Insertion of Isocyanide into Metal−Carbon Bonds of Alkylchloro(pentamethylcyclopentadienyl)niobium- and -tantalum Complexes − X-ray Structure of [TaCp*Cl$_2$(CH$_2$CMe$_2$Ph){η^2-C(CH$_2$CMe$_2$Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] and Unexpected Decomposition of Alkyldichloro(η^2-iminoacyl) Complexes of Tantalum

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Methylation of $NbCp^*Cl_2Me_2$ using excess $ZnMe_2$ gives $NbCp^*ClMe_3$ (**1**) which has been found to exhibit a Berry pseudorotation process on the NMR time scale (log $A = 12.2 \pm 0.3$, $E_a = 12.2 \pm 0.4$ kcal·mol^{-1}, $\Delta H^{\neq} = 11.6 \pm 0.4$ kcal·mol^{-1}, $\Delta S^{\neq} = -4.4 \pm 1.3$ e.u., $\Delta G^{\neq 298K} = 12.9$ kcal·mol^{-1}). Alternatively, lithium dimethylamide reacts with $NbCp^*Cl_2Me_2$ to form $NbCp^*Me_2(NMe_2)_2$ (**2**) which decomposes in solution under the elimination of methane to give the (dimethylamido)methylazaniobacyclopropane derivative $NbCp^*Me(NMe_2)(\eta^2\text{-}CH_2NMe)$ (**3**). Reaction of $NbCp^*Cl_2Me_2$ with 1 equiv. of 2,6-$Me_2C_6H_3NC$ results in a double methyl group migration to give the dichloroazaniobacyclopropane complex $[NbCp^*Cl_2\{\eta^2\text{-}CMe_2N(2,6\text{-}Me_2C_6H_3)\}]$ (**4**). Dialkyldichloro complexes $TaCp^*Cl_2R_2$ [$Cp^* = \eta^5\text{-}C_5Me_5$; R = CH_2SiMe_3 (**5**), CH_2CMe_2Ph (**6**), CH_2CMe_3 (**7**), $CH_2C_6H_5$ (**8**)] were obtained by treating $TaCp^*Cl_4$ with the requisite amounts of the appropriate alkylating agents. Reactions of the dialkyldichloro complexes $TaCp^*Cl_2R_2$ (**5**–**8**) with 1 equiv. of 2,6-$Me_2C_6H_3NC$ resulted in migration of only one of the two alkyl groups to give (alkyl)dichloro(η^2-iminoacyl) complexes $[TaCp^*Cl_2R\{\eta^2\text{-}C(R)=NAr\}]$ [Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3 (**9**), CH_2CMe_2Ph (**10**), CH_2CMe_3 (**11**), $CH_2C_6H_5$ (**12**)]. The molecular structure of complex **10** has been determined by X-ray diffraction analysis. The η^2-iminoacyl complexes **9**–**12** decompose in [D$_6$]benzene or *n*-hexane solutions to give $[TaCp^*Cl_2\{N(2,6\text{-}Me_2C_6H_3)\}]$ and the corresponding *trans* or *cis* olefins R′–CH=CH–CH$_2$–R′ [R′ = $SiMe_3$ (**9o**), CMe_2Ph (**10o**), CMe_3 (**11o**), C_6H_5 (**12o**)]. A mechanism for this reaction is proposed. All the new compounds have been characterized by IR spectrophotometry, ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy, and elemental analysis.

Introduction

Migratory insertion of coordinated unsaturated molecules, such as carbon monoxide[1] or isocyanides,[2] into metal−alkyl bonds and the reactivity[3] of the resulting metal−acyl and metal−iminoacyl functions is one of the most important organometallic reactions, with many synthetic applications stemming from the C−C bond formation under mild reaction conditions. Several years ago, we reported the results of a systematic study[4] concerning the insertion of isocyanides into the tantalum−methyl bonds of various chloro(methyl)(pentamethylcyclopentadienyl) derivatives $TaCp^*Cl_{4-x}Me_x$, which led to the synthesis of η^2-iminoacyl ($x = 1$), azatantalacyclopropane ($x = 2$), and (alkenylamido)imido ($x = 3, 4$) complexes.

In this context, the last years have witnessed a rapid development of early transition metal chemistry associated with imine ligands.[3,5] In these complexes, the imine linkage is typically found to bind strongly to the metal centre in an η^2-CN fashion and therefore they can be described as azametallacyclopropane derivatives. Although iminetantalum complexes have been postulated as intermediates in several organometallic transformations,[3a,3g,3i,6] only a few have been isolated and fully characterized.[4a,7] The formation of η^2-imino ligands at early transition metal centres can be achieved by the cyclometallation of dialkylamido ligands,[3g,3h] by alkyl or hydride reduction of η^2-iminoacyl ligands,[3b,3d,3e,3m,7e] by transfer of a hydrogen atom from an aminemetal complex,[7d] or in a few cases by addition of imines to low-valent metal derivatives.[3j,3k,5a,5j] Such an η^2 geometry has been identified in the crystal structures of some iminetantalum[4a] and -tungsten[3d,3e] complexes, and similar structures have been proposed for imine complexes of tantalum,[3a,8] zirconium,[3b] titanium,[9] and Group 8 metals.[10] Moreover, novel azazirconacyclopropane derivatives have been isolated[11] by orthometallation of 2,6-diethylpyridine with the cationic complex $[ZrCp_2Me(THF)]^+$. The analogous acetonetantalum or oxotantalacyclopropane complexes $TaCp^*X_2(\eta^2\text{-}OCMe_2)$, (X = Cl,[6] Me[1b]) are also thought to involve bonding through both the carbon and oxygen atoms.

In view of the high reactivities[3b,4,5a,5d,12] exhibited by these species, we decided to extend the study to bulky alkyltantalum derivatives. Thus, we report herein on the synthesis, insertion reactions, and intramolecular rearrange-

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ment processes of the complexes obtained by treating dialkyldichloro(pentamethylcyclopentadienyl)niobium- and -tantalum(V) complexes with 2,6-$Me_2C_6H_3NC$.

