Alkylation, Insertion of Isocyanides, and Intramolecular Rearrangement Processes in Azatantalacyclopentene Complexes. X-ray Crystal Structure of [TaCp*Me_2(CHCHCMe_2NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$)§

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Chloro methyl and dimethyl azatantalacyclopentene complexes [TaCp*$Cl_{2-x}Me_x$(CHCHCMe_2NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$; x = 1, 2; 2, 3) can be prepared by reaction of [TaCp*Cl_2(CHCHCMe_2NAr-κ^2C,N)] (**1a**) with dimethylzinc and chloromethylmagnesium, respectively. Reaction of **1a** with dibenzylmagnesium leads to the monoalkylated complex [TaCp*Cl(CH_2Ph)(CHCHCMe_2NAr-κ^2C,N)] (**4**). The alkylation of [TaCp*Cl_2{C(Ph)CHCMe_2NAr-κ^2C,N}] (**1b**) with 2 equiv of chloromethylmagnesium at low temperature gave the dimethyl azatantalacyclopentene complex [TaCp*Me_2{C(Ph)CHCMe_2NAr-κ^2C,N}] (**5**), which at room temperature decomposes, giving the dimethyl(imido) complex [TaCp*Me_2(NAr)] (**7**), identified by NMR spectroscopy. Alkylation of **1b** with 0.5 equiv of dibenzylmagnesium leads to the monobenzyl complex [TaCp*Cl(CH_2Ph){C(Ph)CHCMe_2NAr-κ^2C,N}] (**6**); however treatment with 1 equiv of the alkylating reagent gave the dibenzyl(imido) [TaCp*(CH_2Ph)$_2$(NAr)] (**8**) in a mixture with **6** as minor component. Moreover, **1a** reacts with 1 equiv of isocyanides RNC (R = 2,6-$Me_2C_6H_3$; *t*Bu) to give the dichloro(imido) complex [TaCp*Cl_2(NAr)] (**9**), while the treatment of the chloro methyl azatantalacyclopentene **2** with 2 equiv of isocyanides RNC (R = 2,6-$Me_2C_6H_3$; *t*Bu) at different conditions affords the imido η^2-iminoacyl derivatives [TaCp*Cl(NAr){η^2-C(Me)=NR}] (R = 2,6-$Me_2C_6H_3$, **12**; *t*Bu, **13**) in good yields with simultaneous elimination of *s-trans*-vinylazacumulenes R−N=C=CH−CH=CMe_2 (R = 2,6-$Me_2C_6H_3$, **10**; *t*Bu, **11**). Similarly, the reaction of the dimethyl azatantalacyclopentene **3** with 1 equiv of 2,6-$Me_2C_6H_3$NC produces the alkenylamido imido methyl derivative [TaCp*Me(NAr){η^1-N(Ar)-C(Me)=CH−CH=CMe_2}] (**14**), which with one additional equivalent of isocyanide gives the imido η^2-iminoacyl methyl compound [TaCp*Me(NAr)(η^2-C{CH(CMe=NAr)(CH=CMe_2)}=NAr)] (**15**). All compounds were studied by IR and NMR spectroscopy, and the molecular structure of complex **3** was determined by X-ray diffraction methods.

Introduction

Mono- and bis(cyclopentadienyl) complexes of early transition metals are well established as important types of olefin polymerization catalysts.[1] The 1990s have witnessed a spectacular development of a new generation of "nonmetallocene" catalysts potentially useful to polymerize ethylene on its own and with other olefinic monomers,[2] and several organometallic systems capable of catalyzing the living polymerization of olefins have been designed.[3] Alternatively, also provided were convenient routes to synthetic applications[4] by unsaturated organic derivatives coupling reactions, via metallacyclic intermediates.[5] Several studies related with titanium and zirconium η^2-imine complexes[4a,6] have been re-

§ This paper is dedicated to the memory of Dr. Juan Carlos del Amo, who was a victim of the March 11, 2004, tragedy in Madrid.

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ported but few with monocyclopentadienyl derivatives of group 5 metals.[5f,g] These derivatives may participate in the development of simple and general methods for the synthesis of enantiomerically pure organic compounds such as the following: (i) substituted pyrroles by reaction with CO,[7] (ii) racemic allylic amines from simple amines and unfunctionalized alkynes,[8] (iii) carbocyclic and heterocyclic rings,[9] and (iv) cyclopentylamines and unusual α-amino acids.[10]

Further, the broad success of early transition metal based organic synthesis is due in part to the unique ability of the metal to activate ligands to which it is directly bound through organometallic transformations that are often highly chemo-, regio-, and stereoselective processes. In this context, zirconacycles[9a,b,11] are available from simple organic precursors either by cocyclization of 1,*n*-dienes, enynes, and diynes using a zirconocene fragment or by trapping of metallocene η^2-alkene, -alkyne, and -benzyne complexes with alkenes or alkynes. Methods for further elaboration of these zirconacycles forming carbon−heteroatom bonds include oxygenation, halogenation,[12] and metathesis with a variety of element-dihalides.[13] Carbon−carbon bond forming methods include carbonylation[14] or, more recently, tandem processes involving the insertion of isocyanides and trapping of the resulting zirconocene η^2-imine complexes with unsaturated species.[6p,r,10,15,16a] Further, the intermolecular addition of titanocene vinylidene complexes to alkynes gives titanacyclobutenes, which undergo an insertion-rearrangement with *tert*-butyl isocyanide to afford allenylketenimines.[16b]

In group 5, niobium and tantalum alkyne complexes[17−20] have provided convenient routes to organic products[4b,c,6i,21] via metallacyclic intermediates.[4a,22] Furthermore, alkyne tantalum(III) derivatives react with nitriles, leading to azatantalacyclopentene complexes that may participate in an intermolecular isomerization process to enamines.[4c]

We report herein the synthesis of alkyl azatantalacyclopentene derivatives, their reactivity with isocyanides, and the intramolecular rearrangement processes observed in the resulting complexes. The X-ray molecular structure of the complex [TaCp*Me_2(CHCHCMe_2NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **3**) is also described.

Results and Discussion

Synthesis of Alkyl Azatantalacyclopentene Complexes. [TaCp*$Cl_{2-x}Me_x$(CHCHCMe_2NAr-κ^2C,N)] (Cp*

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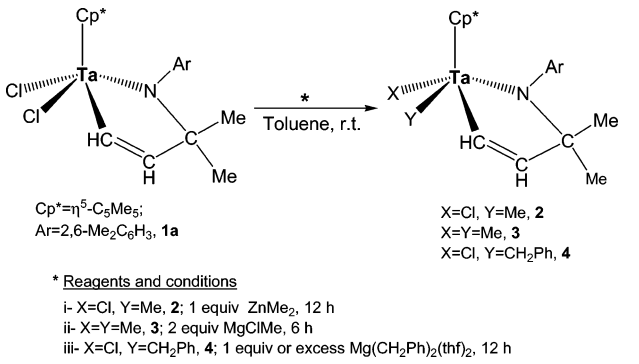
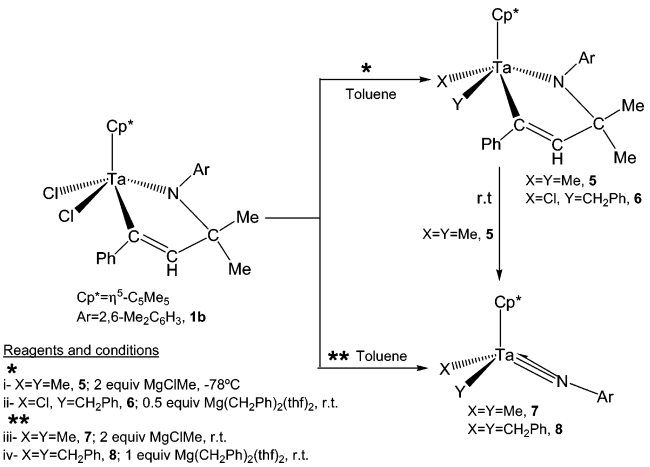
Scheme 1



Scheme 2



$= \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$; x = 1, **2**; 2, **3**) were obtained in good yields by treatment of the dichloro azatantalacyclopentene complex [TaCp*Cl_2(CHCHCMe$_2$-NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **1a**)[23] with 1 equiv of $ZnMe_2$ or 2 equiv of MgClMe in toluene at room temperature (see Scheme 1). Alkylation of **1a** with $Mg(CH_2Ph)_2(thf)_2$, in a 1:1 molar ratio or in excess, gave the monoalkylated derivative [TaCp*Cl(CH_2Ph)-(CHCHCMe$_2$NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **4**) as a red microcrystalline solid.

