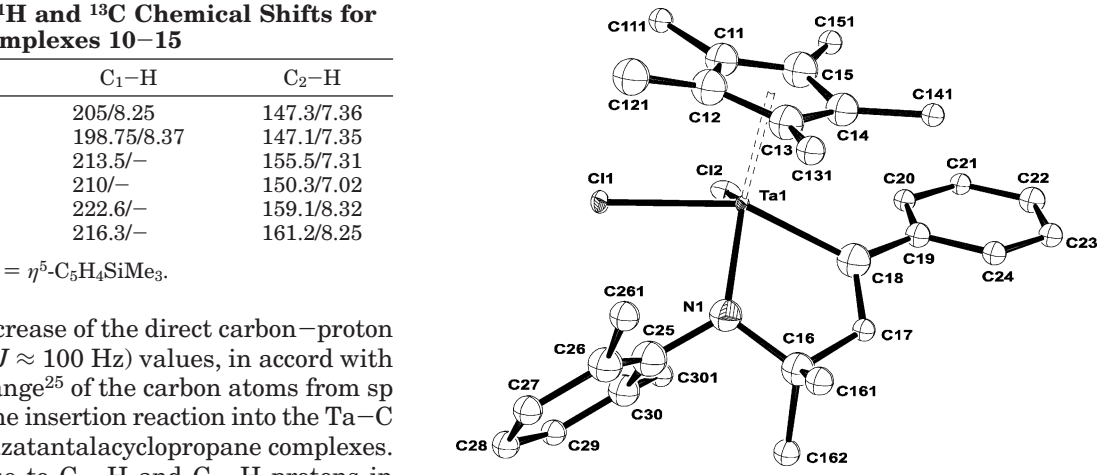

Figure 1. ORTEP drawing of compound **11**.

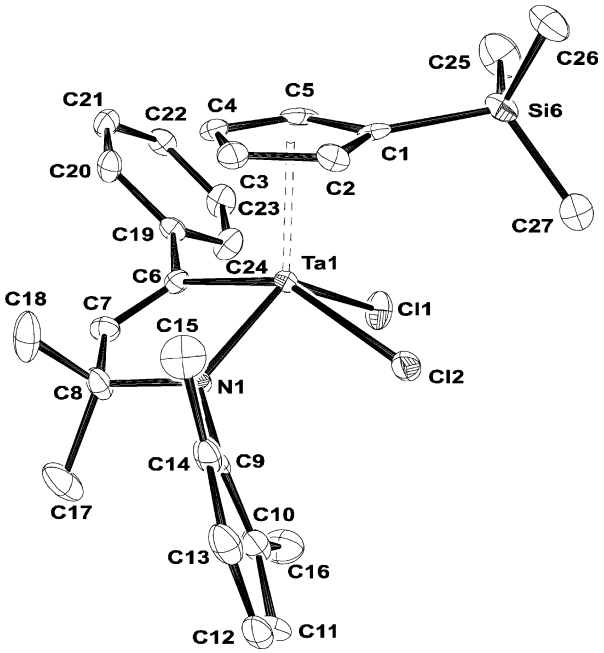

Figure 2. ORTEP drawing of compound **14**.

Ta−N (values 2.010(10) Å for **11** and 1.995(4) Å for **14**) and between the carbon atoms α and β with respect to the tantalum atom (C18−C17 1.338(16) Å for **11** and C6−C7 1.320(6) Å for **14**). The distance Ta−C_α (Ta−C18 2.219(10) Å in **11** and Ta−C6 2.207(4) Å in **14**) is typical for a single bond. The azatantalacyclopentene ring is fairly planar, the corresponding fold angle being defined between the N(1), Ta(1), C_α and N(1), C_α, C_β, $C_{\beta'}$ planes as 15.6(4)° and 14.5(1)°, respectively.

Although in the literature there have been reported a few azatantalacycles, the bonding situation found is different from that observed in complexes **11** and **14**. So, in the complex [TaCpMe{C(Ph)C(Ph)C(Me)N(*t*Bu)}] (Cp = η^5-C_5H_5)[26] the TaC_3N ring is folded 120° and the Ta−C and Ta−N distances in the metallacycle are both 1.98(1) Å and are commensurate with Ta═C and Ta═N double bonds. So, the authors suggest that the ring structure is a derivative of a metallacyclopentatriene. On the other hand, the complexes [TaCp*Cl_2(supine-

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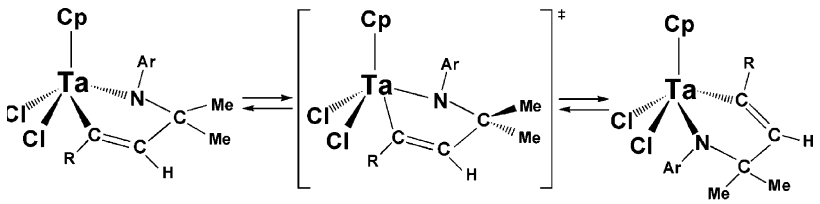
Scheme 7. Isomerization Process in Azatantalacyclopentene Complexes