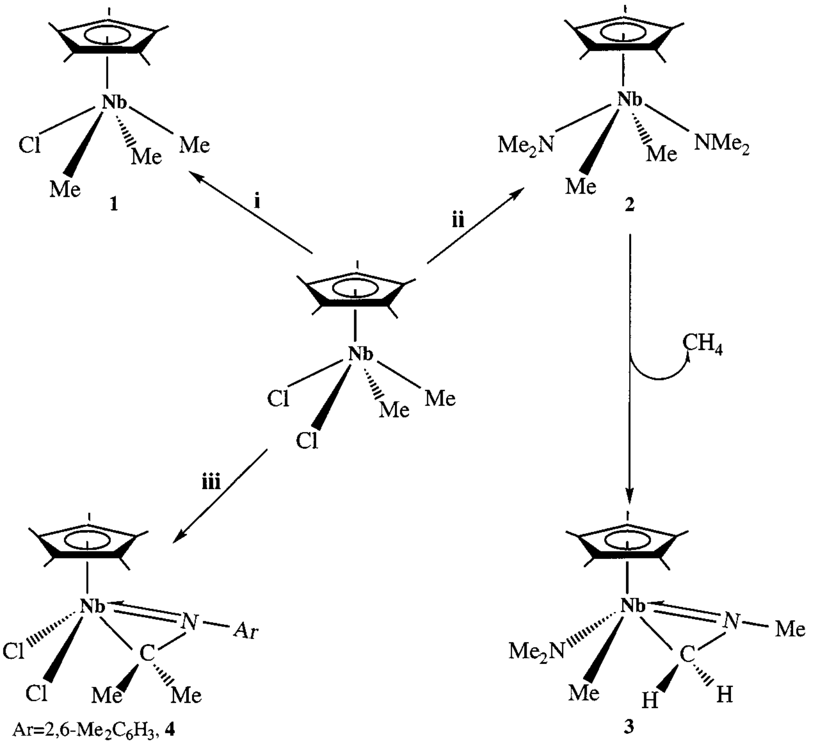
Results and Discussion

Alkylation and Insertion Reactions of NbCp*Cl_2Me_2

The (chloro)trimethyl complex NbCp*$ClMe_3$, **1**, was obtained by treatment of the dichlorodimethyl derivative[13] with an excess of $ZnMe_2$ (see Scheme 1). The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **1** in [D$_6$]benzene solution at room temperature show only one signal for the three methyl groups, whereas the ^{1}H-NMR spectrum in [D$_8$]toluene solution at 223 K shows two narrow resonances in a 1:2 ratio. This NMR behaviour corresponds to a Berry pseudorotation process,[3g,14] akin to that reported for other tantalum complexes,[15] and is consistent with a four-legged piano-stool geometry in the ground state. The kinetic parameters ($\log A = 12.2 \pm 0.3$, $E_a = 12.2 \pm 0.4$ kcal·mol^{-1}, $\Delta H^{\neq} = 11.6 \pm 0.4$ kcal·mol^{-1}, $\Delta S^{\neq} = -4.4 \pm 1.3$ e.u., $\Delta G^{\neq 298\mathrm{K}} = 12.9$ kcal·mol^{-1}), calculated on the basis of the ^{1}H-DNMR data,[16] are consistent with such an intramolecular process with only a small variation in the entropy and thus support our proposed interpretation.

NbCp*Cl_2Me_2 also reacts with 2 equiv. of lithium dimethylamide at room temperature in diethyl ether to give the expected product NbCp*$Me_2(NMe_2)_2$ (**2**), which rapidly decomposes in solution under elimination of methane to give the η^2-imine complex NbCp*Me(NMe_2)(η^2-CH_2NMe) (**3**). Several attempts to separate **2** and **3** as microcrystalline materials proved unsuccessful and their structures have been proposed solely on the basis of ^{1}H-NMR data (see Experimental Section). The ^{1}H-NMR spectrum of **3** features one singlet due to the Cp* ring, one signal due to the NMe_2 moiety, two signals due to the methyl resonances of Nb−Me and N−Me, respectively, and two doublets due to the methylene protons. This NMR behaviour is in accordance with the chiral character of the metal centre. In view of the observation of the resonances of the CH_2 unit at $\delta_{av} = 1.25$ with a typical geminal proton-proton coupling constant value ($^2J_{H-H} = 4.88$ Hz) for a cyclopropane ring,[17] **3** must be described as an azaniobacyclopropane complex (see Scheme 1).

On addition of 1 equiv. of 2,6-$Me_2C_6H_3NC$ to toluene solutions of NbCp*Cl_2Me_2 under rigorously anhydrous conditions, brown-red solutions were obtained, from which [NbCp*Cl_2{η^2-CMe_2N(2,6-$Me_2C_6H_3$)}] (**4**) was recovered as a brown solid on removal of the solvent (Scheme 1). The equivalence of the methyl groups in the NMR spectra is consistent with a C_s-symmetry complex possessing a plane of symmetry defined by the niobium, the nitrogen, and the carbon atoms that is perpendicular to the plane of the pentamethylcyclopentadienyl ring. Previously, we have reported[4a] the synthesis, the mechanism of formation, and the crystal structure of a similar azatantalacyclopropane com-



Reagents and conditions:
i- $ZnMe_2$ excess, n-hexane, RT, 48 h
ii- 2 equiv $LiNMe_2$, diethyl ether, RT, 3 h
iii-1 equiv ArNC, toluene, RT, 30 min

Scheme 1

plex. In the present case, we were unable to obtain adequate single crystals for X-ray diffraction analysis, but like the tantalum analogue the structure must be a distorted trigonal bipyramid with the chlorine and nitrogen atoms occupying the equatorial plane positions and the centroid of the Cp* ring and the azaniobacyclopropane C atom occupying the apical sites.

When the same reaction was repeated at room temperature using 2 equiv. of isocyanide, a different sequence of reactions occurred leading to the diamagnetic pseudooctahedral niobium(III) complex $NbCp^*Cl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)_3$. We have isolated this complex previously[18] by reducing $NbCp^*Cl_4$ with 2 equiv. of Na/Hg in the presence of a stoichiometric amount of isocyanide. This behaviour is in contrast to that observed in the case of $TaCp^*Cl_2Me_2$,[4b] which, in the presence of 2 equiv. of an isocyanide, gives the corresponding dichloro imido complex $TaCp^*Cl_2(NAr)$ (Ar = $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$) under elimination of the arylimine ketene $Ar{-}N{=}C{=}CMe_2$. The same dichloro tris(isocyanide) complex is obtained when 1 equiv. of the appropriate isocyanide is added to a toluene solution of the azaniobacyclopropane complex **4** at room temperature.

Synthesis and Reactivity of Dialkyldichloro(pentamethylcyclopentadienyl)tantalum(V) Complexes

On treating *n*-hexane suspensions of the complex $TaCp^*Cl_4$ with stoichiometric amounts of the alkylating reagents MgClR (R = CH_2SiMe_3, CH_2CMe_2Ph, CH_2Ph) or $Mg(CH_2CMe_3)_2(THF)_2$ under rigorously anhydrous conditions at room temperature, suspensions were obtained from which the dialkyldichloro complexes $TaCp^*Cl_2R_2$ [R = CH_2SiMe_3 (**5**), CH_2CMe_2Ph (**6**), CH_2CMe_3 (**7**), CH_2Ph (**8**)] could be isolated in good yields (see Scheme 2). The dineopentyl and dibenzyl derivatives **7** and **8** have been described previously by Schrock et al.[19] Several attempts to prepare **5**−**8** using stoichiometric amounts of lithium reagents proved unsuccessful and in all cases only unidentified reduction products were obtained. Complexes **5**−**8** were found to be air- and moisture-sensitive, and soluble in both *n*-hexane and aromatic solvents.

When 1 equiv. of the isocyanide $2,6\text{-}Me_2C_6H_3NC$ was added to *n*-hexane solutions of the dialkyldichlorotantalum complexes **5**−**8** under a rigorously dry inert gas or in a sealed NMR tube, reddish solutions were obtained. After work-up, the alkyldichloro(η^2-iminoacyl)tantalum complexes $[TaCp^*Cl_2R\{\eta^2\text{-}C(R){=}NAr\}]$ [Ar = $2,6\text{-}Me_2C_6H_3$; R = CH_2SiMe_3 (**9**), CH_2CMe_2Ph (**10**), CH_2CMe_3 (**11**), CH_2Ph (**12**)] could be recovered (Scheme 2). This behaviour is in contrast to that observed for the dichlorodimethyl derivative,[4] which, in the presence of 1 equiv. of isocyanide, gives a dichloroazatantalacyclopropane complex as a result of a migration of the second methyl group to the electrophilic iminoacyl carbon atom of the dichloro(η^2-iminoacyl)(methyl) intermediate. In the present case, the remaining bulkier alkyl substituent does not migrate. On the other hand, the same η^2-iminoacyl complexes **9**−**12** are obtained upon reaction of 2 equiv. of the isocyanide with the starting dialkyldichloro compounds in [D$_6$]benzene at room temperature and no bis(η^2-iminoacyl) species are detected.