The addition of 2 equiv of MgClMe to toluene solutions of [TaCp*Cl_2{C(Ph)CHCMe$_2$NAr-κ^2C,N}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **1b**)[23] under rigorously anhydrous conditions at −78 °C yields the dimethyl azatantalacyclopentene complex [TaCp*Me_2{C(Ph)-CHCMe$_2$NAr-κ^2C,N}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **5**) (Scheme 2). When the alkylation was carried out at room temperature, complex **5** decomposed, giving a mixture in which the dimethyl(imido) tantalum complex [TaCp*Me_2(NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **7**)[24] was identified by NMR spectroscopy.

On the other hand, **1b** also reacts with 0.5 equiv of $Mg(CH_2Ph)_2(thf)_2$ at room temperature in toluene to give the expected benzyl chloro derivative [TaCp*Cl-(CH_2Ph){C(Ph)CHCMe$_2$NAr-κ^2C,N}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **6**). However, when 1 equiv of Mg-$(CH_2Ph)_2(thf)_2$ is used, the reaction takes place with the rupture of the Ta−C and C−N bonds in the azatantalacyclopentene moiety[23] and leads to a mixture of compounds in which **6** as minor component and the dibenzyl(imido) tantalum complex [TaCp*(CH_2Ph)$_2$-(NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **8**)[25] were identified by NMR spectroscopy. The presence of the dibenzyl imido complex **8** among the reaction products can be explained assuming that the decomposition of the dibenzyl azatantalacyclopentene derivative is faster that its formation rate.

All of the complexes **2**−**6** are soluble in aromatic hydrocarbons and chlorinated solvents and only slightly soluble in saturated hydrocarbons. The IR spectra show the characteristic absorptions due to the ν(C═C),[5c,d,24,26] ν(C−N),[27] ν(C−C)(Cp* ring),[5g,28,29] ν(Ta−N),[27] and ν(Ta−C)[5g,29−31] stretching vibrations at $\bar{\nu}$ 1585, 1175, 1025, 580, and 505 cm^{-1}, respectively. The NMR data of the alkyl azatantalacyclopentene derivatives are in agreement with the expected pseudo-square-pyramidal geometry for **3** and **5** and also with the asymmetrical structure for **2**, **4**, and **6**.

Moreover, at room temperature the ^{1}H NMR spectrum of complex **3** shows some broad signals. When a CD_2Cl_2 solution of **3** was studied by ^{1}H variable-temperature NMR between 203 and 313 K, the mutual exchange of the Ta-Me_2, CMe_2, and 2,6-$Me_2C_6H_3$ resonances, respectively, was observed. Kinetics parameters[32] calculated on the basis of line shape analysis data show that this transformation is an intramolecular process (log A = 12) which consists of the interconversion between two four-legged piano-stool enantiomeric ground states through a trigonal bipyramidal transition state, well-known as Berry pseudorotation and similar to other previously described transformations.[5g,6a,33]

A view of the molecular structure of the dimethyl azatantalacyclopentene complex **3** is shown in the Figure 1. Selected bond distances and angles are presented in Table 1.

Compound **3** can be described as a monomer with a typical four-legged piano-stool environment for the tantalum atom, with the pentamethylcyclopentadienyl ring in the cap position, the legs defined by two methyl groups, and the nitrogen and a carbon atom included

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(32) log A = 11.3 ± 0.25; $E_{act.}$ = 12.00 ± 0.30 kcal/mol (r = 0.998, $F_{6.2}$ = 1645.4); $\Delta H^{\#}$ = 11.80 ± 0.31 kcal/mol, $\Delta S^{\#}$ = −8.23 ± 1.20 eu (r = 0.998, $F_{6.2}$ = 1466.67); $\Delta G^{\#298K}$ = 14.2 kcal/mol.
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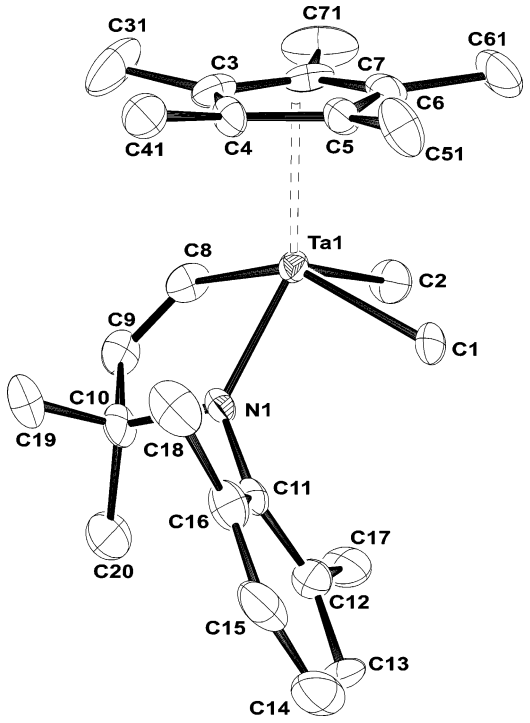


Figure 1. ORTEP drawing of compound **3**.

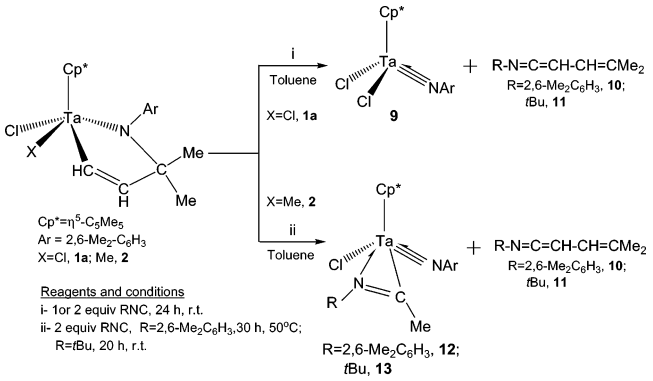
Table 1. Selected Bond Lengths [Å] and Angles [deg] for Compound 3[a]

Ta(1)−N(1)	2.028(4)	Ta(1)−C(8)	2.181(6)
Ta(1)−C(2)	2.209(6)	Ta(1)−C(1)	2.213(6)
Ta(1)−C(3)	2.455(5)	Ta(1)−C(4)	2.402(6)
Ta(1)−C(5)	2.453(6)	Ta(1)−C(6)	2.534(5)
Ta(1)−C(7)	2.519(6)	N(1)−C(11)	1.436(7)
N(1)−C(10)	1.533(7)	C(8)−C(9)	1.314(9)
C(9)−C(10)	1.499(9)	Cp−Ta(1)	2.158
N(1)−Ta(1)−C(8)	76.0(2)	N(1)−Ta(1)−C(2)	112.1(2)
C(8)−Ta(1)−C(2)	79.2(3)	N(1)−Ta(1)−C(1)	85.1(2)
C(8)−Ta(1)−C(1)	143.9(3)	C(2)−Ta(1)−C(1)	79.8(3)
C(8)−C(9)−C(10)	119.5(6)	C(9)−C(8)−Ta(1)	115.9(5)
Cp−Ta(1)−C(8)	106.16	Cp−Ta(1)−N(1)	142.2
Cp−Ta(1)−C(1)	107.6	Cp−Ta(1)−C(2)	105.33