Ar=2,6-$Me_2C_6H_3$
Cp=Cp*=η^5-C_5Me_5, R=Ph, **11**; $SiMe_3$, **12**
Cp=Cp′=η^5-$C_5H_4SiMe_3$, R=Ph, **14**; $SiMe_3$, **15**

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compound 11

Ta(1)−N(1)	2.010(10)	Ta(1)−C(18)	2.219(10)
Ta(1)−Cl(2)	2.366(3)	Ta(1)−Cl(1)	2.441(3)
Ta(1)−C(11)	2.494(12)	Ta(1)−C(12)	2.491(11)
Ta(1)−C(13)	2.408(11)	Ta(1)−C(14)	2.458(12)
Ta(1)−C(15)	2.535(12)	N(1)−C(25)	1.481(14)
N(1)−C(16)	1.527(15)	C(16)−C(17)	1.493(15)
C(17)−C(18)	1.338(16)	C(18)−C(19)	1.516(15)
N(1)−Ta(1)−C(18)	76.7(4)	N(1)−Ta(1)−Cl(2)	113.4(3)
C(18)−Ta(1)−Cl(2)	88.2(3)	N(1)−Ta(1)−Cl(1)	82.4(3)
C(18)−Ta(1)−Cl(1)	152.3(3)	Cl(2)−Ta(1)−Cl(1)	83.6(1)

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Compound 14

Ta(1)−N(1)	1.995(4)	Ta(1)−C(6)	2.207(4)
Ta(1)−Cl(1)	2.346(1)	Ta(1)−Cl(2)	2.413(1)
Ta(1)−C(1)	2.504(5)	Ta(1)−C(2)	2.403(4)
Ta(1)−C(3)	2.381(4)	Ta(1)−C(4)	2.411(4)
Ta(1)−C(5)	2.479(4)	Si(6)−C(1)	1.901(5)
Si(6)−C(25)	1.848(6)	Si(6)−C(26)	1.873(5)
Si(6)−C(27)	1.846(5)	N(1)−C(9)	1.457(5)
N(1)−C(8)	1.521(6)	C(6)−C(7)	1.320(6)
C(6)−C(19)	1.496(6)	C(7)−C(8)	1.483(6)
N(1)−Ta(1)−Cl(1)	119.8(1)	N(1)−Ta(1)−C(6)	76.1(2)
C(6)−Ta(1)−Cl(1)	85.4(1)	N(1)−Ta(1)−Cl(2)	84.9(1)
C(6)−Ta(1)−Cl(2)	150.5(1)	Cl(1)−Ta(1)−Cl(2)	84.7(1)

R_2-AD)] (Cp* = η^5-C_5Me_5; R_2-AD = 1,4-diphenyl-1-aza-1,3-butadiene;[27a] 1-*o*-tolyl-4-phenyl-1-aza-1,3-butadiene[27b]) exhibit a similar structure with typical double bond Ta=N (2.010(7) Å) and C_β=$C_{\beta'}$ (1.39(1) Å) distances. The TaC_3N ring presents an important folding effect of 103.8(3)° but smaller than in the case mentioned above. Further, the three carbon atoms of the cycle have similar bond distances (ranging from 2.322(8) Å for C_α to 2.437(9) Å for C_β), and due to this, the AD ligand coordinates to the tantalum atom with the contribution of the η^1-*N*-η^3-allyl canonical form. In our case, the lack of a π-bonding interaction between the metal center and the three carbon atoms of the cycle is also confirmed by a reinforcement of the Ta−Cl bond trans to the nitrogen atom. Both structures show very short Ta−Cl2 (2.366(3) Å in **11**) and Ta−Cl1 (2.346(1) Å in **14**) bond distances.

The 2,6-$Me_2C_6H_3$ ring bonded to the nitrogen atom is located in both structures quasi perpendicular to the cyclopentadienyl ring plane (62.1(4)° in **11** and 71.8(1)° in **14**), while the phenyl ring bonded to the carbon atom exhibits a very different position, being in complex **11** fairly parallel to the pentamethylcyclopentadienyl ring (10.6(4)°) and in complex **14** bending toward the trimethylsilylcyclopentadienyl ring with an angle between both ring planes of 40.9(1)°, in agreement with the different steric hindrance of the cyclopentadienyl moieties.