All of the complexes **9**−**12** were found to be soluble in most organic solvents, including saturated hydrocarbons. They are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under dry inert gases were found to be imperative for successful preparations.

The molecular structure of compound **10** is shown in Figure 1 and selected bond lengths and angles are given in Table 1. Complex **10** crystallizes in the space group $P2_1/c$ with the two possible enantiomers of the molecule present in the unit cell.

As can be seen, complex **10** is a monomer with the tantalum atom in a pseudooctahedral environment, where the centroid of the pentamethylcyclopentadienyl ring and the carbon atom of the iminoacyl group occupy the axial positions. The tantalum atom is located 0.61(1) Å above the plane formed by the C21, Cl1, Cl2, and N1 atoms.[20] The C=N bond of the iminoacyl group is almost perpendicular [75.0(2)°] to the plane formed by the two chlorine atoms, N1, and C21 of the neopentyl group. The difference between this angle and that for ideal perpendicularity accounts for the fact that two enantiomers are present in the unit cell.

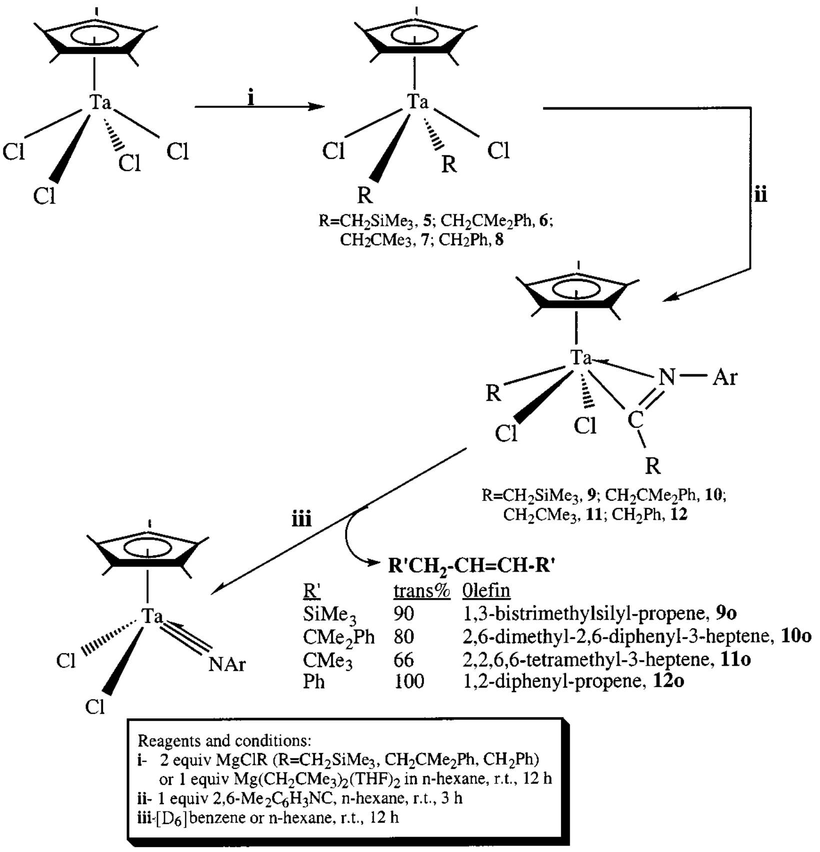
On the other hand, the *trans* effect of the iminoacyl group makes the distances between Ta1 and C11 [2.523(7) Å], C14 [2.528(7) Å], and C15 [2.591(7) Å] longer than the other two Ta−Cl distances [Ta1−C12 2.415(6) Å, Ta1−C13 2.437(6) Å].

Bond lengths in the η^2-iminoacyl group [N1−C41 1.262(7), N1−C42 1.482(7), and C41−C31 1.500(8) Å] are within the range found for other compounds[21] for which a C=N double bond and an η^2 coordination has been proposed. The plane formed by the aromatic ring C42−C47 is rotated by 70.6(2)° with respect to that formed by N1, C41, C42, and C31, partially preventing electronic delocalization over the iminoacyl and aromatic groups.

The IR, ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopic data (see Experimental Section) are consistent with the expected pseudooctahedral geometries of these η^2-iminoacyl complexes. The NMR spectra of **9**−**12** in [D$_6$]benzene solution at room temperature show the expected equivalence of the α-CH_2 protons of the inserted and non-inserted alkyl groups, in accordance with the *trans* disposition of the chlorine atoms and due to fast exchange between the two enantiomeric structures found in the solid state, the transition state of this process having C_s symmetry. Moreover, the $2,6\text{-}Me_2C_6H_3$ ring of the η^2-iminoacyl ligand is characterized by C_{2v} local symmetry (Scheme 3).

The IR spectra of all the complexes show the characteristic absorptions for the pentamethylcyclopentadienyl ring ($\tilde{\nu}_{C-C}$ = 1027 cm^{-1})[22] and the trimethylsilyl substituent {$\tilde{\nu}$ = 1250 cm^{-1} [$\delta_{as}(CH_3)$]}.[23] Absorptions due to the C(R)=N, Ta−C, and Ta−Cl stretching vibrations are observed at $\tilde{\nu}$ = 1559,[23d,24] 525,[23d,25] and 278 cm^{-1},[23c,26] respectively.

In [D$_6$]benzene or *n*-hexane solution, **9**−**12** were found to spontaneously, albeit slowly, decompose at room temperature (see Scheme 4) to give a mixture of two components,



$R'CH_2\text{-}CH{=}CH\text{-}R'$

R'	trans%	Olefin
$SiMe_3$	90	1,3-bistrimethylsilyl-propene, **9o**
CMe_2Ph	80	2,6-dimethyl-2,6-diphenyl-3-heptene, **10o**
CMe_3	66	2,2,6,6-tetramethyl-3-heptene, **11o**
Ph	100	1,2-diphenyl-propene, **12o**

Reagents and conditions:
i- 2 equiv MgClR (R=CH_2SiMe_3, CH_2CMe_2Ph, CH_2Ph) or 1 equiv $Mg(CH_2CMe_3)_2(THF)_2$ in n-hexane, r.t., 12 h
ii- 1 equiv 2,6-$Me_2C_6H_3NC$, n-hexane, r.t., 3 h
iii-[D6]benzene or n-hexane, r.t., 12 h