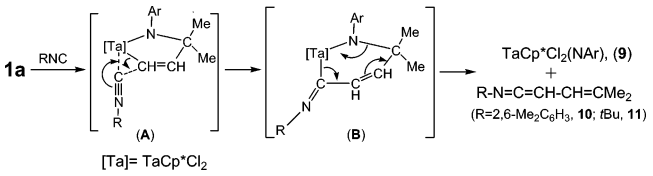
[a] Cp is the centroid of the C3−C4−C5−C6−C7 ring.

in the azatantalacyclopentene moiety TaC_3N. This structure is very similar to that described by us for the dichloro azatantalacyclopentene derivative [$TaCp^*Cl_2$-{C(Ph)CHCMe$_2$NAr-κ^2C,N}] ($Cp^* = \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **1b**).[23] The bonding in the TaC_3N unity corresponds to a diene with a double bond Ta−N (2.028(4) Å), and between the carbon atoms α and β with respect to the tantalum atom the C8−C9 bond distance is 1.314(9) Å. The distance Ta−C8 (2.181(6) Å) is typical of a single bond. The azatantalacyclopentene moiety is fairly planar, with a fold angle defined between the planes N1, Ta1, C8 and N1, C8, C9, C10 of 15.6(2)°. The Ta−C(methyl) distances (Ta−C1 2.213(6) Å, Ta−C2 2.209(6) Å) are in the range corresponding to normal values of a Ta−C[5f,24,29,33a] single bond and are both almost identical, in contrast with the situation in the aforementioned complex **1b**,[23] where clearly different values for the Ta−Cl distances were found. The 2,6-$Me_2C_6H_3$ ring bonded to the nitrogen atom is located quasi perpendicular to the azatantalacyclopentene moiety (80.9(1)°) and to the pentamethylcyclopentadienyl ring planes (61.45(2)°).

Scheme 3



Scheme 4



Reactions with Isocyanides. [$TaCp^*Cl_2$(CHCHCMe$_2$NAr-κ^2C,N)] ($Cp^* = \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **1a**) reacts with 1 equiv of isocyanides RNC (R = 2,6-$Me_2C_6H_3$; *t*Bu) in toluene, giving a reddish solution, which after manipulations affords a mixture of the dichloro(imido) tantalum complex [$TaCp^*Cl_2${N(2,6-$Me_2C_6H_3$)}] ($Cp^* = \eta^5$-C_5Me_5, **9**)[5f] and the *s-trans*-vinylazacumulenes R−N=C=CH−CH=CMe$_2$ (R = 2,6-$Me_2C_6H_3$, **10**; *t*Bu, **11**) in a 1:1 ratio (Scheme 3).

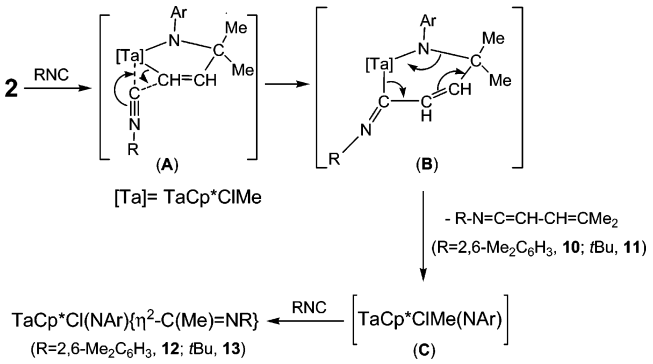
The formation of compounds **9**−**11** probably takes place assuming the coordination[34] of the isocyanide to the metal center of complex **1a** in the first reaction step to give an intermediate adduct **A** (see Scheme 4). The subsequent Ta−C(sp^2) bond rupture and the coupling between two carbon atoms leads to a metallacyclic species **B**, which by an intramolecular rearrangement gives a dichloro(imido) complex **9** and the vinylazacumulenes **10** and **11**.

On the other hand, when a benzene-d_6 solution of the chloro methyl complex **2** is treated with the same isocyanides in a 1:2 ratio (see Scheme 3), in a sealed NMR tube, the formation of the η^2-iminoacyl derivatives [$TaCp^*Cl$(NAr){η^2-C(Me)=NR}] ($Cp^* = \eta^5$-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$; R = 2,6-$Me_2C_6H_3$, **12**;[24] *t*Bu, **13**) and the *s-trans*-vinylazacumulenes **10** and **11** was observed by ^{1}H NMR spectroscopy. Under these conditions, a chloro imido methyl complex, similar to **9**, was not detected, but we suggest (see Scheme 5) that the chloro imido η^2-iminoacyl derivatives **12** (R = 2,6-$Me_2C_6H_3$) and **13** (R = *t*Bu) form from such intermediate species **C** by fast insertion of isocyanide into the Ta−CH_3 bond.

The complexes **12** and **13** are soluble in aromatic, chlorinated, and ethereal solvents but only slightly soluble in saturated hydrocarbons, and their spectroscopic data are consistent with their formulation. Both complexes show the characteristic absorption for the pentamethylcyclopentadienyl ring ($\bar{\nu}_{C-C}$ = 1027 cm^{-1}),[5g,28,29] and the imido η^2-iminoacyl complex **13**

(34) Gómez, M.; Gómez-Sal, P.; Nicolás, M. P.; Royo, P. *J. Organomet. Chem.* **1995**, *491*, 121−125.

Scheme 5



shows the $\nu_{Ta=N}$[24,25,29,31a,36] and $\nu_{C(Me)=N}$[5g,29,37] IR absorptions at 1330 and 1646 cm^{-1}, respectively.

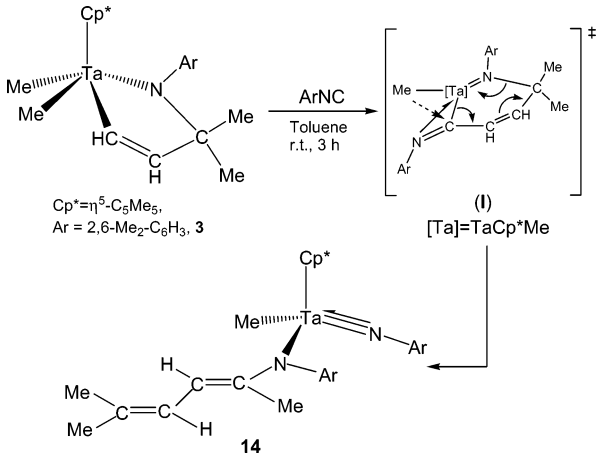
In the IR spectra of R−N=C=CH−CH=CMe_2 (R = 2,6-$Me_2C_6H_3$, **10**; *t*Bu, **11**) were observed absorption bands at 2023 (**10**) and 2015 (**11**) cm^{-1}, which can be assigned to the ν_{CN} stretching vibration.[33a,38] The $^{13}C\{^1H\}$ NMR spectra of both vinylazacumulenes show the typical resonances at δ 190.8, 186.7 (−N=*C*=CH−) and 52.2, 55.8 (−N=C=*C*H−) for **10** and **11**, respectively. In solution, they are mainly present as *s-trans* isomers in accordance with the observed NOE effects and with the vicinal ($^3J_{H-H}$) SSCC values found of 10.7 Hz (**10**) and 10.8 Hz (**11**).