Conclusions

In this paper we report a study of the alkylation and insertion reactions in dichloro azatantalacyclopropane complexes. So, a stable 16-electron chloro(imido) 2-propenyl compound [TaCp*Cl{C(Me)=CH_2}(NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **4**) is obtained by treating the dichloro azatantalacyclopropane complex **1** with different alkylating reagents with elimination of a hydrocarbon and via intermediate alkyl chloro azatantalacyclopropane species [TaCp*ClR(CMe_2NAr-κ^2C,N)] characterized for R = CH_2SiMe_3, **3**. The ethylene and propene insertion reactions into the Ta−C bond of the azatantalacyclopropane system lead to dichloro azatantalacyclopentane complexes [$TaCpCl_2${CH_2CH(R)CMe_2-NAr-κ^2C,N}] (Cp = η^5-C_5Me_5, R = H, **5**; Me, **9**; Cp = η^5-$C_5H_4SiMe_3$, R = H, **6**), being a regioselective and very slow process in the case of the propene insertion. However, complexes **5** and **6** decompose in benzene-d_6 or toluene solutions at room temperature, leading to a dichloro(imido)tantalum compound [$TaCpCl_2$(NAr)] (Cp = η^5-C_5Me_5, **7**; η^5-$C_5H_4SiMe_3$, **8**) with elimination of 2-methyl-2-butene and 3-methyl-1-butene (decomposition of **5**) and only 2-methyl-2-butene (decomposition of **6**). The alkyne insertion reaction is faster and gives dichloro azatantalacyclopentene complexes [$TaCpCl_2$-(CRCHCMe_2NAr-κ^2C,N)] (Cp = η^5-C_5Me_5, R = H, **10**; Ph, **11**; $SiMe_3$, **12**; Cp = η^5-$C_5H_4SiMe_3$, R = H, **13**; Ph, **14**; $SiMe_3$, **15**), which are more stable than the azatantalacyclopentane complexes due to the delocalization of the electronic density along the Ar−N−Ta−C=C bond system. Further, the monosubstitued alkyne insertion reaction is regiospecific and takes place with the formation of the unitary products **11**, **12**, **14**, and **15** with the phenyl and trimethylsilyl groups oriented to the cyclopentadienyl ring, as confirmed by the corresponding structural studies.

Experimental Section

All operations were carried out under a dry argon atmosphere using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glovebox. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: benzene-d_6 and hexane (Na/K alloy) and toluene (Na). Starting materials Ta(η^5-$C_5H_4SiMe_3$)Cl_4,[28] Ta(η^5-$C_5H_4SiMe_3$)Cl_2Me_2,[15] [Ta(η^5-C_5Me_5)Cl_2{CMe_2N(2,6-$Me_2C_6H_3$)-

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(28) Gómez, M.; Royo, P.; Selas, J. M. *J. Organomet. Chem*. **1986**, *314*, 131−138.

κ^2C,N}],[2a] and $Mg(CH_2Ph)_2(thf)_2$[29] were prepared as described previously. Reagent grade C_2H_4 (Air Líquide), $H_2C{=}CH{-}CH_3$ (Air Líquide), C_2H_2 (Air Líquide), RC≡CH (R = Ph, $SiMe_3$, Aldrich), $MgCl(CH_2SiMe_3)$ (1 M in diethyl ether, Aldrich), $ZnMe_2$ (2 M in toluene, Aldrich), and 2,6-$Me_2C_6H_3NC$ (Fluka) were purchased from commercial sources and were used without further purification.

Samples for infrared spectroscopy were prepared as Nujol mulls between CsI pellets or in KBr pellets and recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer (4000−400 cm^{-1}). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Unity-300 and/or Unity Plus-500 (Varian) spectrometer; chemical shifts were referenced to the ^{13}C (δ = 128) and residual ^1H (δ = 7.15) resonances of the benzene-d_6 solvent. Microanalyses (C, H, N) were performed in a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of [Ta(η^5-$C_5H_4SiMe_3$)Cl_2(CMe_2NAr-κ^2C,N)] (Ar = 2,6-$Me_2C_6H_3$, 2). A yellow solution of Ta(η^5-$C_5H_4SiMe_3$)Cl_2Me_2 (1.00 g, 2.38 mmol) in toluene (60 mL) was treated with 2,6-$Me_2C_6H_3NC$ (0.31 g, 2.38 mmol) under rigorously anhydrous conditions for 2 h. The solution was filtered, concentrated to ca. 10 mL, and cooled to −40 °C to give **2** as garnet crystals.

The data for **2** follow. Yield: 1.05 g (81%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2947(m), 1456(s), 1400(m), 1371(m), 1274(s), 1247(s), 1193(m), 1173(s), 1104(m), 1039(m), 906(s), 839(vs), 762(s), 631(m), 576(w), 512(w), 420(m). ^1H NMR (δ ppm, in benzene-d_6): 7.09 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 6.95 [t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-$Me_2C_6\mathbf{H}_3$)−], 6.21 (m, 2H), 5.86 (m, 2H, $C_5\mathbf{H}_4SiMe_3$), 2.23 [s, 6H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 2.20(s, 6H, Ta−C$\mathbf{Me}_2$−), 0.28 (s, 9H, $C_5H_4Si\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 151.6 (C_i), 134.1 (C_o), 129.2 (C_m), 125.7 [C_p, Ta−N(2,6-$Me_2\mathbf{C}_6H_3$)−], 125.2 (C_i), 124.7 ($C_{2,5}$), 112.1 ($C_{3,4}$, $\mathbf{C}_5H_4SiMe_3$), 90.6 (Ta−$\mathbf{C}Me_2$−), 30.7 (Ta−C$\mathbf{Me}_2$−), 20.2 [Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], −0.2 ($C_5H_4Si\mathbf{Me}_3$). Anal. Calcd for $C_{19}H_{28}Cl_2NSiTa$: C, 41.46; H, 5.13; N, 2.55. Found: C, 41.31; H, 5.01; N, 2.63.