Scheme 2

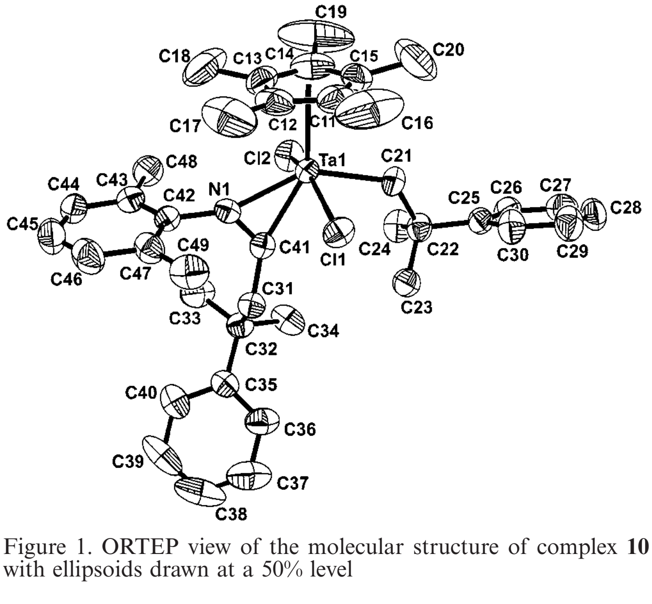


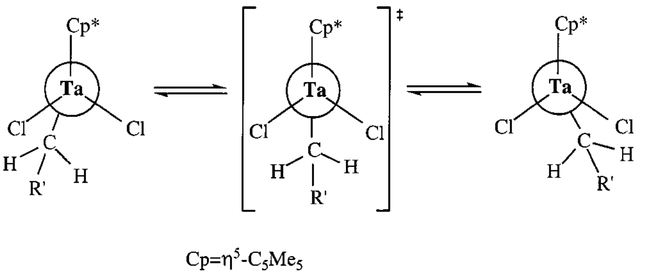
Figure 1. ORTEP view of the molecular structure of complex **10** with ellipsoids drawn at a 50% level

a dichloro(imido)tantalum compound $[TaCp^*Cl_2\{N(2,6\text{-}Me_2C_6H_3)\}]$[4a] together with *cis* and *trans* olefins $R'{-}CH_2{-}CH{=}CH{-}R'$ [R′ = $SiMe_3$ (**9o**), CMe_2Ph (**10o**), CMe_3 (**11o**), Ph (**12o**)],[27] which were fully characterized by NMR spectroscopy (see Experimental Section).

This transformation can be rationalized in terms of migration of the metal-bonded alkyl group to the iminoacyl carbon centre in the first step to give the intermediate dialkylazatantalacyclopropane complexes (see Scheme 4),

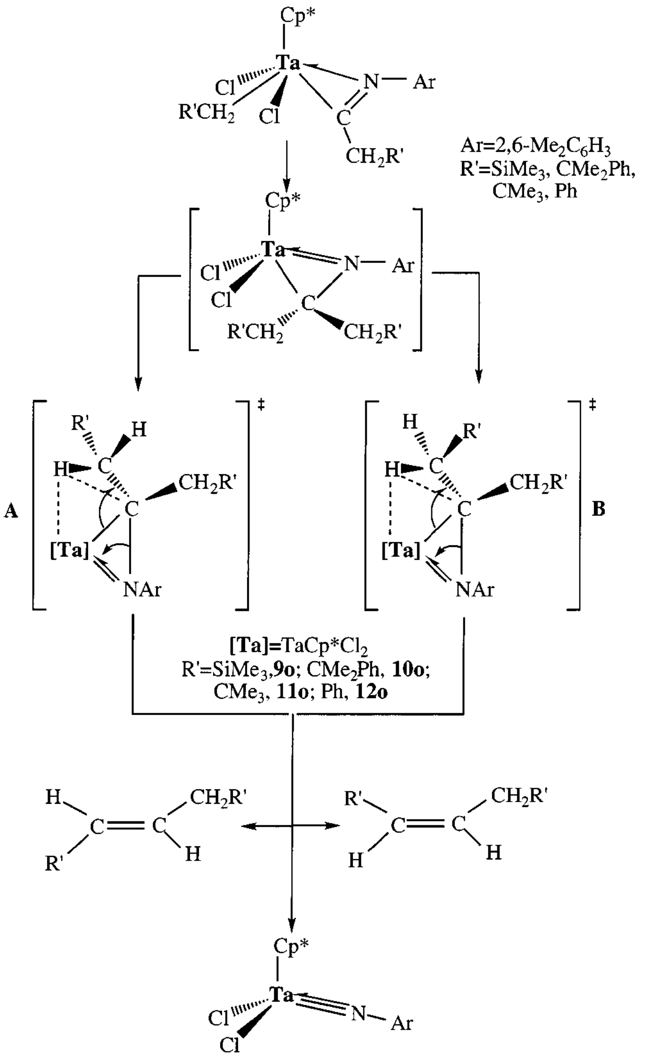
Table 1. Selected bond lengths [Å] and angles [°] for compound **10**

Ta(1)−N(1)	2.154(5)	Ta(1)−C(41)	2.175(6)
Ta(1)−C(21)	2.257(6)	Ta(1)−C(12)	2.415(6)
Ta(1)−Cl(2)	2.418(2)	Ta(1)−C(13)	2.437(6)
Ta(1)−Cl(1)	2.438(2)	Ta(1)−C(11)	2.523(7)
Ta(1)−C(14)	2.528(7)	Ta(1)−C(15)	2.591(7)
N(1)−C(41)	1.262(7)	N(1)−C(42)	1.481(7)
C(31)−C(41)	1.500(8)	C(42)−C(47)	1.396(8)
C(42)−C(43)	1.396(9)		
N(1)−Ta(1)−C(41)	33.89(18)	N(1)−Ta(1)−C(21)	142.4(2)
C(41)−Ta(1)−C(21)	108.8(2)	N(1)−Ta(1)−Cl(2)	85.10(12)
C(41)−Ta(1)−Cl(2)	82.55(14)	C(21)−Ta(1)−Cl(2)	84.04(16)
N(1)−Ta(1)−Cl(1)	89.55(13)	C(41)−Ta(1)−Cl(1)	77.49(14)
C(21)−Ta(1)−Cl(1)	83.17(16)	Cl(2)−Ta(1)−Cl(1)	151.32(6)
C(41)−N(1)−C(42)	128.8(5)	C(41)−N(1)−Ta(1)	73.9(3)
C(42)−N(1)−Ta(1)	156.3(4)	C(22)−C(21)−Ta(1)	131.2(4)
C(41)−C(31)−C(32)	118.6(5)	N(1)−C(41)−C(31)	125.0(5)
N(1)−C(41)−Ta(1)	72.2(3)	C(31)−C(41)−Ta(1)	158.5(4)



Cp=η^5-C_5Me_5
R'=$SiMe_3$, CMe_2Ph, CMe_3, Ph

Scheme 3



Scheme 4

which cannot be detected during monitoring of the entire reaction by ^{1}H-NMR spectroscopy. However, the cyclopropane structure favours agostic interactions between the β-hydrogen atoms of the alkyl groups and the tantalum atom, leading to concerted four-centre transition states **A** and **B**.

Subsequent 2,1-migration of the hydrogen atom, probably through formation of a Ta hydride, and back-rearrangement gives the imido complex[4a] with elimination of the corresponding olefins **9o–12o**. The relative disposition of R′ and CH$_2$R′ groups in **A** and **B** is dependent on the β-hydrogen atom that participates in an agostic interaction with the metal centre and thus determines the stereochemistry of the final olefins.

The data reported here are in contrast to our previous results concerning the insertion of isocyanides into Ta–C bonds of dimethyltantalum derivatives[4a] and show that these are more stable compared to the complexes **9–12**, probably due to steric factors.