The NMR data for the η^2-iminoacyl complex **13** (see Experimental Section) are in agreement with the expected pseudo-square-pyramidal geometry found for similar chiral niobium and tantalum derivatives[24,29] in which a characteristic η^2-iminoacyl carbon resonance appears at δ 233.

The addition of 1 equiv of 2,6-$Me_2C_6H_3NC$ to a toluene solution of the dimethyl azatantalacyclopentene [TaCp*Me_2(CHCHCMe_2NAr-κ^2C,N)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **3**) leads to the formation of the alkenyl-enamido imido methyl derivative [TaCp*Me(NAr){η^1-N(Ar)-C(Me)=CH−CH=CMe_2}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **14**) (Scheme 6).

A similar reaction pathway to that shown in Scheme 4 could explain the formation of **14** from a transition state **I** (Scheme 6). The coordination of the free nitrogen electron pair to the tantalum atom, the migration of the methyl group to the carbon atom of the inserted isocyanide with the concertated rupture of the Ta−C and N−C, and α-migration of the π C=C bonds lead to the resultant product **14**. This behavior is similar to that reported[33a] for the [TaCp*Cl_xMe_{4-x}] (Cp* = η^5-C_5Me_5; x = 1, 0) complexes, which in the presence of 2 equiv of isocyanides afford the chloro and methyl alkenylamido imido compounds [TaCp*X(NAr){η^1-N(Ar)-C(Me)=CMe_2}]

Scheme 6



(X = Cl, Me; Ar = 2,6-$Me_2C_6H_3$). Moreover, when **3** is treated with 2 equiv of 2,6-$Me_2C_6H_3NC$ in the same conditions, an unresolved mixture was obtained.

The presence of the imido ligand in complex **14** was confirmed by the absorption band located at 1305 cm^{-1}, whereas the NMR spectra in C_6D_6 show the presence of a pentamethylcyclopentadienyl ring, one methyl group bonded to the tantalum atom (δ 0.97 (^{1}H); 34.8 (^{13}C)), the expected signals for a N−C(Me)=CH−CH=CMe_2 moiety, and two types of 2,6-$Me_2C_6H_3$ rings (see Experimental Section). The ^{1}H NMR spectrum at room temperature also shows a broad signal at δ 1.67 (6H, $\Delta\nu$ = 9.5 Hz) for −CH=C*Me*$_2$ and another one at δ 2.17 (6H, $\Delta\nu$ = 8.3 Hz) for the Ta−N(2,6-*Me*$_2$$C_6H_3$). Its assignment and the corresponding C_6H_3 signals at δ 6.89 (2H) and 6.60 (1H)) in the amido moiety were realized by observation in the gHMBC spectrum of its coherence cross-peaks, with the broad ($\Delta\nu$ = 25 Hz) resonance at δ 151.7 due to C_1 of the aryl amido ring, whereas the more deshielded C_1 signal for the imido group is observed at δ 153.2. Moreover, the carbon spectrum at 25 °C shows other broad signals at δ 144.0 ($\Delta\nu$ = 8 Hz) and 134.2 ($\Delta\nu$ = 15 Hz) corresponding to the aryl amido and at δ 108.4 ($\Delta\nu$ = 10 Hz) for −H*C*=CMeN− moieties.

The ^{1}H (500 MHz) NMR spectra of **14** in CD_2Cl_2 solution obtained between 178 and 298 K (see Figure 2) show the significant line width variations that are in accordance with typical spin exchange processes of more than two very different populated positions[39] and could be explained by the well-known restricted rotation about C−N and C=C bonds (see Scheme 7) in organic enamines[40] and organometallic enamides.[33a]

We suggest that this behavior, coincidental to that previously observed by us for similar tantalum derivatives,[33a] determines the reactivity of complex **14**. So, when 1 equiv of 2,6-$Me_2C_6H_3NC$ is added to a benzene-d_6 solution of pure **14**, under rigorously anhydrous conditions, a new reaction takes place to give an imido η^2-iminoacyl methyl derivative [TaCp*Me(NAr)(η^2-C{CH(CMe=NAr)(CH=CMe_2)}=NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **15**) in quantitative yield (Scheme 7). After coordination of the isocyanide to the tantalum atom, it forms a transition state **I**, in which a concer-

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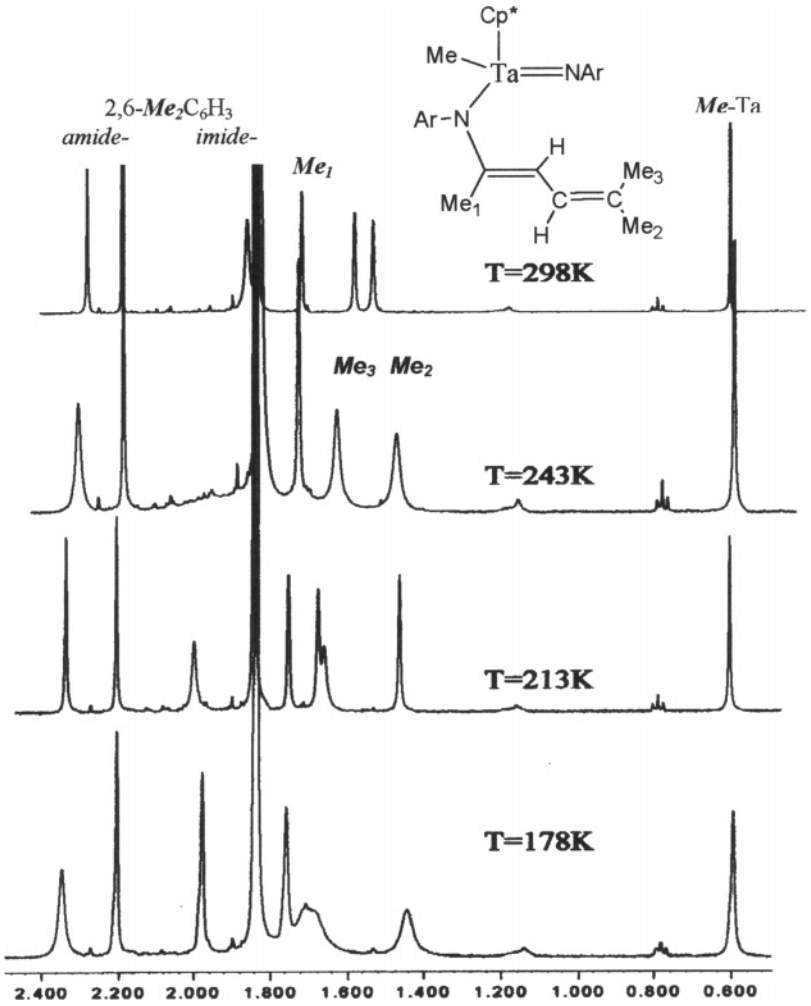
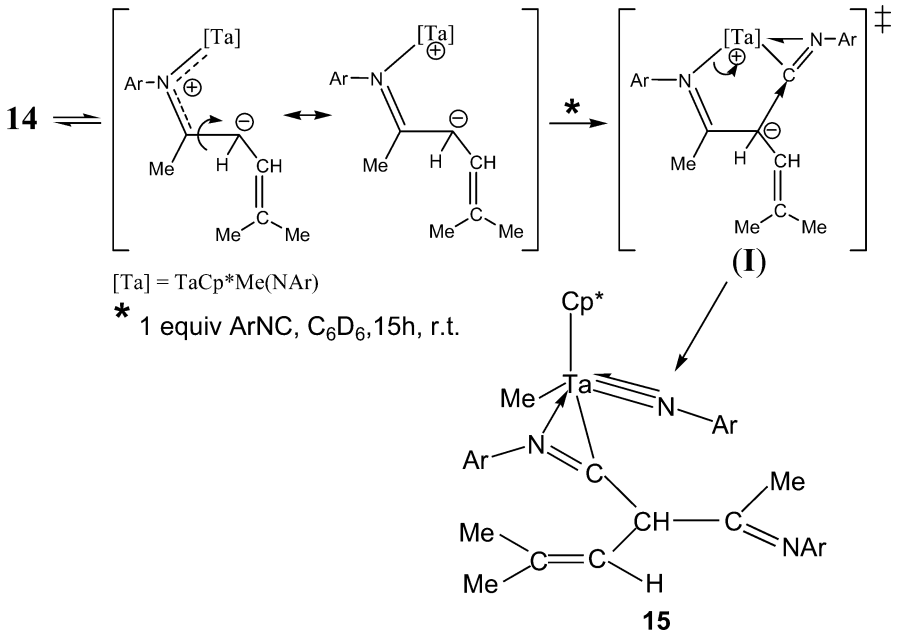


Figure 2. VT ^{1}H NMR spectra of complex **14** in CD_2Cl_2.