Synthesis of [TaCp*Cl(CH_2SiMe_3)(CMe_2NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 3). A 1 M solution of $MgCl(CH_2SiMe_3)$ in OEt_2 (2.00 mL, 2.40 mmol) was added at −78 °C to a solution of **1** (0.50 g, 0.91 mmol) in toluene (30 mL), and the mixture was stirred for 30 min. It was warmed to room temperature for 12 h, the solvent was removed in vacuo, and the residue was extracted into hexane (3 × 10 mL). The solution was concentrated to ca. 10 mL and cooled to −40 °C overnight to give **3** as a yellow microcrystalline solid.

The data for **3** follow. Yield: 0.32 g (59%). IR (Nujol mull, $\bar{\nu}$ cm^{-1}): 1580(w), 1550(m), 1420(m), 1245(s), 1225(m), 1105(m), 1090(m), 1026(m), 975(m), 785(s), 769(s), 574(m), 490(w), 475(w). ^1H NMR (δ ppm, in benzene-d_6): 7.02 [d, 2H, $^3J_{H-H}$ = 7.6 Hz], 6.93 [t, 1H, $^3J_{H-H}$ = 7.6 Hz, Ta−N(2,6-$Me_2C_6\mathbf{H}_3$)−], 2.33 (s, 3H), 2.25 [s, 3H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 2.09 (s, 3H), 2.01 (s, 3H, Ta−C$\mathbf{Me}_2$−), 1.65(s, 15H, $C_5\mathbf{Me}_5$), 1.60, 1.31 (AB, 2H, $^2J_{H-H}$ = 11.3 Hz, Ta−C$\mathbf{H}_2SiMe_3$), 0.30 (s, 9H, Ta−CH_2-Si$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 150.3 (C_i), 133.6 (C_o), 128.7 (C_m), 124.7 [C_p, Ta−N(2,6-$Me_2C_6H_3$)−], 118.5 ($\mathbf{C}_5Me_5$), 91.8 (Ta−$\mathbf{C}Me_2$−), 71.7 (Ta−$\mathbf{C}H_2SiMe_3$), 30, 26.8 (Ta−C$\mathbf{Me}_2$−), 20.8, 20.3 [Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 10.7 ($C_5\mathbf{Me}_5$), 2.8 (Ta−$CH_2Si\mathbf{Me}_3$). Anal. Calcd for $C_{25}H_{41}ClNSiTa$: C, 50.04; H, 6.89; N, 2.33. Found: C, 50.10; H, 6.90; N, 2.30.

Synthesis of [TaCp*Cl{C(Me)=CH_2}(NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 4). A toluene (10 mL) solution of $Mg(CH_2Ph)_2(thf)_2$ (0.32 g, 0.91 mmol or 0.16 g, 0.46 mmol) was added at −78 °C to a solution of **1** (0.50 g, 0.91 mmol) in toluene (25 mL), and the mixture was stirred for 30 min. The color of the mixture changed slowly from reddish to yellow. It was then warmed to room temperature for 10 h, the solvent removed in vacuo, and the resulting residue extracted with hexane (3 × 10 mL). The solution was filtered, concentrated to ca. 10 mL, and cooled to −40 °C to give **4** as a yellow microcrystalline solid. Yield: 0.25 g (54%).

4 can be isolated with a similar yield by treatment of **1** with $Mg(CH_2CMe_3)_2(thf)_2$, MgClR (R = CH_2CMe_2Ph, CH_2Ph, CH_2CMe_3). and/or LiR (R = CH_2CMe_2Ph, CH_2Ph, CH_2CMe_3) in a 1:1 or 1:2 molar ratio or in excess. Alternatively, the benzene-d_6 or toluene solution of complex **3** slowly decomposes at room temperature to give **4** in good yield.

The data for **4** follow. IR (Nujol mull, $\bar{\nu}$ cm^{-1}): 1588(m), 1545(m), 1415(m), 1314(vs), 1285(w), 1158(m), 1137(m), 1095(m), 1025(m), 982(m), 930(m), 902(s), 799(m), 757(s), 624(m), 590(w), 450(w), 440(w). ^1H NMR (δ ppm, in benzene-d_6): 7.03 [d, 2H, $^3J_{H-H}$ = 7.6 Hz], 6.72 [t, 1H, $^3J_{H-H}$ = 7.6 Hz, Ta−N(2,6-$Me_2C_6\mathbf{H}_3$)], 5.83 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^2J_{H-H}$ = 0.6 Hz), 4.96 [dq, 1H, $^4J_{H-H}$ = 1.2 Hz, $^2J_{H-H}$ = 0.6 Hz, Ta−C(Me)=C$\mathbf{H}_2$], 2.55 [s, 6H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)], 2.46 [dd, 3H, $^4J_{H-H}$ = 1.5;1, 2 Hz, Ta−C($\mathbf{Me}$)=CH_2], 1.77 (s, 15H, $C_5\mathbf{Me}_5$). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 212.2 [Ta−$\mathbf{C}$(Me)=CH_2], 153.1 (C_i), 134.6 (C_o), 127.6 (C_m), 123.1 [C_p, Ta−N(2,6-$Me_2\mathbf{C}_6H_3$)], 118.7 [Ta−C(Me)=$\mathbf{C}H_2$], 118.5 ($\mathbf{C}_5Me_5$), 34 [Ta−C($\mathbf{Me}$)=CH_2], 20 [Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)], 11.2 ($C_5\mathbf{Me}_5$). Anal. Calcd for $C_{21}H_{29}ClNTa$: C, 47.27; H, 5.71; N, 2.73. Found: C, 47.36; H, 5.81; N, 2.70.

