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PAPER

Tri-chlorido, 2-methylallyl and 2-butenyl *tert*-butylimido niobium and tantalum complexes: Synthesis, multinuclear NMR spectroscopy and reactivity†

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Pseudooctahedral complexes $[MCl_3(NtBu)L_2]$ (M = Nb, L = py **1**, $\frac{1}{2}$ tmeda **3**; M = Ta, L = py **2**, $\frac{1}{2}$ tmeda **4**) have been studied by spectroscopic methods. By a VT ^{1}H NMR experiment a mutual exchange process between the py_{ax} and py_{free} in the complexes **1–2** was observed, whereas ^{13}C and ^{15}N NMR studies showed in the complexes **3–4** a tmeda ligand with an axial/equatorial coordination mode. The reaction of **2** with 3 equiv of Grignard reagent produces the methathesis products $[TaR_3(NtBu)]$ (R = CH_2CMeCH_2 **5**, $CH_2CHCHCH_3$ **6**) in which 2-methylallyl and 2-butenyl groups appear with a η^3- and σ-coordination mode, respectively. When, toluene solutions of the compounds **5–6** were treated with 2 equiv of 2,6-dimethylphenylisocyanide the imido bisiminoacyl compounds $[TaR(NtBu)\{C(R)NAr\text{-}\kappa^1C\}_2]$ (Ar = 2,6-$Me_2C_6H_3$; R = CH_2CMeCH_2 **7**, $CH_2CHCHCH_3$ **8**) can be isolated, *via* an imido iminoacyl intermediate $[TaR_2(NtBu)\{C(R)NAr\text{-}\kappa^1C\}]$ (Ar = 2,6-$Me_2C_6H_3$; R = CH_2CMeCH_2 **9**) as we have observed in the treatment of **5** with 1 equiv of isocyanide; however, the analogous reaction between **5** and $COPh_2$ leads to the formation of the trisalkoxo imido compound $[Ta(OCPh_2R)_3(NtBu)]$ (R = CH_2CMeCH_2 **10**). All new complexes were studied by IR and multinuclear NMR spectroscopy.

Introduction

High-valent early transition metal complexes containing strong π-donor organoimido substituents[1] are being intensively studied in relation to their potential applications in catalytic and stoichiometric processes. A lot of examples show that over the last few years we have witnessed an extensive development of imido group 5 nonmetallocene chemistry.[2]

Protonated lithium amides[3] together with other synthetic strategies[4] have been extensively used to generate the imido ligand and in this context, neutral niobium and tantalum complexes have been synthesized[5] and their functionalities[6] were used as both ancillary and reactive sites. Although as ancillary ligands they have been electronically compared with cyclopentadienide,[6a,7] a series of important stoichiometric transformations such as, protonations of metal amides,[6e] additions of hydrogen to metal–alkyl groups,[6j,6k] insertions of unsaturated molecules (CO, ArNC) into metal–alkyl bonds,[6b–6d,6f–6h,6l] imido-to-oxo ligand exchange and the activation of benzene C–H bonds[6h] have been observed.

In this paper, some trichlorido *tert*-butylimido niobium and tantalum complexes were studied by multinuclear NMR spectroscopy and the nature of ^{15}N chemical shifts analyzed. In addition, by alkylation reactions 2-methylallyl and 2-butenyl *tert*-butylimido derivatives were prepared and their reactivity investigated with unsaturated organic substrates as isocyanides and ketones.

Results and discussion

Although the first metal-imido complexes of the type $[MX_3(NR)L_2]$ (M = Nb, Ta; R = alkyl, aryl; X = halide; L = neutral σ-donor ligand)[8] were synthesized twenty years ago, their structural study is incomplete and only some molecular structure,[8c,9] reactivity[8b] and luminescent properties[9] have been previously reported. Pseudooctahedral trichlorido imido compounds $[MCl_3(NtBu)py_2]$ (M = Nb **1**, Ta **2**) were prepared in better yields by a modification of the reported method[8c] (see Experimental) when toluene solutions containing 1 equivalent of the pentachlorides MCl_5 were treated with 2 equivalents of $NH(tBu)(SiMe_3)$ in the presence of an excess of pyridine. In addition, reactions of **1–2** with stoichiometric amounts of *N,N,N′,N′*-tetramethylethylenediamine (tmeda) give solutions from which the adducts $[MCl_3(NtBu)(tmeda)]$ (M = Nb **3**, Ta **4**) can be isolated in good yield as yellow and white microcrystalline solids, respectively (Scheme 1). **1–4** are soluble in most organic solvents, including saturated hydrocarbons. They are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under an

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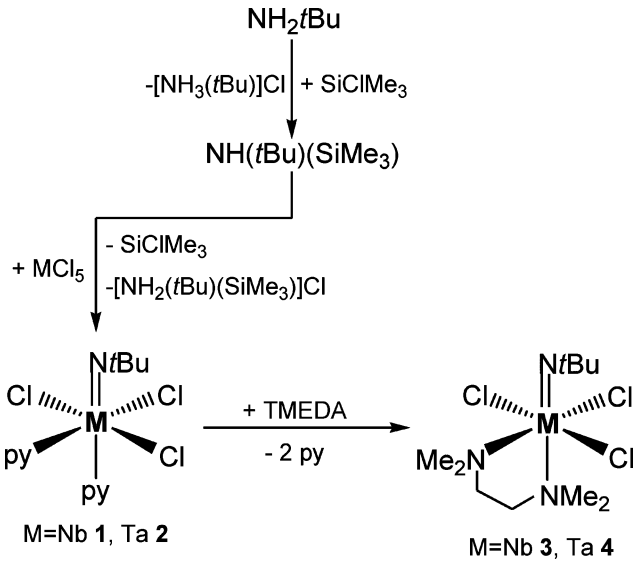
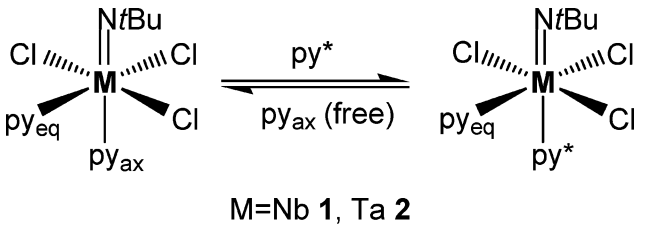
† This paper is dedicated to the memory of Dr Amelio Vázquez de Miguel who died April 20, 2010 and whom we remember with affection.