Scheme 7



tated carbon−carbon coupling, a tantalum−nitrogen bond rupture, and the nitrogen free electron pair coordination to the metal to give the final product **15** take place.

The NMR spectra of **15** show all the expected resonances (see Experimental Section) due to the η^2-iminoacyl (δ^{13}C 239.5) and the vinylimine moieties, three sets for the 2,6-$Me_2C_6H_3$ rings and one for the penta-

methylcyclopentadienyl ring and the methyl group bonded to the tantalum atom (δ^1H 0.56; δ^{13}C 21.3). Moreover, for the =C*H*−C*H*− vinylimine moiety, the ^{1}H NMR spectrum shows an AB system ($^3J_{H-H}$ = 10.7 Hz) at δ 5.58 and 5.01, in which the first doublet is desdoubled in septuplet by allylic coupling with both methyl protons ($^4J_{H-H}$ = 1.2 Hz), whereas its carbon resonances are observed at δ 121.4 and 60.1, in agreement with the gHMQC data.

Conclusions

The direct alkylation of [TaCp*Cl_2{C(R)CHCMe$_2$NAr-κ^2*C*,*N*}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$; R = H, **1a**; Ph, **1b**) with the appropriate amount of alkylating reagent and in different conditions leads to the formation of the alkyl azatantalacyclopentene complexes [TaCp*$Cl_{2-x}R'_x${C(R)CHCMe$_2$NAr-κ^2*C*,*N*}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$; R = H, x = 1, R′ = Me, **2**; CH_2Ph, **4**; x = 2, R′ = Me, **3**; R = Ph, x = 1, R′ = CH_2Ph, **6**; x = 2, R′ = Me, **5**). Reaction of **1a** with 1 equiv of isocyanides RNC (R = 2,6-$Me_2C_6H_3$; *t*Bu) probably takes place through the initial formation of nonstable adducts whose intramolecular rearrangement gave a dichloro imido tantalum compound [TaCp*Cl_2(NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **9**) and the *s-trans*-vinylazacumulenes R−N=C=CH−CH=CMe$_2$ (R = 2,6-$Me_2C_6H_3$, **10**; *t*Bu, **11**). When a toluene solution of **2** was treated with 2 equiv of isocyanides, the organic product **10** (R = 2,6-$Me_2C_6H_3$) or **11** (R = *t*Bu) and the chloro imido η^2-iminoacyl complexes [TaCp*Cl(NAr){η^2-C(Me)=NR}] (Cp* = η^5-C_5Me_5; R = 2,6-$Me_2C_6H_3$, **12**; *t*Bu, **13**) were obtained, probably via coordination, insertion, and intramolecular rearrangement processes. Treatment of the dimethyl azatantalacyclopentene **3** with 1 equiv of 2,6-$Me_2C_6H_3$NC produces the alkenylenamido imido methyl derivative [TaCp*Me(NAr){η^1-N(Ar)−C(Me)=CH−CH=CMe$_2$}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **14**), but the intermediate species were not observed when the reaction was followed by ^{1}H NMR spectroscopy. **14** reacts with 1 equiv of isocyanide, giving the imido η^2-iminoacyl methyl derivative [TaCp*Me(NAr)-(η^2-C{CH(CMe=NAr)(CH=CMe$_2$)}=NAr)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **15**) in quantitative yield.

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_5Me_5)Cl_2(CRCHCMe$_2$NAr-κ^2*C*,*N*)]) (Ar = 2,6-$Me_2C_6H_3$; R = H, **1a**; Ph, **1b**)[23] and the alkylating reagent [Mg(CH_2Ph)$_2$(thf)$_2$][41] were prepared as described previously. Reagent grade $MCl_{2-x}R_x$ (M = Zn, R = Me, x = 2, 2 M in toluene; M = Mg, R = Me, x = 1, 3 M in THF; Aldrich) and RNC (R = 2,6-$Me_2C_6H_3$, Fluka; *t*Bu, Aldrich) were purchased from commercial sources and were used without further purification.

Samples for IR spectroscopy were prepared as KBr pellets and recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer (4000−400 cm^{-1}). NMR spectra were recorded on Unity-300 and Varian Unity-Plus 500 spectrometers ("Varian NMR Systems"); chemical shifts were referenced to the solvent signals. Microanalyses (C, H, N) were performed in a LECO CHNS 932 microanalyzer.

Synthesis of [TaCp*ClMe(CHCHCMe$_2$NAr-κ^2*C*,*N*)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 2). A 2 M toluene solution of $ZnMe_2$ (0.65 mL, 1.30 mmol) was added at room temperature to a yellow solution of **1a** (0.75 g, 1.30 mmol) in toluene (40 mL), and the mixture was stirred for 12 h. The resulting suspension was filtered, the solvent reduced to dryness, and the residue extracted with hexane (3 × 15 mL). Subsequently, the solution was concentrated to ca. 10 mL and cooled to −40 °C overnight to afford **2** as an extremely air-sensitive microcrystalline yellow solid.

The data for **2** follow. Yield: 0.45 g (62%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2913(vs), 1635(w), 1577(m), 1456(vs), 1375(s), 1348(w), 1305(m), 1184(vs), 1163(s), 1138(m), 1098(s), 1024(s), 958(m), 907(s), 882(m), 814(m), 764(s), 687(w), 599(w), 544(w), 507(m), 482(m), 434(w). ^{1}H NMR (δ ppm, in benzene-d_6): 7.68(d, 1H), 7.24(d, 1H, $^2J_{H-H}$ = 10.6 Hz, Ta−C*H*=C*H*−), 7.10(d, 2H), 6.97[t, 1H, $^3J_{H-H}$ = 7.2 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 2.99(s, 3H), 2.14[s, 3H, Ta−N(2,6-*Me*$_2C_6H_3$)−], 1.81(s, 15H, C_5*Me*$_5$), 1.14(s, 3H), 0.97(s, 3H, =CH−C*Me*$_2$−), 0.73(s, 3H, Ta-*Me*). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 204.6(Ta−*C*H=CH−), 147.2(Ta−CH=*C*H−), 157.4(C_1), 138($C_{2,6}$), 132.5($C_{3,5}$), 128.9[C_4, Ta−N(2,6-$Me_2C_6H_3$)−], 121.9(C_5Me_5), 81.3(=CH−*C*Me$_2$−), 51.64(Ta−*Me*), 31.5, 25.7(=CH−C*Me*$_2$−), 22.7, 21.3[Ta−N(2,6-*Me*$_2C_6H_3$)−], 11.84(C_5*Me*$_5$). Anal. Calcd for $C_{24}H_{35}ClNTa$: C, 52.03; H, 6.37; N, 2.52. Found: C, 52.09; H, 6.38; N, 2.62.