Synthesis of [TaCpCl_2($CH_2CH_2CMe_2NAr$-κ^2C,N)] (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, 5; η^5-$C_5H_4SiMe_3$, 6). A solution of **1** or **2** (1.00 g, 1.81 mmol) in toluene (40 mL) was placed into a Schlenk tube and the argon atmosphere replaced by ethylene (1 atm). Under rigorously anhydrous conditions the solution was stirred for 2 h and the resulting reddish solution was concentrated to ca. 10 mL and cooled overnight at −40 °C to yield **5** or **6** as red microcrystalline solids.

The data for **5** follow. Yield: 0.68 g (65%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2910(vs), 1646(w), 1586(w), 1452(vs), 1376(s), 1258(m), 1172(vs), 1147(s), 1098(s), 1073(m), 1023(s), 949(m), 864(m), 796(w), 765(s), 596(w), 524(w), 492(w). ^1H NMR (δ ppm, in benzene-d_6): 7.05 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 6.92 [t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-$Me_2C_6\mathbf{H}_3$)−], 3.30 (m, 1H, −C$\mathbf{H}_2$−CMe_2−), 3.10 [s, 3H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 2.70 (m, 1H, Ta−C$\mathbf{H}_2$−), 2.16 (m, 1H, −C$\mathbf{H}_2$−CMe_2−), 2.08 (m, 1H, Ta−C$\mathbf{H}_2$−), 2.07 [s, 3H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)], 1.96 (s, 15H, $C_5\mathbf{Me}_5$), 1.08 (s, 3H, −CH_2−C$\mathbf{Me}_2$−), 0.81 (s, 3H, −CH_2−C$\mathbf{Me}_2$−). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 158.92 (C_i), 128.74 (C_o), 127.45 (C_m), 124.64 [C_p, Ta−N(2,6-$Me_2\mathbf{C}_6H_3$)], 126.08 ($\mathbf{C}_5Me_5$), 79.38 (Ta−$\mathbf{C}H_2$−), 78.03 (−CH_2−$\mathbf{C}Me_2$−), 43.73 (−$\mathbf{C}H_2$−CMe_2−), 30.45, 26.94 (−CH_2−C$\mathbf{Me}_2$−), 22.94, 21.23 [Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 12.40 ($C_5\mathbf{Me}_5$). Anal. Calcd for $C_{23}H_{34}Cl_2NTa$: C, 47.93; H, 5.95; N, 2.43. Found: C, 47.86; H, 5.60; N, 2.39.

The data for **6** follow. Yield: 0.89 g (86%). ^1H NMR (δ ppm, in benzene-d_6): 6.98 (d, 2H, $^3J_{H-H}$ = 7.4 Hz), 6.86 [t, 1H, $^3J_{H-H}$ = 7.4 Hz, Ta−N(2,6-$Me_2C_6\mathbf{H}_3$)−], 6.17 (br, 4H, $C_5\mathbf{H}_4SiMe_3$), 3.05−2.59 (m, 4H, Ta−C$\mathbf{H}_2$−C$\mathbf{H}_2$−), 2.4 [br, 6H, Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], 0.89 (s, 6H, −CH_2−C$\mathbf{Me}_2$−), 0.26 (s, 9H, C_5H_4-Si$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 155.88 (C_i), 135.0 (C_o), 128.84 (C_m), 125.52 [C_p, Ta−N(2,6-$Me_2\mathbf{C}_6H_3$)−], 128.6 (C_i, $\mathbf{C}_5H_4SiMe_3$), 116.15 ($\mathbf{C}_5H_4SiMe_3$), 75.93 (−CH_2−$\mathbf{C}Me_2$−), 72.11 (Ta−$\mathbf{C}H_2$−), 38.25 (−$\mathbf{C}H_2$−CMe_2−), 27.47 (−CH_2−C$\mathbf{Me}_2$−), 22.07 [Ta−N(2,6-$\mathbf{Me}_2C_6H_3$)−], −0.13 (C_5H_4-Si$\mathbf{Me}_3$). Repeated attempts to obtain a satisfactory microanalysis on this material were unsuccessful.

Synthesis of [TaCpCl_2(CHCHCMe$_2$NAr-κ^2C,N)] (Ar = 2,6-$Me_2C_6H_3$; Cp = η^5-C_5Me_5, 10; η^5-$C_5H_4SiMe_3$, 13). Under rigorously anhydrous conditions, a toluene (35 mL) solution of **1** or **2** (1.00 g, 1.81 mmol) was placed into a Schlenk tube and the argon atmosphere replaced by acetylene (1 atm). The reaction mixture was stirred at room temperature 4 h. The resulting solution was filtered, and the filtrate was concentrated to a volume of ca. 10 mL. Cooling at −40 °C overnight led to the deposition of microcrystalline yellow solids identified as **10** and **13**

(29) Schrock, R. R. *J. Organomet. Chem*. **1976**, *122*, 209−225.