Scheme 1 Preparation of complexes **1–4**.



Scheme 2 Exchange process between py_{ax} and free py*.

argon atmosphere were found to be imperative for successful preparations.

Compounds **1–4** were characterized by analytical and spectroscopic methods, and the data are in agreement with a *mer*, *cis*-pseudooctahedral structure. The IR spectra of all complexes show the characteristic absorption corresponding to the M=N-stretching vibration[5a,6g,10] at $\tilde{\nu} \approx 1358$ cm^{-1}. At room temperature, the ^{1}H NMR spectrum of the complexes **1–2** shows two signals set with different width, probably due to an intermolecular exchange process between the py coordinated in only one position and a small amount of free undetected py. A *noesy 1d* experiment with selective excitation of *t*Bu resonance showed that the well resolved multiplets corresponding to the py_{eq} and therefore, only the py_{ax} participate in the spin exchange process (see Scheme 2).

When a C_7D_8 solution of **1–2** and pyridine in an 1 : 1.5 molar ratio was studied by ^{1}H VT NMR spectroscopy between 223 and 343 K (Fig. 1), the proposed mutual exchange process[6c,11] between the axial pyridine (py_{ax}) and free pyridine (py*) was confirmed and free Gibbs energy values were obtained in the collapse point (**1**, $\Delta G^{\ddagger 313\,K} = 15.3$ kcal mol^{-1}; **2**, $\Delta G^{\ddagger 317\,K} = 15.4$ kcal mol^{-1}).

The $^{13}C\{^1H\}$ NMR spectra of both complexes **1–2** (see Experimental) are in agreement with the observed behaviour by ^{1}H NMR spectroscopy and although it hardly shows any differences between the py_{ax} and py_{eq} carbon atom resonances, the quaternary carbon resonances of the *t*Bu moiety are different: δ 72.6 (**1**), 67.0 (**2**). Moreover, in the gHMBCd2_N15 spectra we observe the signals for the imido nitrogen atom at δ 64.2 (**1**) and 30.8 (**2**), and the corresponding signals for the equatorial pyridine ligand at δ 112.6 (**1**) and 113.1 (**2**), whereas the cross-peaks for the axial pyridine ligand were not detected in both complexes probably due to the spin exchange process.

The NMR spectra of complexes **3–4** show two carbon (^{13}C) and two nitrogen (^{15}N) resonances for tmeda in agreement with a C_s symmetry and with the presence of a bidentate ligand coordinated to the axial/equatorial positions of a metal centre in a pseudooctahedral environment. Moreover, in the ^{1}H NMR spectra we have observed very well resolved multiplets for the –CH_2-CH_2– moiety and there is no inter- and/or intramolecular exchange process in the NMR time scale.

The ^{15}N resonances of Ta≡N*t*Bu moiety (see Scheme 3) are remarkably more shielding ($\Delta\delta \approx -34$) with respect to the

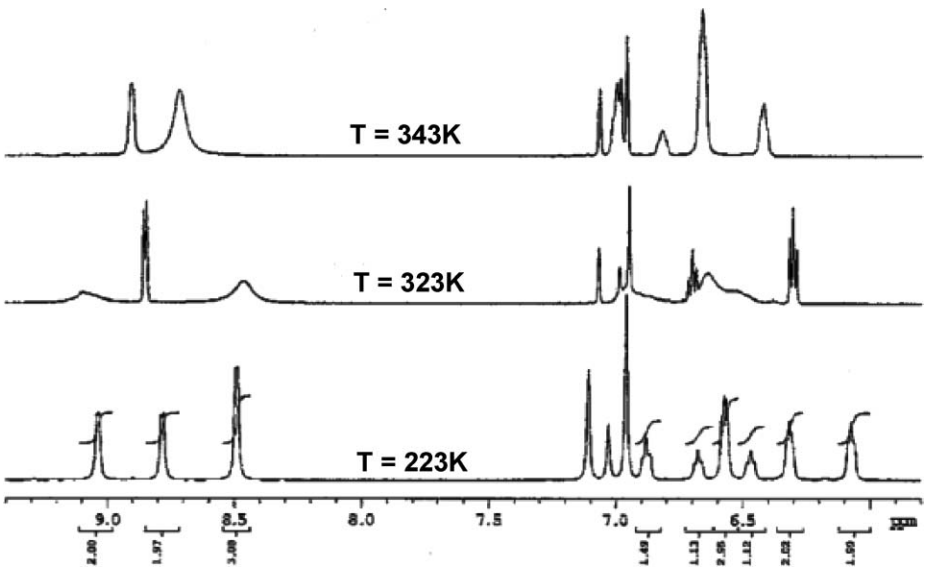
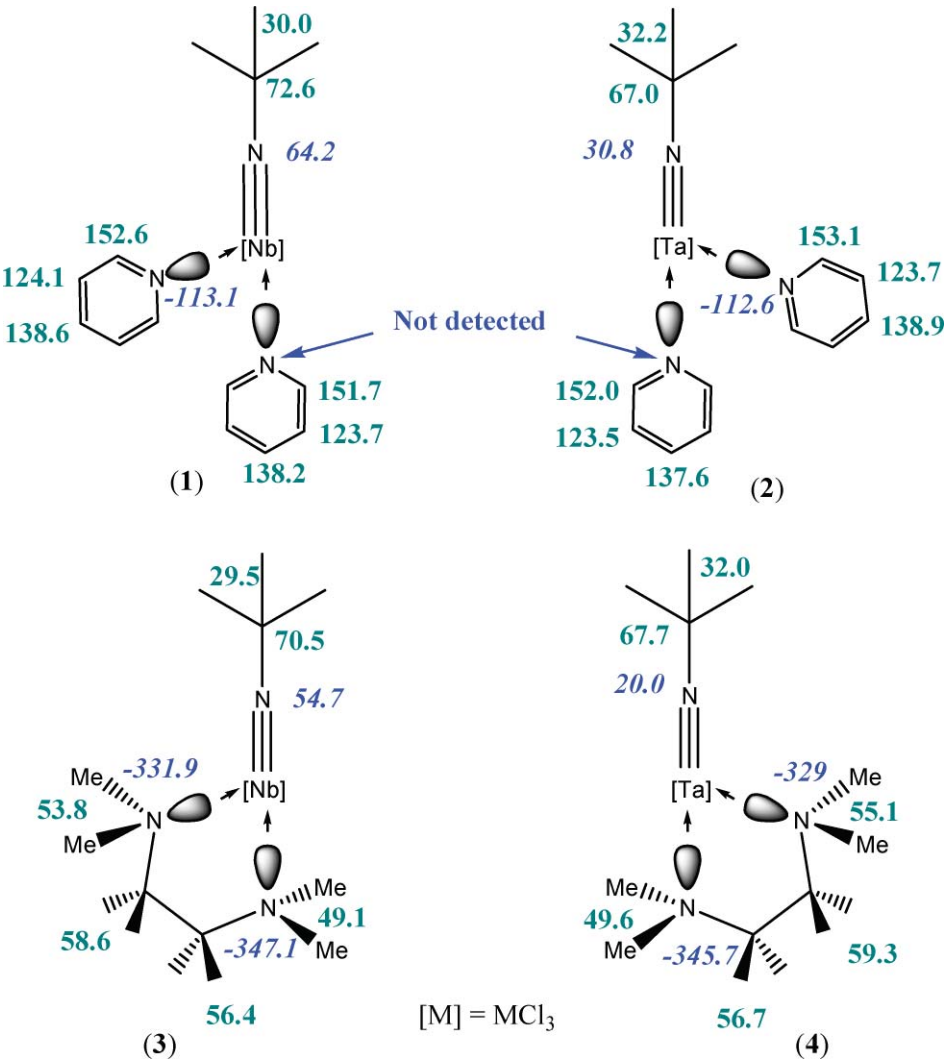