Experimental Section

General: All reactions and manipulations were carried out under argon using standard Schlenk-tube and cannula techniques or in a conventional argon-filled MBraun glove-box.[28] Solvents were refluxed over appropriate drying agents and distilled and degassed prior to use: diethyl ether (sodium/benzophenone), *n*-hexane and [D$_6$]benzene (Na/K alloy). Literature methods were employed for the syntheses of the starting materials NbCp*Cl$_2$Me$_2$,[13] TaCp*Cl$_2$R$_2$ [19] [R = CH$_2$CMe$_3$ (**3**), CH$_2$Ph (**4**)], TaCp*Cl$_4$,[29] and Mg(CH$_2$CMe$_3$)$_2$(THF)$_2$.[30] 2 M ZnMe$_2$ in toluene (Aldrich), LiNMe$_2$ (Aldrich), 2,6-Me$_2$C$_6$H$_3$NC (Aldrich), and MgClR (R= CH$_2$SiMe$_3$, 1 M in diethyl ether; CH$_2$CMe$_2$Ph, 0.5 M in diethyl ether; CH$_2$Ph 2 M in THF) (Aldrich) were purchased as reagent-grade materials and were used without further purification.

Infrared spectra were recorded with a Perkin–Elmer 583 spectrophotometer (4000–200 cm^{-1}) with samples as Nujol mulls between CsI plates or in polyethylene pellets. – ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with Varian Unity 300 and Varian Unity 500 Plus spectrometers; chemical shifts were referenced to the ^{13}C (δ = 128) and residual ^{1}H (δ = 7.15) resonances of the [D$_6$]benzene solvent. – C, H, N analyses were carried out with a Perkin–Elmer 240C microanalyzer.

Synthesis of NbCp*ClMe$_3$ (1): A 2 M solution of ZnMe$_2$ in toluene (6.00 mmol, 3 mL) was added dropwise to NbCp*Cl$_2$Me$_2$ (1.00 g, 3.06 mmol) in *n*-hexane (100 mL) at room temperature to give an orange suspension. After stirring for 48 h, all volatiles were removed under reduced pressure and the residual red-orange solid was extracted with *n*-hexane (3 × 10 mL). The combined extracts were filtered and the filtrate was concentrated to a volume of 10 mL; on cooling overnight at –40 °C, **1** was deposited as a red-orange microcrystalline solid. Yield 0.37 g (40%). – IR (Nujol): $\tilde{\nu}$ = 1024 cm^{-1} s, 803 w, 723 w, 467 s, 326 s. – ^{1}H NMR (C$_6$D$_6$, 20 °C): δ = 1.54 (s, 15 H, C$_5$Me$_5$), 1.25 (s, 9 H, Nb–Me). – ^{1}H NMR (C$_7$D$_8$, –50 °C): δ = 1.44 (s, 15 H, C$_5$Me$_5$), 1.22 (s, 6 H, Nb–Me), 1.12 (s, 3 H, Nb–Me). – ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ = 119.6 (*C*$_5$Me$_5$), 64.9 (br., Nb–Me), 11.6 (C$_5$*Me*$_5$). – C$_{13}$H$_{24}$ClNb (308.694): calcd. C 50.58, H 7.84; found C 50.68, H 7.79.

Reaction of NbCp*Cl$_2$Me$_2$ with LiNMe$_2$: NbCp*Cl$_2$Me$_2$ (0.50 g, 1.53 mmol) and LiNMe$_2$ (0.16 g, 3.14 mmol) were stirred in diethyl ether (50 mL) at room temperature for 3 h. The resulting suspension was filtered and the solvent was removed from the filtrate to leave an oily residue. ^{1}H-NMR analysis showed this to consist of a mixture of [NbCp*Me$_2$(NMe$_2$)$_2$] (**2**) and [NbCp*Me(NMe$_2$)(η^2-CH$_2$NMe)] (**3**) in a 1:2 molar ratio. All attempts to separate the compounds by recrystallization were unsuccessful. – ^{1}H NMR (C$_6$D$_6$, 20 °C): **2**: δ = 3.00 (s, 12 H, Me$_2$N–Nb), 1.65 (s, 15 H, C$_5$Me$_5$), 0.38 (s, 6 H, Me–Nb); **3**: δ = 3.63 (s, 3 H, CH$_2$N*Me*), 2.72 (s, 6 H, Me$_2$N–Nb), 1.73 (s, 15 H, C$_5$Me$_5$), 1.51 (d, 1 H), 1.01 (d, $^2J_{H-H}$ = 4.88 Hz, 1 H, C*H*$_2$NMe), 0.53 (s, 3 H, Me–Nb).

Synthesis of [NbCp*Cl$_2${η^2-CMe$_2$–N(2,6-Me$_2$C$_6$H$_3$)}] (4): A solution of NbCp*Cl$_2$Me$_2$ (0.50 g, 1.53 mmol) in toluene (20 mL) was treated with (2,6-Me$_2$C$_6$H$_3$)NC (0.20 g, 1.53 mmol) under rigorously anhydrous conditions. The mixture was stirred for 30 min and then filtered. The filtrate was concentrated to dryness and the residue was washed with cold *n*-hexane (2 × 10 mL) to leave **4** as a brown microcrystalline solid. Yield 0.53 g (76%). – IR (Nujol): $\tilde{\nu}$ = 1259 cm^{-1} m, 1023 m, 768 m, 723 m, 371 m. – ^{1}H NMR (C$_6$D$_6$, 20 °C): δ = 6.94 (br., 3 H, *H*$_3$C$_6$Me$_2$N), 2.10 (s, 6 H, *Me*$_2$C$_6$H$_3$N), 2.00 (s, 6 H, Me$_2$C), 1.63 (s, 15 H, C$_5$Me$_5$). – ^{13}C{^{1}H} NMR

($\mathrm{C_6D_6}$, 20 °C): δ = 150.0, 132.2, 128.8, 124.0 (C_i, C_o, C_m, C_p, $\mathrm{\mathit{C}_6H_3Me_2N}$), 122.8 ($\mathrm{\mathit{C}_5Me_5}$), not observed ($\mathrm{\mathit{C}Me_2}$), 28.7 ($\mathrm{\mathit{Me}_2C}$), 20.4 ($\mathrm{\mathit{Me}_2C_6H_3N}$), 11.1 ($\mathrm{C_5\mathit{Me}_5}$). − $\mathrm{C_{21}H_{30}Cl_2NNb}$ (460.29): calcd. C 54.80, H 6.57, N 3.04; found C 54.94, H 6.62, N 3.17.

Synthesis of $\mathrm{TaCp^{*}Cl_2R_2}$ [R = $\mathrm{CH_2SiMe_3}$ (5), $\mathrm{CH_2CMe_2Ph}$ (6)]: A 1.0 M (**5**) or 0.5 M (**6**) solution of MgClR in diethyl ether (4.36 mmol; R = $\mathrm{CH_2SiMe_3}$, 4.36 mL; $\mathrm{CH_2CMe_2Ph}$, 8.73 mL) was added to a suspension of $\mathrm{TaCp^{*}Cl_4}$ (1.00 g, 2.18 mmol) in *n*-hexane (40 mL) at room temperature and the mixture was stirred for 12 h. The $\mathrm{MgCl_2}$ formed was removed by filtration and the resulting filtrate was concentrated to a volume of ca. 10 mL. On cooling to −40 °C, orange (**5**) or red (**6**) microcrystalline solids were deposited.