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The data for **10** follow. Yield: 0.75 g (72%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2910(s), 1650(w), 1582(m), 1457(s), 1375(s), 1305(w), 1251(w), 1182(vs), 1159(s), 1097(m), 1021(m), 949(m), 901(s), 879(m), 813(m), 760(s), 547(w), 508(m), 426(w). ^{1}H NMR (δ ppm, in benzene-d_6): 8.25 (d, 1H, $^2J_{H-H}$ = 9.8 Hz, Ta−C**H**=CH−), 7.36 (d, 1H, $^2J_{H-H}$ = 9.8 Hz, Ta−CH=C**H**−), 7.07 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 6.92 [t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 2.98 (s, 3H), 2.09 [s, 3H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−],1.96 (s, 15H, C$_5$**Me**$_5$), 0.98 (s, 6H, −CH=CH−C**Me**$_2$−). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 205 (Ta−**C**H=CH−), 147.3 (Ta−CH=**C**H−), 138.3 (C$_i$), 131.0 (C$_o$), 128.7 (C$_m$), 126.5 [C$_p$, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 124.7 (**C**$_5$Me$_5$), 85.0 (−CH=CH−**C**Me$_2$−), 32, 26.6 (−CH=CH−C**Me**$_2$−), 22.9, 21.1 [Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 12.5 (C$_5$**Me**$_5$). Anal. Calcd for C$_{23}$H$_{32}$Cl$_2$NTa: C, 48.09; H, 5.62; N, 2.44. Found: C, 48.03; H, 5.90; N, 2.61.

The data for **13** follow. Yield: 0.30 g (30%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2977(m), 1585(m), 1458(s), 1380(m), 1250(s), 1177(s), 1100(m), 1046(m), 905(s), 842(vs), 766(s), 631(w), 510(w), 418(w). ^{1}H NMR (δ ppm, in benzene-d_6): 8.37 (d, 1H, $^2J_{H-H}$ = 9.5 Hz, Ta−C**H**=CH−), 7.35 (d, 1H, $^2J_{H-H}$ = 9.5 Hz, Ta−CH=C**H**−), 7.05 (d, 2H, $^3J_{H-H}$ = 7.3 Hz), 6.88 [t, 1H, $^3J_{H-H}$ = 7.3 Hz, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 6.33 (m, 2H), 6.30 (m, 2H, C$_5$**H**$_4$SiMe$_3$), 2.47 [s, 6H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 0.94 (s, 6H, −CH=CH−C**Me**$_2$−), 0.24 (s, 9H, C$_5$H$_4$Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 198.75 (Ta−**C**H=CH−), 159.47 [C$_i$, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 147.09 (Ta−CH=**C**H−), 134.27 (C$_i$, **C**$_5$H$_4$SiMe$_3$), 132.06 (C$_o$), 128.44 (C$_m$), 125.16 [C$_p$, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 124.36 (C$_{2,5}$), 117.63 (C$_{3,4}$, **C**$_5$H$_4$SiMe$_3$), 85.8 (−CH=CH−**C**Me$_2$−), 25.45 (−CH=CH−C**Me**$_2$−), 21.69 [Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], −0.41 (C$_5$H$_4$Si**Me**$_3$). Anal. Calcd for C$_{21}$H$_{30}$Cl$_2$NSiTa: C, 43.75; H, 5.24; N, 2.43. Found: C, 43.85; H, 5.14; N, 2.60.

Synthesis of [TaCpCl$_2${C(Ph)CHCMe$_2$NAr-κ^2*C*,*N*}] (Ar = 2,6-Me$_2$C$_6$H$_3$; Cp = η^5-C$_5$Me$_5$, 11; η^5-C$_5$H$_4$SiMe$_3$, 14). A solution of **1** or **2** (0.50 g, 0.91 mmol) in toluene (30 mL) was treated with excess PhC≡CH (0.15 mL, 1.36 mmol) under rigorously anhydrous conditions. The mixture was stirred for 15 h and then filtered. The filtrate was concentrated to ca. 5 mL, and cooling overnight at −40 °C produced **11** or **14**, deposited as a red microcrystalline solids.