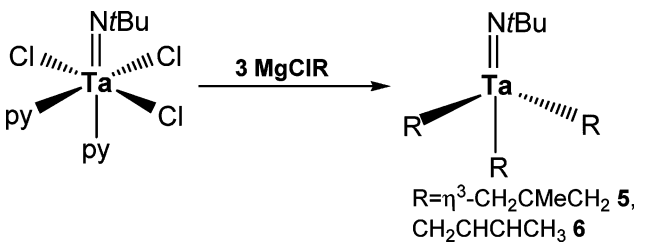
Fig. 1 VT ^{1}H NMR spectra of the mixture **2** + 1.5 **py*** in C_7D_8.



Scheme 3 NMR data assignment for complexes **1–4**.

analogous niobium complexes ($\Delta\delta_{2\text{-}1}$ = 30.8–64.2 = –33.4; $\Delta\delta_{4\text{-}3}$ = 20.0–54.7 = –34.7). We propose that the coincident $\Delta\delta$ (^{15}N) value is basically due to the change of the diamagnetic component of the magnetic shielding constant in agreement with Lamb's formalism for a M≡N- direct bond. On the other hand, the axial position in the complexes **3** and **4** is characterized by more shielding resonances ($\Delta\delta = \delta_{ax} - \delta_{eq}$) in the ^{15}N (**N**Me$_2$) [$\Delta\delta$ = –15.2 (**3**), –16.7 (**4**)] and the ^{13}C (N**Me**$_2$) [$\Delta\delta$ = –4.7 (**3**), –5.5 (**4**)] spectra due to the well known *trans* effect of the M≡N- triple bond.[6g] Moreover, the pyridine by tmeda substitution also causes a notable shielding of the ^{15}N imido resonance ($\Delta\delta_{3\text{-}1}$ = 54.7–64.2 = –9.5; $\Delta\delta_{4\text{-}2}$ = 20.0–30.8 = –10.8) probably due to the major donor character of the axial nitrogen amino atom in the *trans* position with respect to the imido group in comparison with the pyridine ligand implied in a coordination–decoordination process. In addition, the carbon chemical shift corresponding to the quaternary carbon atom of the *t*Bu moiety in niobium complexes (**1,3**) is larger ($\Delta\delta_{1\text{-}2}$ = 5.6; $\Delta\delta_{3\text{-}4}$ = 2.8) in agreement with the major electronic density of the imido nitrogen atom in the tantalum compounds (**2,4**).

Trialkylated imido tantalum complexes [TaR$_3$(N*t*Bu)] (R = CH_2CMeCH_2 **5**, $CH_2CHCHCH_3$ **6**) were obtained (Scheme 4) at

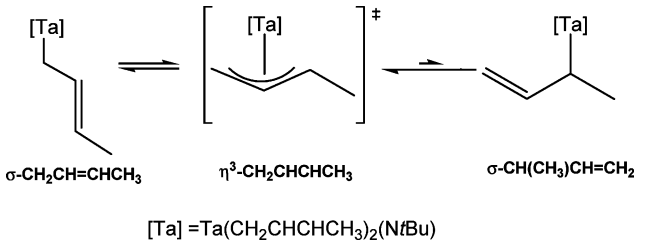


Scheme 4 Preparation of complexes **5–6**.

room temperature by treatment of diethyl ether solutions of **2** with a stoichiometric amount of the corresponding Grignard reagent. They are soluble in most organic solvents, including saturated hydrocarbons and in addition, are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under an argon atmosphere were found to be imperative for successful preparations.

Compounds **5–6** were characterized by spectroscopic methods and the data are in agreement with the proposed structures. The IR spectra show the characteristic absorption for the Ta═N- stretching vibration[5a,6g,10] at $\tilde{\nu} \approx 1351$ cm^{-1}. The different