Data for 5: Yield: 0.73 g (60%). − IR (Nujol): $\tilde{\nu}$ = 1327 cm^{-1} s, 1241 vs, 1024 m, 952 vs, 835 vs, 749 vs, 716 vs, 681 vs, 615 w, 567 m, 453 m, 365 m, 332 s, 269 vs. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 1.89 (s, 15 H, $\mathrm{C_5Me_5}$), 0.79 (s, 4 H, $\mathrm{\mathit{H}_2CSiMe_3}$), 0.42 (s, 18 H, $\mathrm{\mathit{Me}_3SiCH_2}$). − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 124.78 ($\mathrm{\mathit{C}_5Me_5}$), 94.57 ($\mathrm{\mathit{C}H_2SiMe_3}$), 12.83 ($\mathrm{C_5\mathit{Me}_5}$), 3.36 ($\mathrm{\mathit{Me}_3SiCH_2}$). − $\mathrm{C_{18}H_{37}Cl_2Si_2Ta}$ (561.52): calcd. C 38.50, H 6.64; found C 38.46, H 6.54.

Data for 6: Yield: 0.85 g (60%). − IR (Nujol): $\tilde{\nu}$ = 1597 cm^{-1} w, 1260 w, 1176 m, 1078 s, 1026 s, 804 w, 767 vs, 699 vs, 359 m, 301 vs. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 7.46 (d, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 2 H), 7.25 (t, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 2 H), 7.06 (t, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 1 H, $\mathrm{\mathit{H}_5C_6CMe_2CH_2}$), 1.83 (s, 6 H, $\mathrm{CH_2C\mathit{Me}_2Ph}$), 1.73 (s, 15 H, $\mathrm{C_5Me_5}$), 1.35 (s, 2 H, $\mathrm{\mathit{H}_2CCMe_2Ph}$). − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 158.0, 125.75, 125.2, 116.05 (C_i, C_o, C_m, C_p, $\mathrm{\mathit{C}_6H_5Me_2CCH_2}$), 124.34 ($\mathrm{\mathit{C}_5Me_5}$), 44.05 ($\mathrm{\mathit{C}H_2CMe_2Ph}$), 32.76 ($\mathrm{CH_2C\mathit{Me}_2Ph}$), 31.4 ($\mathrm{CH_2\mathit{C}Me_2Ph}$), 12.63 ($\mathrm{C_5\mathit{Me}_5}$). − $\mathrm{C_{30}H_{41}Cl_2Ta}$ (653.512): calcd. C 55.14, H 6.32; found C 54.96, H 6.18.

Synthesis of [$\mathrm{TaCp^{*}Cl_2R\{\eta^2\text{-}C(R){=}NAr\}}$] [Ar = 2,6-$\mathrm{Me_2C_6H_3}$; R = $\mathrm{CH_2SiMe_3}$ (9), $\mathrm{CH_2CMe_2Ph}$ (10), $\mathrm{CH_2CMe_3}$ (11), $\mathrm{CH_2Ph}$ (12)]

9−11: Under rigorously anhydrous conditions, *n*-hexane (20 mL) was added to a mixture of the complex $\mathrm{TaCp^{*}Cl_2R_2}$ (0.50 g; R = $\mathrm{CH_2SiMe_3}$, 0.89 mmol; $\mathrm{CH_2CMe_2Ph}$, 0.76 mmol; $\mathrm{CH_2CMe_3}$, 0.94 mmol) and CN(2,6-$\mathrm{Me_2C_6H_3}$) (R = $\mathrm{CH_2SiMe_3}$, 0.116 g, 0.89 mmol; $\mathrm{CH_2CMe_2Ph}$, 0.10 g, 0.76 mmol; $\mathrm{CH_2CMe_3}$, 0.123 g, 0.94 mmol) in a Schlenk tube. The color quickly changed to dark red and after stirring for 3 h at room temperature, 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 solids identified as **9**, **10** (red), and **11** (red-orange).

Data for 9: Yield: 0.26 g (43%). − IR (Nujol): $\tilde{\nu}$ = 1553 cm^{-1} m, 1250 s, 1175 s, 1094 m, 1024 m, 980 s, 852 vs, 726 s, 672 m, 602 w, 573 w, 518 w, 449 w, 342 m, 268 s. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 6.90 (t, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 1 H), 6.81 [d, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 2 H, $\mathrm{\mathit{H}_3C_6Me_2N{=}C(CH_2SiMe_3)}$], 3.44 [s, 2 H, $\mathrm{H_3C_6Me_2N{=}C(C\mathit{H}_2SiMe_3)}$], 2.05 [s, 6 H, $\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2SiMe_3)}$], 1.93 (s, 15 H, $\mathrm{C_5Me_5}$), 0.60 (s, 2 H, $\mathrm{Ta{-}C\mathit{H}_2SiMe_3}$), 0.52 (s, 9 H, $\mathrm{Ta{-}CH_2Si\mathit{Me}_3}$), 0.10 [s, 9 H, $\mathrm{H_3C_6Me_2N{=}C(CH_2Si\mathit{Me}_3)}$]. − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 256.73 [$\mathrm{H_3C_6Me_2N{=}\mathit{C}(CH_2SiMe_3)}$], 141.32, 132.92, 127.02, 125.41 [C_i, C_o, C_m, C_p, $\mathrm{H_3\mathit{C}_6Me_2N{=}C(CH_2SiMe_3)}$], 129.45 ($\mathrm{\mathit{C}_5Me_5}$), 51.76 [$\mathrm{H_3C_6Me_2N{=}C(\mathit{C}H_2SiMe_3)}$], 31.32 ($\mathrm{Ta{-}\mathit{C}H_2SiMe_3}$), 20.13 [$\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2SiMe_3)}$], 11.64 ($\mathrm{C_5\mathit{Me}_5}$), 4.05 ($\mathrm{Ta{-}CH_2Si\mathit{Me}_3}$), 0.66 [$\mathrm{H_3C_6Me_2N{=}C(CH_2Si\mathit{Me}_3)}$]. − $\mathrm{C_{27}H_{46}Cl_2NSi_2Ta}$ (692.698): calcd. C 46.82, H 6.69, N 2.02; found C 47.00, H 6.80, N 2.11.