The data for **11** follow. Yield: 0.42 g (71%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2914(s), 1631(w), 1590(w), 1570(w), 1456(vs), 1377(s), 1298(w), 1253(w), 1176(vs), 1137(s), 1098(m), 1026(m), 963(m), 876(s), 806(m), 766(vs), 705(m), 599(w), 545(w), 476(w). ^{1}H NMR (δ ppm, in benzene-d_6): 7.65 [m, 2H, Ta−C(C$_6$**H**$_5$)=CH−], 7.31 [s, 1H, Ta−C(Ph)=C**H**−], 7.27 [t, 2H, Ta−C(C$_6$**H**$_5$)=CH], 7.14 [m, 1H, Ta−C(C$_6$**H**$_5$)=CH−], 7.10 (d, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.91 [t, 1H, $^3J_{H-H}$ = 7.2 Hz, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 3.01 (s, 3H), 2.18 [s, 3H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 1.94 (s, 15H, C$_5$**Me**$_5$), 1.13 (s, 3H), 0.81 (s, 3H, =CH−C**Me**$_2$−). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 213.6 [Ta−**C**(Ph)=CH−], 155−126 [several phenyl, Ta−C(**C**$_6$H$_5$)=CH−], 155−126 [several phenyl, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 146.53 [Ta−C(Ph)=**C**H−], 124.8 (**C**$_5$Me$_5$), 77.9 (=CH−**C**Me$_2$−), 32.9, 27.9 (=CH−C**Me**$_2$−), 22.9, 21.0 [Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 12.95 (C$_5$**Me**$_5$). Anal. Calcd for C$_{29}$H$_{36}$Cl$_2$NTa: C, 53.55; H, 5.58; N, 2.15. Found: C, 53.47; H, 5.49; N, 2.21.

The data for **14** follow. Yield: 0.35 g (62%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2966(s), 1829(w), 1768(w), 1590(s), 1460(s), 1323(w), 1289(w), 1247(s), 1172(s), 1137(s), 1098(m), 1075(m), 1053(m), 962(m), 905(s), 840(vs), 760(vs), 702(s), 629(m), 543(w), 482(w), 414(m). ^{1}H NMR (δ ppm, in benzene-d_6): 7.47−6.64 [several phenyl, Ta−C(C$_6$**H**$_5$)=CH−, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 7.02 [s, 1H, Ta−C(Ph)=C**H**−], 6.40 (m, 1H), 6.32 (m, 1H), 6.19 (m, 1H), 5.72 (m, 1H, C$_5$**H**$_4$SiMe$_3$), 2.94 (br, 3H), 2.16 [br, 3H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 0.92 (br, 6H, =CH−C**Me**$_2$−), 0.14 (s, 9H, C$_5$H$_4$Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 210 [Ta−**C**(Ph)=CH−], 160.33 [Ta−C(Ph)=**C**H−], 151.9−129.2 [several phenyl, Ta−C(**C**$_6$H$_5$)=CH−, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 126.1 (C$_i$), 125.5, 125.2, 123.3, 118.5 (**C**$_5$H$_4$SiMe$_3$), 82.1 (=CH−**C**Me$_2$−), 31.78 (br, =CH−C**Me**$_2$−), 26.54, 21.75 [br, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], −0.70 (C$_5$H$_4$Si**Me**$_3$). Anal. Calcd for C$_{27}$H$_{34}$Cl$_2$NSiTa: C, 49.69; H, 5.25; N, 2.15. Found: C, 49.73; H, 5.10; N, 2.23.

Table 4. Crystal Data and Structure Refinement for 11 and 14

	11	**14**
chem formula	C$_{29}$H$_{36}$NCl$_2$Ta·C$_6$H$_6$	C$_{27}$H$_{34}$NCl$_2$SiTa·C$_7$H$_8$
fw	728.55	744.63
T, K	100(2)	153(2)
λ (Mo, Kα), Å	0.71073	0.71073
cryst syst, space group	orthorhombic, *Pbca*	monoclinic, *P*2$_1$/*n*
a, Å	15.544(2)	17.621(1)
b, Å; β, deg	19.634(3)	8.3557(7); 102.76(1)
c, Å	20.140(7)	22.317(3)
V, Å^3	6147(2)	3204.7(6)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.575	1.545
μ, mm^{-1}	3.775	3.658
cryst size, mm	0.58 × 0.35 × 0.24	0.4 × 0.3 × 0.3
θ range, deg	3.18 to 27.5	5.01 to 27.51
index ranges	−19 ≤ *h* ≤ 19, −25 ≤ *k* ≤ 24, −25 ≤ *l* ≤ 25	−22 ≤ *h* ≤ 22, −10 ≤ *k* ≤ 10, −28 ≤ *l* ≤ 25
no. of data collected	37934	19331
no. of unique data	6304 [*R*(int) = 0.159]	7257 [*R*(int) = 0.108]
no. of obsd reflns [$I > 2\sigma(I)$]	4287	5685
absorp corr	Gaussian	semiempirical from equivalents
max. and min. transmn	0.293 and 0.172	1.644 and 0.580
no. of params refined	323	352
goodness-of-fit on F^2	1.060	1.009
final *R* indices[a]	R1 = 0.073, wR2 = 0.170	R1 = 0.040, wR2 = 0.093
R indices (all data)	R1 = 0.118, wR2 = 0.199	R1 = 0.061, wR2 = 0.101
largest diff peak and hole, e Å^{-3}	1.979 and −1.796	2.444 and −1.921

[a] R1 = $\sum||F_o| - |F_c||/[\sum|F_o|]$; wR2 = $\{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

Synthesis of [TaCp*Cl$_2${C(SiMe$_3$)CHCMe$_2$NAr-κ^2*C*,*N*}] (Cp* = η^5-C$_5$Me$_5$; Ar = 2,6-Me$_2$C$_6$H$_3$, 12). A 100 mL ampule (Teflon stopcock) was charged with **1** (0.40 g, 0.73 mmol), an excess of trimethylsilylacetylene (0.15 mL, 1.06 mmol), and toluene (20 mL). After the reaction mixture had been stirred at room temperature for 6 days the volatile components were removed under reduced pressure. The resultant oily reddish solid was washed with hexane (2 × 5 mL) and identified by ^{1}H NMR spectroscopy as a mixture of **12**, the starting material **1**, and the dichloro(imido) complex **7**. By successive recrystallization in toluene complex **12** can be isolated as a red solid but always impurified with **1** and the dichloro(imido) complex **7** as minority components.