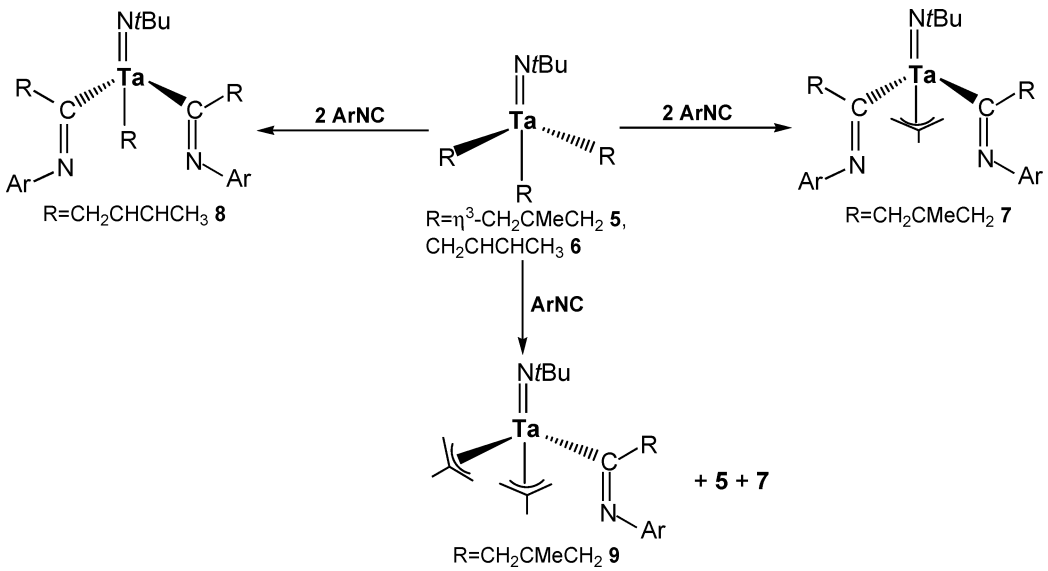
coordination mode of the 2-methylallyl and 2-butenyl groups to the pseudotetrahedral metal centre in the complexes **5–6** was deduced by NMR spectroscopic studies. Complex **5** shows in its ^{1}H NMR spectra one singlet at δ 0.85 (9H) for the *t*-butyl group, two narrow resonances at δ 3.11 (12H) and 1.70 (9H) for the three equivalent η^3-coordinated 2-methylallyl groups.[12] The $^{13}C\{^{1}H\}$ NMR spectrum (see Experimental) is in agreement with the proposed structure showing the -C**H**$_2$- resonance at δ 73.4 and in addition, in the ^{15}N NMR spectrum the imido nitrogen signal appears at δ 13.2. Although the Grignard reagent used MgCl(CH$_2$CMeCH$_2$) is seemingly described in the Aldrich catalogue as a magnesium compound with a σ-coordinated methylallyl group, we propose a η^3-coordination mode for this ligand as we deduced after studying a C_6D_6 solution of the reagent by NMR spectroscopy.[13] In contrast, the ^{1}H NMR spectrum of **6** shows a narrow singlet at δ 0.97 (9H) for the *t*-butyl substituent, a resolved doublet at δ 2.34 (6H) and a doublet of triplets at δ 5.1 (3H) ($^{3}J_d$ = 15, $^{3}J_t$ = 10.6 Hz) for -CH$_2$–C**H** = resonances, also a broad signal ($\Delta\nu$ = 18 Hz) at δ 1.84 (9H) and another very broad ($\Delta\nu$ = 40 Hz) at δ 3.8 (≈ 3H) for the CH$_3$–C**H** = moiety. In the $^{13}C\{^{1}H\}$ spectrum all signals for the 2-butenyl group appear as slightly wide resonances at δ 125.6 ($\Delta\nu \approx 5$ Hz) for –CH$_2$-**C**H═, 97.5 ($\Delta\nu$ = 12.5 Hz) for = **C**H–CH$_3$, 44.4 ($\Delta\nu$ = 14.3 Hz) for –**C**H$_2$–CH═, 17.8 ($\Delta\nu$ = 5.4 Hz) for **C**H$_3$–CH═, whereas the resonance at δ 32.2 corresponding to -C**Me**$_3$ is characterized by a natural line width ($\Delta\nu$ = 1.2 Hz). The $^{13}C\{^{1}H\}$ spectrum of **6** exhibits significant chemical shift differences with respect to the Grignard reagent MgCl(CH$_2$CHCHCH$_3$).[14] So, while the resonances for α-CH$_2$ and CH$_3$ groups are deshielding $\Delta\delta = \delta_{Ta} - \delta_{Mg}$ = +26.9 and $\Delta\delta$ = +2.8, the resonances corresponding to carbons β- and γ-**C**H = **C**H- have a shielding of $\Delta\delta$ = –15.3 and –3.7, respectively. Furthermore, the chemical shift of the methylene carbon atom δ 44.4 (**6**) has really the same value as that in the methylallyl complex δ 42.4 (**5**) and, in addition, the imido nitrogen resonance in **6** was observed at δ 6.7 [$\Delta\delta = \delta$(**6**) – δ(**5**) = –8.2]. Assuming the anomaly a large value of vicinal SSCC between –C**H**$_2$–C**H** = protons (^{3}J = 10.4 Hz) and observation of some broad signals in ^{1}H NMR, we proposed that the spectral behaviour of **6** in a C_6D_6 solution can be described by a typical σ1–σ3 isomerization process of the 2-butenyl group coordinated to the metal center in which the population of σ1 ground state is very much larger than σ3, as shown in Scheme 5.



Scheme 5 Isomerization process of complex **6**.

Unfortunately, we do not observe this process for complex **6** by a ^{1}H VT NMR experiment. However, an important spectral variation was detected at 173–253 K in a CD_2Cl_2 solution of starting Grignard reagent MgCl(CH$_2$CHCHCH$_3$) in the presence of tetrahydrofuran. The VT ^{1}H NMR spectra show a typical two spin exchange process corresponding to very different populations. The more significant experimental data comprise the detection at 183 K of a new signal for the methyl group (1 : 6 ratio) in accordance with the tocsy 1d and ASAPHMQC spectra (^{1}H, δ 1.47; ^{13}C, δ 20). We suggest that this resonance is due to the MgC(**C**H$_3$)CHCH$_2$ moiety in the σ3-isomeric structure (see Scheme 5).

Complexes **5** and **6** react with xilylisocyanide in an 1 : 1 or 1 : 2 molar ratio (Scheme 6) at room temperature in toluene to give, in good yields, the bisiminoacyl compounds [TaR(N*t*Bu){C(R)NAr-κ^{1}C}$_2$] (Ar = 2,6-Me$_2$C$_6$H$_3$; R = CH$_2$CMeCH$_2$ **7**, CH$_2$CHCHCH$_3$ **8**), as result of a double isocyanide insertion reaction into the two different Ta–C bonds of the starting trialkylated derivatives. However, **5** reacts with 1 equivalent of isocyanide leading to a mixture in which the main product is a di(2-methylallyl) imido iminoacyl derivative



Scheme 6 Preparation of complexes **7–9**.