Data for 10: Yield: 0.24 g (40%). − IR (Nujol): $\tilde{\nu}$ = 1536 cm^{-1} m, 1493 m, 1324 s, 1187 m, 1096 m, 1028 m, 982 m, 764 vs, 701 vs, 577 w, 548 w, 394 w, 350 s, 315 m, 285 m. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 7.70 (m, 2 H), 7.32 (m, 2 H), 7.11 (m, 2 H), 6.97 [m, 4 H, $\mathrm{H_3C_6Me_2N{=}C(CH_2CMe_2C_6\mathit{H}_5)}$ and $\mathrm{Ta{-}CH_2CMe_2C_6\mathit{H}_5}$], 6.80 (t, $^{3}J_{\mathrm{H-H}}$ = 7.69 Hz, 1 H), 6.65 [d, $^{3}J_{\mathrm{H-H}}$ = 7.69 Hz, 2 H, $\mathrm{\mathit{H}_3C_6Me_2N{=}C(CH_2CMe_2Ph)}$], 4.19 [s, 2 H, $\mathrm{H_3C_6Me_2N{=}C(C\mathit{H}_2CMe_2Ph)}$], 2.07 [s, 6 H, $\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2CMe_2Ph)}$], 1.82 (s, 15 H, $\mathrm{C_5Me_5}$), 1.80 (s, 6 H, $\mathrm{Ta{-}CH_2C\mathit{Me}_2Ph}$), 1.75 (s, 2 H, $\mathrm{Ta{-}C\mathit{H}_2CMe_2Ph}$), 1.49 [s, 6 H, $\mathrm{H_3C_6Me_2N{=}C(CH_2C\mathit{Me}_2Ph)}$]. − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 259.26 [$\mathrm{H_3C_6Me_2N{=}\mathit{C}(CH_2CMe_2Ph)}$], 181.96−124.86 [several phenyl, $\mathrm{H_3C_6Me_2N{=}C(CH_2CMe_2\mathit{C}_6H_5)}$ and $\mathrm{Ta{-}CH_2CMe_2\mathit{C}_6H_5}$], 159.15−119.26 [several phenyl, $\mathrm{H_3\mathit{C}_6Me_2N{=}C(CH_2CMe_2C_6H_5)}$], 125.57 ($\mathrm{\mathit{C}_5Me_5}$), 88.56 [$\mathrm{H_3C_6Me_2N{=}C(\mathit{C}H_2CMe_2Ph)}$], 51.10 ($\mathrm{Ta{-}\mathit{C}H_2CMe_2Ph}$), 43.80 ($\mathrm{Ta{-}CH_2\mathit{C}Me_2Ph}$), 40.18 [$\mathrm{H_3C_6Me_2N{=}C(CH_2\mathit{C}Me_2Ph)}$], 32.81 ($\mathrm{Ta{-}CH_2C\mathit{Me}_2Ph}$), 30.95 [$\mathrm{H_3C_6Me_2N{=}C(CH_2C\mathit{Me}_2Ph)}$], 11.14 ($\mathrm{C_5\mathit{Me}_5}$). − $\mathrm{C_{39}H_{50}Cl_2NTa}$ (784.685): calcd. C 59.69, H, 6.42, N 1.78; found C 59.83, H 6.40, N 1.76.

Data for 11: Yield: 0.25 g (40%). − IR (Nujol): $\tilde{\nu}$ = 1556 cm^{-1} s, 1233 s, 1166 s, 1096 m, 1019 m, 830 m, 769 vs, 724 w, 649 m, 603 w, 510 w, 340 s, 279 vs, 231 m. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 6.83 (m, 1 H), 6.77 [m, 2 H, $\mathrm{\mathit{H}_3C_6Me_2N{=}C(CH_2CMe_3)}$], 3.64 [s, 2 H, $\mathrm{H_3C_6Me_2N{=}C(C\mathit{H}_2CMe_3)}$], 2.02 [s, 6 H, $\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2CMe_3)}$], 1.90 (s, 15 H, $\mathrm{C_5Me_5}$), 1.59 [s, 9 H, $\mathrm{H_3C_6Me_2N{=}C(CH_2C\mathit{Me}_3)}$], 1.54 (s, 2 H, $\mathrm{Ta{-}C\mathit{H}_2CMe_3}$), 1.07 (s, 9 H, $\mathrm{Ta{-}CH_2C\mathit{Me}_3}$). − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 260.94 [$\mathrm{H_3C_6Me_2N{=}\mathit{C}(CH_2CMe_3)}$], 141.70, 132.63, 129.50, 127.00 [C_i, C_o, C_m, C_p, $\mathrm{H_3\mathit{C}_6Me_2N{=}C(CH_2CMe_3)}$], 125.74 ($\mathrm{C_5\mathit{Me}_5}$), 88.10 [$\mathrm{H_3C_6Me_2N{=}C(\mathit{C}H_2CMe_3)}$], 50.36 ($\mathrm{Ta{-}\mathit{C}H_2CMe_3}$), 37.41 [$\mathrm{H_3C_6Me_2N{=}C(CH_2\mathit{C}Me_3)}$], 36.10 [$\mathrm{H_3C_6Me_2N{=}C(CH_2C\mathit{Me}_3)}$], 34.22 ($\mathrm{Ta{-}CH_2\mathit{C}Me_3}$), 31.70 ($\mathrm{Ta{-}CH_2C\mathit{Me}_3}$), 20.19 [$\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2CMe_3)}$], 11.66 ($\mathrm{C_5\mathit{Me}_5}$). − $\mathrm{C_{29}H_{46}Cl_2NTa}$ (660.548): calcd. C 52.73, H 7.02, N 2.12; found C 52.93, H 7.04, N 2.28.

12: A solution of $\mathrm{TaCp^{*}Cl_2(CH_2Ph)_2}$ (0.50 g, 0.88 mmol) in *n*-hexane (15 mL) was treated with the isocyanide (2,6-$\mathrm{Me_2C_6H_3}$)NC (0.115 g, 0.88 mmol) under rigorously anhydrous conditions. The color of the solution rapidly changed from brown-green to purple and after 2 h, a red microcrystalline precipitate had separated. This was collected by filtration, washed with a small volume of cold *n*-hexane, and dried in vacuo.

Data for 12: Yield: 0.31 g (50%). − IR (Nujol): $\tilde{\nu}$ = 1614 cm^{-1} m, 1590 m, 1290 m, 1262 s, 1162 s, 1100 s, 1064 s, 1024 s, 804 s, 724 vs, 690 s, 352 m, 280 m. − ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 7.84 (m, 3 H), 7.52 [m, 2 H, $\mathrm{H_3C_6Me_2N{=}C(CH_2C_6\mathit{H}_5)}$], 6.96 (m, 2 H), 6.50 [m, 1 H, $\mathrm{\mathit{H}_3C_6Me_2N{=}C(CH_2Ph)}$], 6.70 (m, 5 H, $\mathrm{Ta{-}CH_2C_6\mathit{H}_5}$), 3.86 [s, 2 H, $\mathrm{H_3C_6Me_2N{=}C(C\mathit{H}_2Ph)}$], 2.11 (s, 2 H, $\mathrm{Ta{-}C\mathit{H}_2C_6H_5}$), 1.89 (s, 15 H, $\mathrm{C_5Me_5}$), 1.61 [s, 6 H, $\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2Ph)}$]. − ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20 °C): δ = 258 [$\mathrm{H_3C_6Me_2N{=}\mathit{C}(CH_2Ph)}$], 152.58−122.31 [several phenyl, $\mathrm{H_3\mathit{C}_6Me_2N{=}C(CH_2\mathit{C}_6H_5)}$ and $\mathrm{Ta{-}CH_2\mathit{C}_6H_5}$], 124.94 ($\mathrm{C_5\mathit{Me}_5}$), 70.53 [$\mathrm{H_3C_6Me_2N{=}C(\mathit{C}H_2Ph)}$], 37.74 ($\mathrm{Ta{-}\mathit{C}H_2C_6H_5}$), 20.45 [$\mathrm{H_3C_6\mathit{Me}_2N{=}C(CH_2Ph)}$], 11.39 ($\mathrm{C_5\mathit{Me}_5}$). − $\mathrm{C_{33}H_{38}Cl_2NTa}$ (700.528): calcd. C 56.58, H 5.47, N 2.00; found C 56.48, H 5.63, N 2.28.