The data for **12** follow. ^{1}H NMR (δ ppm, in benzene-d_6): 8.32 [s, 1H, Ta−C(SiMe$_3$)=C**H**−], 7.11 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 6.88 [t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 2.92 (s, 3H), 2.20 [s, 3H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 2.04 (s, 15H, C$_5$**Me**$_5$), 1.02 (s, 3H), 0.86 (s, 3H, =CH−C**Me**$_2$−), 0.37 [s, 9H, Ta−C(Si**Me**$_3$)=CH−]. ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 222.6 [Ta−**C**(SiMe$_3$)=CH−], 159.1 [Ta−C(SiMe$_3$)=**C**H−], 160−126 [several phenyl, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 124.7 (**C**$_5$Me$_5$), 84.5 (=CH−**C**Me$_2$−), 29.2, 27.8(=CH−C**Me**$_2$−), 22.9, 20.8 [Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 12.97 (C$_5$**Me**$_5$), 2.92 [Ta−C(Si**Me**$_3$)=CH−].

Synthesis of [TaCp′Cl$_2${C(SiMe$_3$)CHCMe$_2$NAr-κ^2*C*,*N*}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$, 15). A 100 mL Schlenk flask was charged with **2** (0.40 g, 0.73 mmol), excess Me$_3$SiC≡CH (0.15 mL, 1.06 mmol), and toluene (25 mL). After the mixture had been stirred at room temperature for 10 h,

the volume of the solution was concentrated to ca. 10 mL under reduced pressure. The resulting solution was cooled to −40 °C overnight to afford orange crystals of **15**.

The data for **15** follow. Yield: 0.32 g (68%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2949(s), 1585(w), 1553(m), 1461(m), 1410(m), 1371(m), 1287(w), 1245(s), 1179(s), 1138(m), 1096(m), 1049(m), 957(w), 878(s), 836(vs), 756(s), 648(m), 628(m), 589(w), 468(w), 442(w), 416(w). ^{1}H NMR (δ ppm, in benzene-d_6): 8.25 [s, 1H, Ta−C(SiMe$_3$)=C**H**−], 7.03 (d, 2H, $^3J_{H-H}$ = 7.4 Hz), 6.85 [t, 1H, $^3J_{H-H}$ = 7.4 Hz, Ta−N(2,6-Me$_2$C$_6$**H**$_3$)−], 6.5 (br, 4H, C$_5$**H**$_4$SiMe$_3$), 2.50 [br, 6H, Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 0.91 (br, 6H, =CH−C**Me**$_2$−), 0.36 [s, 9H, Ta−C(Si**Me**$_3$)=CH−], 0.26 (s, 9H, C$_5$H$_4$Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 216.32 [Ta−**C**(SiMe$_3$)=CH−], 157.93 [Ta−C(SiMe$_3$)=**C**H−], 161.17(C$_i$), 132.94 (C$_o$), 128.16 (C$_p$), 125.16 [C$_m$, Ta−N(2,6-Me$_2$**C**$_6$H$_3$)−], 124.9(C$_i$), 122.8 (**C**$_5$H$_4$SiMe$_3$), 86.79 (=CH−**C**Me$_2$−), 28.9 (=CH−C**Me**$_2$−), 21.57 [Ta−N(2,6-**Me**$_2$C$_6$H$_3$)−], 1.66 [Ta−C(Si**Me**$_3$)=CH−], 0.1 (C$_5$H$_4$Si**Me**$_3$). Anal. Calcd for C$_{24}$H$_{38}$Cl$_2$NSi$_2$Ta: C, 44.40; H, 5.90; N, 2.16. Found: C, 43.85; H, 5.99; N, 2.16.

Crystal Structure Determination of Compounds 11 and 14. Crystals suitable for the X-ray analyses were obtained by recrystallization from benzene (**11**) and toluene (**14**) solutions. The crystallographic and experimental details of the crystal structure determinations are given in Table 4. Suitable crystals of complexes **11** and **14** were covered with mineral oil and mounted in the N_2 stream of a Bruker-Nonius Kappa CCD diffractometer, and data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was performed at low temperature (see Table 4), in the case of compound **11** with an exposure time of 8 s per frame (3 sets; 286 frames) and compound **14** with an exposure time of 7 s per frame (4 sets; 316 frames). Raw data were corrected for Lorentz and polarization effects.

Both structures were solved by direct methods, completed by the subsequent difference Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL-97).[30] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms expect for seven atoms in compound **11**, which have some of the thermal parameters fixed in the last cycle of refinement. The hydrogen atoms were included from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.[31]

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Supporting Information Available: Tables of experimental details of the X-ray studies, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **11** and **14** and in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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