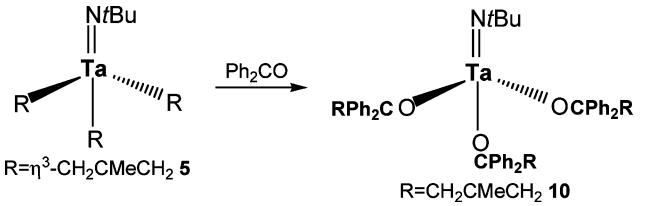
$[TaR_2(NtBu)\{C(R)NAr\text{-}\kappa^1C\}]$ (Ar = 2,6-$Me_2C_6H_3$; R = CH_2CMeCH_2 **9**) together with small amounts of the bisiminoacyl complex **7** and starting material **5**.

This result is in contrast with to that observed for $[TaCp^*Cl_{4-x}Me_x]$ (x = 2–4)[6b,6c] which in the presence of 1 or 2 equivalents of isocyanide leads to the formation of azatantalacyclopropane $[TaCp^*XY(CMe_2NAr\text{-}\kappa^2C,N)]$ (x = 2, 4; X = Y = Cl, Me; x = 3, X = Cl, Y = Me; Ar = 2,6-$Me_2C_6H_3$) or chloride/methyl imido alkenylamido $[TaCp^*X(NAr)\{NAr(CMeCMe_2)\text{-}\kappa^1N\}]$ (x = 3, 4; X = Cl, Me; Ar = 2,6-$Me_2C_6H_3$) species, respectively. In the present case, the first step consists in the insertion of the first coordinated isocyanide molecule with migration of an 2-methylallyl or 2-butenyl group to give the corresponding iminoacyl complex **9**, as we have detected by NMR spectroscopy and subsequently, the coordination of a second isocyanide to the vacant position is followed by the migration of the second group to the electrophilic isocyanide carbon atom leading to bisiminoacyl complexes **7**–**8**. The remaining 2-methylallyl or 2-butenyl group does not migrate, probably because it would lead to a much less favourable unsaturated electron deficient compound and in both cases (R = CH_2CMeCH_2, $CH_2CHCHCH_3$), we do not detect the formation of azatantalacyclopropane or imido alkenylamido systems.

The IR spectra of the imido iminoacyl complexes **7**–**9** show the characteristic absorption due to the Ta═N-imido stretching vibration[5a,6g,10] at $\tilde{\nu} \approx 1352$ cm^{-1}, but the corresponding absorption bands due to the C═C[6d] and C(R) = N-[6g] moieties cannot be unambiguously assigned because both appear around $\tilde{\nu} \approx$ 1600 cm^{-1} together with other more intense absorption bands corresponding to the 2,6-$Me_2C_6H_3$ substituent. However, the NMR data (see Experimental) of the complexes **7**–**8** are in agreement with the structural proposal indicated in the Scheme 6, as pseudotetrahedral complexes with a C_s symmetry. The ^{15}N imide resonance appears at δ +5.1 [$\Delta\delta = \delta(\mathbf{7}) - \delta(\mathbf{5}) = -8.1$] and δ +3.8 [$\Delta\delta = \delta(\mathbf{8}) - \delta(\mathbf{6}) = -2.9$]. The iminoacyl moiety shows carbon-13 signals[6g,15] located at $\delta \approx 254$ for the complexes **7**–**8** and the ^{15}N resonance at δ –91 for **7**, whereas this signal for **8** is not detected. The methylene proton resonances of the migrated allyl groups are diastereotopics[16] in both complexes [$\delta_{av.}$ 3.28, 4H, $^2J_{H-H}$ = 15.7 Hz (**7**); $\delta_{av.}$ 3.34, 4H, $^2J_{H-H}$ = 16.2 Hz (**8**)] due to the prochiral character of the metal centre, while the carbon resonances of $\mathbf{C}H_2$ appear at δ 45 (**7**) and 41.5 (**8**). In complex **7** the allyl group bonded to the tantalum atom appears as one singlet at δ 2.05 and a broad resonance ($\Delta\nu$ = 25 Hz) at δ 3.3 for $\mathbf{C}H_3$ and $\mathbf{C}H_2$ moieties, respectively, in accordance with a η^3-coordinated methylallyl group but with a slower σ1–σ3 isomerization process with respect to the starting tris-η^3-methylallyl complex **5**. The formation of the monoinsertion compound **9** can be observed when the reaction is followed by NMR spectroscopy. The observation of two inequivalent methyl groups for the 2,6-$Me_2C_6H_3$ ring of the iminoacyl ligand is consistent with the restricted rotation of the aryl group around the N–C_i(aryl) bond.[6g]

Contrary to the isocyanide insertion, diphenyl ketone reacts with **5** (Scheme 7) in a molar ratio 3 : 1 at room temperature to give in good yield the trialkoxo imido complex $[Ta(OCPh_2R)_3(NtBu)]$ (R = CH_2CMeCH_2 **10**).

The ^1H NMR spectrum shows one singlet at δ 0.99 (9H) for the *t*Bu moiety, three characteristic multiplets at δ 7.46 (12H), 7.12 (12H), and 7.04 (6H) for *o*-, *m*- and *p*- proton resonances



Scheme 7 Insertion of Ph_2CO in complex **5**.

corresponding to the phenyl ring, and also four signals at δ 1.47 (9H), 3.2 (6H), 4.84 (3H) and 4.91 (3H) for the 2-methylallyl group in accordance with a pseudotetrahedral tantalum(V) complex with a C_{3v} symmetry. The $^{13}C\{^1H\}$ spectrum displays all expected signals (see Experimental, δ 65.2, 34.1 $\mathbf{C}Me_3$; 50.6, 141.6, 24.9, 116.6 $\mathbf{C}H_2\mathbf{C}MeCH_2$; 148.1, 129.0, 127.4, 126.9 C_i, C_o, C_m, C_p $\mathbf{C}_6H_5$; 88.1 $O\mathbf{C}Ph_2R$) whereas the ^{15}N imido resonance is detected at δ –30.2 and is very shielding [$\Delta\delta$ = 43.4] with respect to the precursor tris(methylallyl) complex **5**. We propose that the observed difference in the ^{15}N chemical shift is due to the major back donation (p_π–d_π hyperconjugation) of oxygen free electron pairs to the imido nitrogen atom, which increases their electronic density.