Synthesis of [TaCp*Me$_2$(CHCHCMe$_2$NAr-κ^2*C*,*N*)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 3). Under rigorously anhydrous conditions, a 3 M solution of MgClMe in THF (1 mL, 3 mmol) was added at −78 °C to a solution of **1a** (0.75 g, 1.30 mmol) in toluene (40 mL), and the reaction mixture was stirred for 30 min. It was warmed to room temperature for 6 h, the solvent evaporated to dryness, and the residue extracted with hexane (3 × 10 mL). The solution was concentrated to ca. 10 mL and cooled to −40 °C overnight to give **3** as yellow crystals.

The data for **3** follow. Yield: 0.60 g (83%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2915(vs), 1844(w), 1653(w), 1566(m), 1488(m), 1456(s), 1423(s), 1374(s), 1347(m), 1302(w), 1249(w), 1232(w), 1189(vs), 1164(s), 1097(m), 1068(w), 1024(m), 957(m), 898(s), 810(m), 768(s), 746(m), 697(w), 668(w), 597(w), 566(w), 543(w), 499(m), 484(m), 440(m). ^{1}H NMR (δ ppm, in benzene-d_6): 7.98(d, 1H), 7.04(d, 1H, $^2J_{H-H}$ = 10.9 Hz, Ta−C*H*=C*H*−), 7.12(d, 2H), 6.95[t, 1H, $^3J_{H-H}$= 7.5 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 2.50[br, 6H, Ta−N(2,6-*Me*$_2C_6H_3$)−], 1.74(s, 15H, C_5*Me*$_5$), 1.11(br, 6H, =CH−C*Me*$_2$−), 0.20(br, 6H, Ta-*Me*$_2$). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 203.9(Ta−*C*H=CH−), 146.5(Ta−CH=*C*H−), 154.7(C_1), 129.9($C_{2,6}$), 128.6($C_{3,5}$), 124.1[C_4, Ta−N(2,6-$Me_2C_6H_3$)−], 119.1(C_5Me_5), 79.5(=CH−*C*Me$_2$−), 51.6(Ta−*Me*$_2$), 31.8(=CH−C*Me*$_2$−), 21.6[Ta−N(2,6-*Me*$_2C_6H_3$)−], 11.4(C_5*Me*$_5$). Anal. Calcd for $C_{25}H_{38}NTa$: C, 56.28; H, 7.17; N, 2.62. Found: C, 56.16; H, 7.03; N, 2.66.

Synthesis of [TaCp*Cl(CH_2Ph)(CHCHCMe$_2$NAr-κ^2*C*,*N*)] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 4). Toluene (40 mL) was added to a mixture of **1a** (0.50 g, 0.87 mmol) and Mg(CH_2Ph)$_2$(thf)$_2$ (0.30 g, 0.87 mmol) at room temperature, and the mixture was stirred for 12 h under rigorously anhydrous conditions (glovebox). The suspension was removed by filtration, and the resulting solution was evaporated to dryness. The residue was extracted with a toluene/hexane mixture (2 × 15 mL) and the solution concentrated to ca. 10 mL and cooled to −40 °C overnight to give a microcrystalline red solid identified as **4**.

The data for **4** follow. Yield: 0.36 g (66%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2964(vs), 2907(s), 1650(w), 1586(m), 1488(s), 1457(vs), 1375(s), 1314(w), 1259(w), 1205(m), 1176(vs), 1160(s), 1099(s), 1024(m), 955(w), 910(m), 879(w), 813(m), 768(s), 755(s), 697(s), 666(m), 601(w), 544(m), 507(m), 428(m). ^{1}H NMR (δ ppm, in benzene-d_6): 7.76(d, 1H), 7.36(d, 1H, $^2J_{H-H}$ = 10.8 Hz, Ta−C*H*=C*H*−), 7.32(m, 2H$_m$), 7.28(m, 2H$_o$), 6.912(tt, 1H$_p$, Ta−$CH_2C_6H_5$), 7.12(dd, 1H), 7.01(dd, 1H, $^4J_{H-H}$ = 1.13 Hz), 6.905[t,

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

1H, $^3J_{H-H}$= 7.5 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 2.08(s, 3H), 1.98-[s, 3H, Ta−N(2,6-$Me_2C_6H_3$)−], 1.76(s, 15H, C_5Me_5), 1.69, 1.40-(AB, 2H, $^2J_{H-H}$ = 10.6 Hz, Ta−$CH_2C_6H_5$), 1.01(s, 3H), 0.85(s, 3H, =CH−CMe_2−). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 203.4(Ta−*C*H=CH−), 148.5(Ta−CH=*C*H−), 156(C_1), 138.5, 133.1($C_{2,6}$), 129.8, 127.3($C_{3,5}$), 124.6[C_4, Ta−N(2,6-$Me_2C_6H_3$)−], 148.6(C_1), 130.7($C_{2,6}$), 127.4($C_{3,5}$), 123.4(C_4, Ta−$CH_2C_6H_5$), 122.5(C_5Me_5), 82.3(=CH−*C*Me_2−), 78.5(Ta−$CH_2C_6H_5$), 29.4, 24.4(=CH−CMe_2−), 22.4, 22.2[Ta−N(2,6-$Me_2C_6H_3$)−], 12.1-(C_5Me_5). Anal. Calcd for $C_{30}H_{39}ClNTa$: C, 57.19; H, 6.24; N, 2.22. Found: C, 57.49; H, 6.52; N, 2.35.

Synthesis of [TaCp*Me_2{C(Ph)CHCMe$_2$NAr-κ^2*C,N*}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 5). A sample of **1b** (0.40 g, 0.61 mmol) was dissolved in 30 mL of toluene in a Schlenk tube and at −78 °C was treated with a 3 M solution of MgClMe in THF (0.50 mL, 1.50 mmol). The mixture was stirred at low temperature 6 h, and after, the resulting suspension was decanted and filtered. The filtrate was concentrated to ca. 10 mL and cooled to −40 °C to give **5** as a microcrystalline yellow solid.

The data for **5** follow. Yield: 0.22 g (59%). ^1H NMR (δ ppm, in benzene-d_6): 7.28−7.01[d, 2H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 7.28−7.01[m, 5H, Ta−C(C_6H_5)=CH−], 6.95[t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 6.76[s, 1H, Ta−C(Ph)=C*H*−], 3.06(s, 3H), 2.12[s, 3H, Ta−N(2,6-$Me_2C_6H_3$)−], 1.66(s, 15H, C_5Me_5), 1.30(s, 3H), 0.94(s, 3H, =CH−CMe_2−), 0.68(s, 3H), −0.13(s, 3H, Ta−Me_2).

Synthesis of [TaCp*Cl(CH_2Ph){C(Ph)CHCMe$_2$NAr-κ^2*C,N*}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 6). At room temperature, toluene (50 mL) was added to a mixture of compound **1b** (0.40 g, 0.61 mmol) and Mg(CH_2Ph)$_2$(thf)$_2$ (0.10 g, 0.30 mmol). The mixture was stirred for 12 h, the magnesium chloride, $MgCl_2$, formed removed by filtration, and the filtrate concentrated to a volume of ca. 10 mL. Cooling at −40 °C overnight led to the deposition of a microcrystalline yellow solid identified as **6**.