Decomposition Reaction of [$\mathrm{TaCp^{*}Cl_2R\{\eta^2\text{-}C(R){=}NAr\}}$] [Ar = 2,6-$\mathrm{Me_2C_6H_3}$; R = $\mathrm{CH_2SiMe_3}$ (9), $\mathrm{CH_2CMe_2Ph}$ (10), $\mathrm{CH_2CMe_3}$ (11), $\mathrm{CH_2Ph}$ (12)]: A solution of **9−12** (0.50 mmol) in [$\mathrm{D_6}$]benzene was placed in a valved NMR tube under rigorously anhydrous conditions. The reaction was monitored by ^{1}H- and ^{13}C-NMR spectroscopy until no further change was observed (ca. 12 h). The final spectrum was indicative of complete transformation of the starting material to a mixture of the two components, i.e. a dichloro(imido) complex $TaCp^{*}Cl_2(NAr)$ and an olefin **9o**−**12o** (*cis*/*trans* isomers).[27]

X-ray Structure Determination of 10: A red, block-shaped crystal of compound **10**, crystallized from *n*-hexane at −40°C, was mounted in a glass capillary in a random orientation on an Enraf−Nonius CAD-4 four-circle automatic diffractometer and examined with graphite-monochromated Mo-K_{α} radiation (λ = 0.71073 Å). Crystallographic and experimental details for **10** are summarized in Table 2. Intensities were corrected for Lorentz and polarization effects in the usual manner. Intensity measurements were performed by ω-θ scans in the range $6° < 2\theta < 50°$.

Table 2. Crystal and X-ray structural analysis data for the compound $[TaCp^{*}Cl_2(CH_2CMe_2Ph)\{\eta^2\text{-}C(CH_2CMe_2Ph)=N(2,6\text{-}Me_2\text{-}C_6H_3)\}]$ (**10**)

Empirical formula	$C_{39}H_{50}Cl_2NTa$
Molecular mass	784.65
Temperature [K]	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, *b*, *c* [Å]	16.602(4), 11.411(5), 20.522(4)
β [°]	112.66(4)
Volume; *Z*	3587(2) Å^3; 4
Density (calculated)	1.453 g/cm^3
μ (Mo-K_{α})	3.240 mm^{-1}
F(000)	1592
Crystal size	0.40 × 0.35 × 0.32 mm
Index ranges	$0 < h < 19$, $0 < k < 13$, $-24 < l < 22$
Reflections collected	6507
Independent reflections	6276 (R_{int} = 0.0454)
Observed reflections [$I > 2\sigma(I)$]	5251
Data/restraints/parameters	6276/0/399
Goodness-of-fit on F^2	0.903
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.040$, $wR2 = 0.101$
R indices (all data)	$R1 = 0.054$, $wR2 = 0.110$
Largest diff. peak and hole	1.828 and −1.793 eÅ^{-3}

The structure was solved by direct methods (SHELXS-97)[31] using the WINGX package and refined by least-squares against F^2 (SHELXL-97). Of the 6507 measured reflections, 6276 were independent; $R1 = 0.040$ and $wR2 = 0.101$ [for 5251 reflections with $F > 4\sigma(F)$]. The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.081)^2 + 9.023P]$, $P = (F_o^2 + 2F_c^2)/3$, and σ was obtained from the counting statistics. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced in calculated positions in the final cycle of the refinement and refined using a riding model with thermal parameters fixed at U = 0.08 Å^2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139661. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[27] NMR data for olefins $R'{-}C^1H_2{-}C^2H{=}C^3H{-}R'$ (**9o**−**12o**). − ^1H NMR (C_6D_6, 20 °C): **9o** ($R' = SiMe_3$), *trans* isomer: $\delta = 6.38$ (dt, $^3J_{H2-H1} = 6.8$ Hz, $^3J_{H2-H3} = 14.1$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 5.48 (dt, $^3J_{H2-H3} = 14.1$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 2.20 (d, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$), 0.19 (s, 9 H, $R'{-}CH_2{-}CH{=}CH{-}Si\mathit{Me}_3$), −0.01 (s, 9 H, $\mathit{Me}_3Si{-}CH_2{-}CH{=}CH{-}R'$). − **10o** ($R' = CMe_2Ph$), *trans* isomer: $\delta = 5.51$ (dt, $^3J_{H3-H1} = 2$ Hz, $^3J_{H2-H3} = 15.5$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 5.27 (dt, $^3J_{H2-H1} = 15.5$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 2.26 (dd, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$), 1.22 (s, 12 H, $Ph\mathit{Me}_2C{-}CH_2{-}CH{=}CH{-}C\mathit{Me}_2Ph$); *cis* isomer: $\delta = 5.59$ (dt, $^3J_{H2-H3} = 11.7$ Hz, $^4J_{H3-H1} = 2$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 5.16 (dt, $^3J_{H2-H3} = 11.7$ Hz, $^3J_{H2-H1} = 7$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 2.01 (dd, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$), 1.32 (s, 6 H), 1.03 (s, 6 H, $Ph\mathit{Me}_2C{-}CH_2{-}CH{=}CH{-}C\mathit{Me}_2Ph$). − **11o** ($R' = CMe_3$), *trans* isomer: $\delta = 5.46$ (dt, $^3J_{H2-H3} = 12.2$ Hz, $^4J_{H1-H3} = 1.8$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 5.31 (dt, $^3J_{H2-H3} = 12.2$ Hz, $^3J_{H1-H2} = 6.5$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 2.12 (dd, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$), 1.12 (s, 9 H, $R'{-}CH_2{-}CH{=}CH{-}C\mathit{Me}_3$), 0.90 (s, 9 H, $\mathit{Me}_3C{-}CH_2{-}CH{=}CH{-}R'$) [$^{13}C\{^1H\}$ DEPT NMR data: **11o**, *trans* isomer: $\delta = 141.23$ (C^3), 126.14 (C^2), 42.13 (C^1); *cis* isomer: $\delta = 144.58$ (C^3), 122.25 (C^2), 47.4 (C^1)]; *cis* isomer: $\delta = 5.47$ (dt, $^3J_{H2-H3} = 12$ Hz, $^4J_{H1-H3} = 1.8$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 5.42 (dt, $J_{H2-H3} = 12$ Hz, $^3J_{H1-H2} = 6.5$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 1.88 (dd, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$), 1.01 (s, 9 H, $R'{-}CH_2{-}CH{=}CH{-}C\mathit{Me}_3$), 0.88 (s, 9 H, $\mathit{Me}_3C{-}CH_2{-}CH{=}CH{-}R'$). − **12o** ($R' = Ph$), *trans* isomer: $\delta = 6.30$ (dt, $^3J_{H2-H3} = 16$ Hz, $^4J_{H1-H3} = 1$ Hz, 1 H, $R'{-}CH_2{-}CH{=}C\mathit{H}{-}R'$), 6.18 (dt, $^3J_{H2-H3} = 16$ Hz, $^3J_{H1-H2} = 6.9$ Hz, 1 H, $R'{-}CH_2{-}C\mathit{H}{=}CH{-}R'$), 3.30 (dd, 2 H, $R'{-}C\mathit{H_2}{-}CH{=}CH{-}R'$). (For **10o** and **12o**: The spectral region corresponding to the phenyl protons cannot be analyzed, but the integral is 10 H for each isomer of **10o** and for the *trans* isomer of **12o**.)

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