Conclusions

NMR spectroscopic studies in $[MCl_3(NtBu)(tmeda)]$ (M = Nb, Ta) complexes show a mutual exchange process between axial pyridine and free pyridine and confirm a pseudooctahedral geometry for $[MCl_3(NtBu)(tmeda)]$ (M = Nb, Ta) with a bidentate ligand coordinated in an axial/equatorial fashion. Alkylation of the trichlorido imido tantalum compounds with Grignard reagents produces trialkylated imido derivatives $[TaR_3(NtBu)]$ (R = η^3-CH_2CMeCH_2, σ-$CH_2CHCHCH_3$), which in the presence of 2,6-$Me_2C_6H_3NC$ and $COPh_2$ leads to 2-methylallyl/2-butenyl imido bisiminoacyl and trialkoxo imido compounds, respectively, by conventional insertion processes.

Experimental

All operations were carried out under a dry argon atmosphere using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glove-box. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: C_6D_6 and hexane (Na/K alloy), diethyl ether (Na/benzophenone) and toluene (Na). Starting materials $[MCl_3(NtBu)py_2]$ (M = Nb, Ta)[8c] were prepared by a modification of the method described previously. Reagent grade MCl_5 (M = Nb, Ta), $SiClMe_3$, $tBuNH_2$, py, tmeda, 2,6-$Me_2C_6H_3NC$ and MgClR (R = CH_2CMeCH_2, $CH_2CHCHCH_3$; 0.5 M in diethyl ether, 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}). The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Mercury^{Plus}-300 and Unity^{Plus}-300 spectrometers. The inverse detection (ASAPHMQ, gc2hsqcsc13 and gHMBC_d215), selective excitation and VT experiments were realized in a three channel VNMRS-500 spectrometer. The ^1H and ^{13}C chemical shifts were referenced to TMS by using the solvent signals and

^{15}N chemical shifts to external CH_3NO_2. Microanalyses (C, H, N) were performed in a LECO CHNS 932 microanalyzer.

Synthesis of [MCl_3(N*t*Bu)py_2] (M = Nb 1, Ta 2)

To a toluene (40 mL) solution of *t*$BuNH_2$ (2.60 mL, 25 mmol) was added $SiClMe_3$ (1.50 mL, 12 mmol), which immediately produced a white precipitate of [NH_3(*t*Bu)]Cl. This mixture was stirred at room temperature for 15 min, the suspension was filtered through Celite and the filtrate was added to a toluene (M = Nb 30 mL, Ta 100 mL) suspension of MCl_5 (5.50 mmol; M = Nb 1.45 g, Ta 2.20 g). The reaction mixture was stirred for 1 h and a large excess of pyridine (1.60 mL, 21 mmol) was added. The resulting yellow suspension was stirred for 12 h and filtered, and the filtrate was pumped to dryness giving **1–2** as yellow microcrystalline solids.

1. Yield 2.10 g (89%). IR (KBr): $\tilde{\nu}$ = 2972(vs), 1606(vs), 1444(vs), 1359(s), 1247(vs), 1066(s), 758(vs), 697(vs), 425(w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 9.20(br, 2H, $\mathbf{H}_o$, py_{ax}), 8.83(2H, $\mathbf{H}_o$, py_{eq}), 6.81(1H, $\mathbf{H}_p$, py_{ax}), 6.64(1H, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.6 Hz, $\mathbf{H}_p$, py_{eq}), 6.50(2H, $\mathbf{H}_m$, py_{ax}), 6.27(m, 2H, $\mathbf{H}_m$, py_{eq}), 1.48(s, 9H, N***t*Bu**).^{13}C{^{1}H} NMR (C_6D_6): δ = 152.6($\mathbf{C}_o$, py_{eq}), 151.7($\mathbf{C}_o$, py_{ax}), 138.6($\mathbf{C}_m$, py_{ax}), 138.1($\mathbf{C}_m$, py_{eq}) 123.7($\mathbf{C}_p$, py_{eq}), 124.1($\mathbf{C}_p$, py_{ax}), 72.0(N**C**Me_3), 30.7(NC**Me**$_3$). ^{15}N gHMBC NMR (C_6D_6): δ = 65.2(**N***t*Bu), –108(**N**py_{eq}), not detected(**N**py_{ax}).

2. Yield 2.32 g (82%). IR (KBr): $\tilde{\nu}$ = 2971(vs), 1609(vs), 1444(vs), 1357(s), 1281(vs), 1067(s), 758(vs), 697(vs), 427(w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 9.17(br, 2H, $\mathbf{H}_o$, py_{ax}), 8.90(m, 2H, $^3J_{H-H}$ = 5.2 Hz, $^4J_{H-H}$ = 1.6 Hz, $\mathbf{H}_p$, py_{ax}), 6.80(m, 1H, $\mathbf{H}_p$, py_{ax}), 6.61(m, 1H, $\mathbf{H}_p$, py_{eq}), 6.47(br, 2H, $\mathbf{H}_m$, py_{ax}), 6.23(m, 2H, $\mathbf{H}_m$, py_{eq}), 1.53(s, 9H, N***t*Bu**).^{13}C{^{1}H} NMR (C_6D_6): δ = 153.2($\mathbf{C}_o$, py_{ax}), 152.0($\mathbf{C}_o$, py_{eq}), 139.1($\mathbf{C}_m$, py_{ax}), 138.1($\mathbf{C}_m$, py_{eq}), 124.0($\mathbf{C}_p$, py_{ax}), 123.8($\mathbf{C}_p$, py_{eq}), 66.6(N**C**Me_3), 32.2(NC**Me**$_3$). ^{15}N gHMBC NMR (C_6D_6): δ = 30.8(**N***t*Bu), –113.2(**N**py_{eq}), not detected (**N**py_{ax}).

Synthesis of [MCl_3(N*t*Bu)(Me_2N-CH_2-CH_2-NMe_2-κ^2*N*,*N*)] (M = Nb 3, Ta 4)

A toluene (25 mL) solution of [MCl_3(N*t*Bu)py_2] (M = Nb, 0.16 g, 0.45 mmol; Ta, 0.20 g, 0.38 mmol) was treated at room temperature with tmeda (M = Nb, 0.10 mL, 0.67 mmol; Ta, 0.11 mL, 0.58 mmol) and the mixture was stirred for 12 h. The resulting suspension was filtered, the solution was concentrated to *ca.* 5 mL and cooled to –40 °C overnight to afford **3** and **4** as yellow and white air-sensitive microcrystalline solids, respectively.