The data for **6** follow. Yield: 0.31 g (72%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2913(vs), 1593(m), 1487(s), 1458(vs), 1375(s), 1322(vs), 1263-(m), 1204(w), 1158(m), 1098(m), 1068(m), 1026(s), 984(m), 917-(w), 867(w), 803(m), 765(vs), 701(vs), 588(m), 507(w), 484(w). ^1H NMR (δ ppm, in benzene-d_6): 7.12−6.86[several phenyl, 10H, Ta−$CH_2C_6H_5$, Ta−C(C_6H_5)=CH−], 6.98(d, 2H), 6.69[t, 1H, $^3J_{H-H}$ = 7.5 Hz, Ta−N(2,6-$Me_2C_6H_3$)−], 5.60[s, 1H, Ta−C(Ph)=C*H*−], 2.67, 2.61(AB, 2H, $^2J_{H-H}$ = 13 Hz, Ta−CH_2Ph), 2.25[s, 6H, Ta−N(2,6-$Me_2C_6H_3$)−], 1.84(s, 15H, C_5Me_5), 0.96-(s, 3H), 0.83(s, 3H, =CH−CMe_2−). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 209.6[Ta−*C*(Ph)=CH−], 187.7[Ta−C(Ph)=*C*H−], 149−131[several phenyl, Ta−$CH_2C_6H_5$, Ta−C(C_6H_5)=CH−], 138.4(C_1), 126.4($C_{2,6}$), 125.2($C_{3,5}$), 123.3[C_4, Ta−N(2,6-$Me_2C_6H_3$)−], 117.9(C_5Me_5), 50(=CH−*C*Me_2−), 41.3(Ta−*C*$H_2C_6H_5$), 29.5, 28.2(=CH−CMe_2−), 19.5[Ta−N(2,6-$Me_2C_6H_3$)−], 11.5-(C_5Me_5). Anal. Calcd for $C_{36}H_{43}ClNTa$: C, 61.23; H, 6.14; N, 1.98. Found: C, 61.15; H, 6.05; N, 2.08.

Reaction of 1a with Isocyanides RNC (R = 2,6-$Me_2C_6H_3$; *t*Bu). RNC (0.52 mmol; R = 2,6-$Me_2C_6H_3$, 0.07 g; *t*Bu, 0.06 mL) was added at room temperature to a solution of **1a** (0.30 g, 0.52 mmol) in toluene (25 mL), and the mixture was stirred for 24 h (R = 2,6-$Me_2C_6H_3$) and 10 h (R = *t*Bu). The reaction was checked by ^1H NMR spectroscopy until total conversion of the tantalum starting complex. The reddish solution was evaporated to dryness, and the ^1H NMR analysis of the crude residue showed this to consist of a mixture of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (Cp* = η^5-C_5Me_5, **9**[5f]) and the organic material *s-trans*-R−N=C=CH−CH=CMe_2 (R = 2,6-$Me_2C_6H_3$, **10**; *t*Bu, **11**) in a 1:1 molar ratio.

The data for **10** follow. ^1H NMR (δ ppm, in benzene-d_6): 6.86(m, 3H, 2,6-$Me_2H_3C_6$−N=), 5.66(dsept, 1H, $^3J_{H-H}$ = 10.7 Hz, −C*H*=CMe_2), 4.60(d, 1H, $^3J_{H-H}$ = 10.7 Hz, −N=C=C*H*−), 2.24(s, 6H, 2,6-$Me_2H_3C_6$−N=), 1.65(s, 3H), 1.47(s, 3H, −CH=CMe_2). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 190.8(=*C*=CH−), 150−131.5(several phenyl, 2,6-$Me_2H_3C_6$−N=), 114.5(−*C*H=CMe_2), not observed(−CH=*C*Me_2), 52.2(=C=*C*H−), 25.9, 18.3-(−CH=C*Me*$_2$), 18.7(2,6-$Me_2H_3C_6$−N=). The data for **11** follow. ^1H NMR (δ ppm, in benzene-d_6): 5.64(d, 1H, $^3J_{H-H}$= 10.8 Hz, −C*H*=CMe$_2$), 4.60(d, 1H, $^3J_{H-H}$ = 10.8 Hz, =C=C*H*−), 1.64-(s, 3H), 1.49(s, 3H, −CH=C*Me*$_2$), 1.15(s, 9H, *Me*$_3$C−N=). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 186.7(=*C*=CH−), 116.2(−*C*H=CMe$_2$), 58.3(Me$_3$*C*−N=), 55.8(=C=*C*H−), 30(*Me*$_3$C−N=), 25.8, 17.9(−CH=C*Me*$_2$).

Reaction of 2 with 2,6-$Me_2C_6H_3$NC. A solution of **2** (0.20 g, 0.36 mmol) in toluene (20 mL) was treated with 2,6-$Me_2C_6H_3$NC (0.09 g, 0.72 mmol) under rigorously anhydrous conditions. The mixture was heated for 30 h at 50 °C and then filtered. The filtrate was concentrated to dryness and the residue extracted with hexane (2 × 10 mL). The solution was concentrated to ca. 5 mL and cooled to −40 °C to give a yellow microcrystalline solid identified as a mixture of **10** and the η^2-iminoacyl complex [TaCp*Cl(NAr){η^2-C(Me)=NAr}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, **12**[24]) in a 1:1 ratio.

Reaction of 2 with *t*BuNC. *t*BuNC (0.11 mL, 1.02 mmol) was added to a solution of **2** (0.25 g, 0.45 mmol) in toluene (20 mL) at room temperature, and the mixture was stirred for 20 h. The resulting solution was filtered and the filtrate concentrated to dryness. The residue solid was washed with hexane (2 × 10 mL), and the resulting yellow suspension was decanted and filtered. The yellow microcrystalline solid was dried in vacuo and identified as the η^2-iminoacyl complex [TaCp*Cl-(NAr){η^2-C(Me)=N*t*Bu}] (Cp* = η^5-C_5Me_5, **13**). The filtrate was concentrated to ca. 5 mL and cooled to −40 °C to give the organic product **11** impurified with a small portion of the complex **13**.

The data for **13** follow. Yield: 0.13 g (51%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2908(s), 1890(w), 1828(w), 1772(w), 1646(s), 1588(m), 1459-(vs), 1366(s), 1330(vs), 1243(m), 1200(s), 1121(m), 1095(m), 1026(m), 980(m), 851(m), 805(w), 759(s), 650(w), 561(w), 508-(w), 463(m), 412(w). ^1H NMR (δ ppm, in benzene-d_6): 7.04(d, 2H), 6.71[t, 1H, $^3J_{H-H}$= 7.5 Hz, Ta=N(2,6-$Me_2C_6H_3$)], 2.51[s, 6H, Ta=N(2,6-*Me*$_2C_6H_3$)], 2.38[s, 3H, Ta−C(*Me*)=N*t*Bu], 1.83-(s, 15H, C_5Me_5), 1.22[s, 9H, Ta−C(Me)=N(C*Me*$_3$)]. $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 233[Ta−*C*(Me)=N*t*Bu], 154.4-(C_1), 131.9($C_{2,6}$), 127.2($C_{3,5}$), 120.8[C_4, Ta=N(2,6-$Me_2C_6H_3$)], 115(C_5Me_5), 63.9[Ta−C(Me)=N(*C*Me$_3$)], 29.9[Ta−C(Me)=N(C*Me*$_3$)], 20.1[Ta−C(*Me*)=N(CMe$_3$)], 19.9[Ta=N(2,6-*Me*$_2C_6H_3$)], 11.1(C_5Me_5). Anal. Calcd for $C_{24}H_{36}ClN_2Ta$: C, 50.66; H, 6.38; N, 4.92. Found: C, 50.99; H, 6.51; N, 5.09.

Synthesis of [TaCp*Me(NAr){η^1-N(Ar)−C(Me)=CH−CH=CMe$_2$}] (Cp* = η^5-C_5Me_5; Ar = 2,6-$Me_2C_6H_3$, 14). A stirred yellow solution of **3** (0.40 g, 0.75 mmol) in toluene (20 mL) was treated with 2,6-$Me_2C_6H_3$NC (0.13 g, 1.00 mmol) under rigorously anhydrous conditions for 3 h. The color of the mixture changed quickly from yellow to dark red. The solution was filtered, concentrated to ca. 5 mL, and cooled to −40 °C to give **14** as a brown microcrystalline solid.