3. Yield 0.16 g (91%). IR (KBr): $\tilde{\nu}$ = 2974(vs), 1474(s), 1402(m), 1358(m), 1243(s), 1010(m), 951(m), 797(s) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 2.47(s, 6H, Me_2N_{eq}–C_2H_4–N_{ax}**Me**$_2$), 2.26(s, 6H, **Me**$_2N_{eq}$–C_2H_4–$N_{ax}Me_2$), 1.54(2H), 1.59(2H, AA′BB′, Me_2N_{eq}–**C**H_2-**C**H_2-$N_{ax}Me_2$), 1.29(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 70.5(N**C**Me_3), 58.6(Me_2N_{eq}-CH_2-**C**H_2–$N_{ax}Me_2$), 56.4(Me_2N_{eq}-**C**H_2-CH_2–$N_{ax}Me_2$), 53.8(**Me**$_2N_{eq}$–C_2H_4–$N_{ax}Me_2$), 49.1(Me_2N_{eq}–C_2H_4–N_{ax}**Me**$_2$), 29.5(NC**Me**$_3$). ^{15}N gHMBC NMR (C_6D_6): δ = 54.7(**N**CMe_3), –331.9(Me_2**N**$_{eq}$-C_2H_4–$N_{ax}Me_2$), –347.1(Me_2N_{eq}–C_2H_4-**N**$_{ax}Me_2$). Anal. Calcd. for $C_{10}H_{25}N_3Nb$: C, 31.08; H, 6.47; N, 10.87. Found: C, 30.87; H, 6.44; N, 10.40%.

4. Yield 0.16 g (87%). IR (KBr): $\tilde{\nu}$ = 2969(vs), 1475(s), 1356(m), 1280(s), 1008(m), 950(m), 799(s) cm^{-1}.^{1}H NMR (C_6D_6): δ = 2.49(s, 6H, Me_2N_{eq}–C_2H_4–N_{ax}**Me**$_2$), 2.39(s, 6H, **Me**$_2N_{eq}$–C_2H_4–$N_{ax}Me_2$), 1.85(AA′BB′, 4H, Me_2N_{eq}–**C**H_2-**C**H_2-$N_{ax}Me_2$), 1.38(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 67.7(N**C**Me_3), 59.3(Me_2N_{eq}-**C**H_2-CH_2–$N_{ax}Me_2$), 56.7(Me_2N_{eq}-CH_2-**C**H_2–$N_{ax}Me_2$), 55.1(**Me**$_2N_{eq}$–C_2H_4–$N_{ax}Me_2$), 49.7(Me_2N_{eq}–C_2H_4–N_{ax}**Me**$_2$), 32.0(NC**Me**$_3$). ^{15}N gHMBC NMR (C_6D_6): δ = 20.0(**N**CMe_3), –329.0(Me_2**N**$_{eq}$-C_2H_4–$N_{ax}Me_2$), –345.7(Me_2N_{eq}–C_2H_4-**N**$_{ax}Me_2$). Anal. Calcd. for $C_{10}H_{25}N_3Ta$: C, 25.31; H, 5.26; N, 8.85. Found: C, 25.27; H, 5.26; N, 8.78%.

Synthesis of [Ta(CHCMeCH_2)$_3$(N*t*Bu)] (5)

Under rigorously anhydrous conditions, a 0.5 M solution of Mg$Cl(CH_2CMeCH_2)$ in diethyl ether (4.94 mL, 2.47 mmol) was added at room temperature to a solution of **2** (0.43 g, 0.82 mmol) in diethyl ether (15 mL) and the reaction mixture was stirred for 12 h. The resulting suspension was decanted and the magnesium salt filtered off. The filtrate was evaporated to dryness and the residue extracted with hexane (3 × 10 mL). The solution was concentrated to *ca.* 5 mL and cooled to –40 °C overnight to give **5** as a dark red microcrystalline solid.

Yield 0.19 g (48%). IR (KBr): $\tilde{\nu}$ = 2946(s), 1606(m), 1445(m), 1376(m), 1354(vs), 1263(vs), 1032(w), 884(m), 697(w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 3.11(br, 12H, C**H**$_2$CMeC**H**$_2$), 1.69(s, 9H, CH_2C**Me**CH_2), 0.84(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 146.3(CH_2**C**$MeCH_2$), 67.6(N**C**Me_3), 42.4(**C**H_2CMe**C**H_2), 32.2(NC**Me**$_3$), 25.5(CH_2C**Me**CH_2). ^{15}N gHMBC NMR (C_6D_6): δ = 14.9(**N**CMe_3). Anal. Calcd. for $C_{16}H_{30}NTa$: C, 46.07; H, 7.19; N, 3.35. Found: C, 45.86; H, 7.21; N, 3.26%.

Synthesis of [Ta(CH_2CHCHCH_3)$_3$(N*t*Bu)] (6)

A sample of **2** (0.43 g, 0.82 mmol) was dissolved in 15 mL of diethyl ether in a Schlenk tube and at –78 °C was treated with a 0.5 M solution of Mg$Cl(CH_2CHCHCH_3)$ in diethyl ether (4.94 mL, 4.94 mmol), and the mixture was stirred for 1 h. 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 filtrate was concentrated to *ca.* 10 mL and cooled to –40 °C to give **6** as a brown microcrystalline solid.

Yield 0.18 g (46%). IR (KBr): $\tilde{\nu}$ = 2961(s), 1605(m), 1445(vs), 1376(m), 1353(m), 1273(vs), 1022(w), 838(w), 757(w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 5.08(dt, 3H, $^3J_{H-H}$ = 14.69 Hz, $^3J_{H-H}$ = 10.47 Hz, CH_2–C**H** = CH-CH_3), 3.82(br, 3H, CH_2-CH=C**H**-CH_3), 2.34(d, 6H, $^3J_{H-H}$ = 10.47 Hz, C**H**$_2$-CH=CH-CH_3), 1.62(br, 9H, CH_2-CH=CH–C**H**$_3$), 0.96(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 125.38(CH_2-**C**H=CH-CH_3), 97.42(CH_2-CH = **C**H-CH_3), 65.73(N**C**Me_3), 44.26(**C**H_2-CH=CH-CH_3), 31.94(NC**Me**$_3$), 17.63(CH_2-CH=CH-**C**H_3). ^{15}N gHMBC NMR (C_6D_6): δ = 6.7(**N**CMe_3). Anal. Calcd. for $C_{16}H_{30}NTa$: C, 46.07; H, 7.19; N, 3.35. Found: C, 45.88; H, 7.23; N, 3.29%.