The data for **14** follow. Yield: 0.29 g (58%). IR (KBr, $\bar{\nu}$ cm^{-1}): 2912(vs), 1709(w), 1587(m), 1462(vs), 1432(s), 1376(s), 1305-(vs), 1251(w), 1213(w), 1191(s), 1151(s), 1098(m), 1024(m), 980(w), 899(m), 849(w), 762(s), 673(w), 593(m), 526(w), 480-(m), 397(w). ^1H NMR (δ ppm, in benzene-d_6): 7.00(dd, 2H), 6.79(dd, 1H, $^4J_{H-H}$=1.98 Hz), 6.83[t, 1H, $^3J_{H-H}$= 7.4 Hz, Ta=N(2,6-$Me_2C_6H_3$)], 6.88(d, 2H), 6.60[t, 1H, $^3J_{H-H}$ = 7.4 Hz, Ta−N(2,6-$Me_2C_6H_3$)], 6.01(dsept, 1H, $^4J_{H-H}$ = 1.43 Hz, −C*H*=CMe$_2$), 5.55[d, 1H, $^3J_{H-H}$ = 10.9 Hz, −C(Me)=C*H*−], 2.48(s, 3H), 2.32[s, 3H, Ta=N(2,6-*Me*$_2C_6H_3$)], 2.17[br, 6H, Ta−N(2,6-*Me*$_2C_6H_3$)], 1.77(s, 15H, C_5Me_5), 1.76[s, 3H, −C(*Me*)=CH−], 1.67(br, 6H, −CH=C*Me*$_2$), 0.97(s, 3H, Ta−*Me*). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene-d_6): 153.2[C_1, Ta=N(2,6-$Me_2C_6H_3$)], 151.7-[C_1, Ta−N(2,6-$Me_2C_6H_3$)], 136, 134.2, 130.9, 129.6, 128.1, 127.2, 125.1, 121.9[several phenyl carbons, Ta=N(2,6-$Me_2C_6H_3$), Ta−N(2,6-$Me_2C_6H_3$)], 145.6[−N−*C*(Me)=CH−], 133.2(−CH=*C*Me$_2$), 122.7(−*C*H=CMe$_2$), 115.7(C_5Me_5), 108.4[−C(Me)=*C*H−], 34.8(Ta−*Me*), 26.4, 18.6(−CH=C*Me*$_2$), 19.99, 19.94[Ta=N(2,6-*Me*$_2C_6H_3$)], 19.85[Ta−N(2,6-*Me*$_2C_6H_3$)], 17.8[−C(*Me*)=CH−],

Table 2. Crystal Data and Structure Refinement for Compound 3

chem formula	$C_{25}H_{38}NTa$
fw	533.51
T (K)	200(2)
λ (Mo Kα), Å	0.71073
cryst syst, space group	orthorhombic, $P2_12_12_1$
a, Å	8.3124(10)
b, Å	10.5190(7)
c, Å	26.0587(18)
V, Å^3	2278.5(4)
Z	4
ρ_{calcd}, g cm^{-3}	1.555
μ, mm^{-1}	4.883
cryst size, mm	0.35 × 0.2 × 0.2
F(000)	1072
θ range, deg	5.01 to 27.52
index ranges	$-4 \le h \le 10$, $-13 \le k \le 13$, $-31 \le l \le 33$
no. of data collected	10 010
no. of unique data	5155 [R(int) = 0.0662]
no. of obsd reflns [$I > 2\sigma(I)$]	4588
absorp corr	semiempirical from equivalents
max. and min. transmn	1.284 and 0.821
no. of params refined	252
goodness-of-fit on F^2	1.036
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0351, wR2 = 0.0644
R indices (all data)[a]	R1 = 0.0454, wR2 = 0.0670
largest diff peak and hole, e Å^{-3}	0.807 and −1.032

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

10.9(C_5Me_5). Anal. Calcd for $C_{34}H_{47}N_2Ta$: C, 61.45; H, 7.12; N, 4.21. Found: C, 61.22; H, 6.80; N, 4.41.

Synthesis of [TaCp*Me(NAr)(η^2-C{CH(CMe=NAr)(CH=CMe$_2$)}=NAr)] (Cp* = η^5-C$_5$Me$_5$; Ar = 2,6-Me$_2$C$_6$H$_3$, 15). Benzene-d_6 (0.60 mL) was added to a mixture of complex **14** (0.035 g, 0.052 mmol) and 2,6-$Me_2C_6H_3NC$ (0.007 g, 0.052 mmol) in a NMR valved tube. The reaction was monitored by ^{1}H NMR spectroscopy until no further change was observed. After 15 h the spectrum showed the presence of **15** in quantitative yield.

The data for **15** follow. ^{1}H NMR (δ ppm, in benzene-d_6): 7.08−6.56[m, 9H, Ta=N(2,6-$Me_2C_6H_3$), Ta−C{CH(CMe=N(2,6-$Me_2C_6H_3$)(CH=CMe$_2$)}=N(2,6-$Me_2C_6H_3$)], 5.58(dsept, 1H, $^3J_{H-H}$ = 10.7 Hz, $^4J_{H-H}$ = 1.2 Hz, Me_2C=CH−CH−), 5.01(d, 1H, $^3J_{H-H}$ = 10.7 Hz, Me_2C=CH−CH−), 2.49(s, 6H), 2.06(s, 3H), 1.93(s, 3H), 1.79(s, 3H), 1.78[s, 3H, Ta=N(2,6-$Me_2C_6H_3$), Ta−C{CH(CMe=N(2,6-$Me_2C_6H_3$)(CH=CMe$_2$)}=N(2,6-$Me_2C_6H_3$)], 1.96(s, 15H, C_5Me_5), 1.57(s, 3H, −CMe=NAr), 1.46(s, 3H), 1.38-(s, 3H, Me_2C=CH−CH−), 0.56(s, 3H, Ta−Me). ^{13}C{^{1}H} NMR (δ ppm, in benzene-d_6): 239.5[Ta−C{CH(CMe=N(2,6-$Me_2C_6H_3$)-(CH=CMe$_2$)}=N(2,6-$Me_2C_6H_3$)], 169.1[−CMe=N(2,6-$Me_2C_6H_3$)], 155.1−119.9[several phenyl carbons, Ta=N(2,6-$Me_2C_6H_3$), Ta−C{CH(CMe=N(2,6-$Me_2C_6H_3$)(CH=CMe$_2$)}=N(2,6-$Me_2C_6H_3$)], 119.8(Me_2C=CH−CH−), not observed (Me_2C=CH−CH−), 113.4(C_5Me$_5$), 60.1(Me_2C=CH−CH−), 25.7, 17.9(Me_2C=CH−CH-), 21.3(Ta−Me), 19.4[−CMe=N(2,6-$Me_2C_6H_3$)], 20.2, 20.1, 18.8, 18.6, 18.3, 17.6[Ta=N(2,6-$Me_2C_6H_3$), Ta−C{CH(CMe=N(2,6-$Me_2C_6H_3$)(CH=CMe$_2$)}=N(2,6-$Me_2C_6H_3$)], 11.5(C_5Me_5).

Crystal Structure Determination of Compound 3. Crystallographic and experimental details of the crystal structure determinations are given in Table 2. Suitable crystals for the X-ray analyses of complex **3** were obtained by recrystallization from a hexane solution and then covered with mineral oil and mounted in the N_2 stream in a Bruker-Nonius Kappa CCD diffractometer. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was performed at 200 K (see Table 2) with an exposure time of 6 s per frame (4 sets, 582 frames). Raw data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL-97).[42] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms. Hydrogen atoms were included from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.[43]

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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 **3** (Tables S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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