Synthesis of [TaR(N*t*Bu){C(R′)NAr-κ^1*C*}$_2$] (R = η^3-CH_2C**Me**CH_2, R′ = CH_2C**Me**CH_2, Ar = 2,6-$Me_2C_6H_3$ 7)

A solution of **5** (0.18 g, 0.41 mmol) in toluene (20 mL) was treated with 2,6-$Me_2C_6H_3NC$ (0.12 g, 0.82 mmol) under rigorously anhydrous conditions. The mixture was stirred for 12 h and then filtered. The filtrate was concentrated to *ca.* 5 mL and cooling overnight at –40 °C produced **7** as a garnet microcrystalline solid.

Yield 0.24 g (80%). IR (KBr): $\tilde{\nu}$ = 2963(s), 1590(s), 1467(vs), 1353(s), 1260(vs), 1091(m), 764(w) cm^{-1}. ^1H NMR (C_6D_6): δ = 6.93[m, 6H, TaC(CH_2CMeCH_2)$NC_6\mathbf{H}_3Me_2$], 4.18[av, m, 4H, TaC($CH_2CMeC\mathbf{H}_2$)NAr], 3.30(br, 4H, Ta–C$\mathbf{H}_2$CMeC$\mathbf{H}_2$), 3.34, 3.22[AB, 4H, $^2J_{H-H}$ = 14.55 Hz, TaC(C$\mathbf{H}_2$CMeCH_2)NAr], 2.14(s, 6H), 1.73[s, 6H, TaC(CH_2CMe-CH_2)$NC_6H_3\mathbf{Me}_2$], 2.05(s, 3H, Ta-$CH_2C\mathbf{Me}CH_2$), 1.92[t, 6H, $^4J_{H-H}$ = 1.27 Hz, TaC($CH_2C\mathbf{Me}CH_2$)NAr], 1.32(s, 9H, NC$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 254.4[Ta**C**(CH_2CMeCH_2)-NAr], 156(Ta$CH_2\mathbf{C}$MeCH_2), 141[TaC($CH_2\mathbf{C}$MeCH_2)NAr], 153.8(C_i), 141(C_p), 129.2, 128.1(C_m), 122, 121(C_o)[TaC(CH_2CMe-CH_2)$NC_6H_3Me_2$], 114[TaC(CH_2CMe**C**H_2)NAr], 66.5(N**C**Me_3), 45.7[TaC(**C**H_2CMeCH_2)NAr], 34.3(NC$\mathbf{Me}_3$), 26.9(Ta$CH_2C\mathbf{Me}$-CH_2), 23.7[TaC($CH_2C\mathbf{Me}CH_2$)NAr], 18.7, 18.3[TaC(CH_2CMe-CH_2)$NC_6H_3\mathbf{Me}_2$], not observed(Ta**C**H_2CMe**C**H_2). ^{15}N gHMBC NMR (C_6D_6): δ = 5.8(**N**CMe_3), –90.6[TaC(CH_2CMeCH_2)**N**Ar]. Anal. Calcd. for $C_{34}H_{48}N_3Ta$: C, 60.11; H, 7.06; N, 6.18. Found: C, 59.88; H, 6.78; N, 6.24%.

Synthesis of [TaR(N*t*Bu){C(R)NAr-κ^1*C*}$_2$] (R = $CH_2CHCHCH_3$; Ar = 2,6-$Me_2C_6H_3$ 8)

A 100 mL Schlenk flash was charged with a toluene (30 mL) solution of **6** (0.18 g, 0.42 mmol) and treated with 2,6-$Me_2C_6H_3NC$ (0.11 g, 0.84 mmol) under rigorously anhydrous conditions. After the mixture had been stirred at room temperature for 12 h, the volume of the solution was concentrated to *ca.* 5 mL under reduced pressure. The resulting solution was cooled to –40 °C overnight to afford a brown microcrystalline solid of **8**.

Yield 0.22 g (77%). IR (KBr): $\tilde{\nu}$ = 2915(s), 1612(vs), 1458(vs), 1373(s), 1351(m), 1266(s), 964(s), 728(s) cm^{-1}. ^1H NMR (C_6D_6): δ = 6.90[m, 6H, TaC($CH_2CHCHCH_3$)$NC_6\mathbf{H}_3Me_2$], 5.95(br, 2H, $TaCH_2\mathbf{C}HCHCH_3$), 5.85[m, 2H, TaC($CH_2\mathbf{C}HCHCH_3$)NAr], 5.52[m, 2H, TaC($CH_2CHC\mathbf{H}CH_3$)NAr], 4.60(br, 1H, $TaCH_2CHC\mathbf{H}CH_3$), 3.30(m, 2H, Ta**C**$H_2CHCHCH_3$), 3.30[m, AB, 4H, TaC(C$\mathbf{H}_2$CHCHCH_3)NAr], 2.13(s, 6H), 1.72[s, 6H, TaC($CH_2CHCHCH_3$)$NC_6H_3\mathbf{Me}_2$], 1.60[m, 6H, TaC($CH_2CHCHC\mathbf{H}_3$)NAr], 1.58(m, 3H, $TaCH_2CHCHC\mathbf{H}_3$), 1.29(s, 9H, NC$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 254.1[Ta**C**(CH_2-$CHCHCH_3$)NAr], not observed(C_i), 142.5(C_p), 130, 129(C_m), 128.1, 128(C_o)[TaC(CH_2CMeCH_2)N**C**$_6H_3Me_2$], 127.8[TaC(CH_2-$CH\mathbf{C}HCH_3$)NAr], 125.6[TaC($CH_2\mathbf{C}HCHCH_3$)NAr], 66.1-(N**C**Me_3), 40.8[Ta(**C**$H_2CHCHCH_3$)], 40.5[TaC(**C**$H_2CHCHCH_3$)-NAr], 34.2(NC$\mathbf{Me}_3$), 19.5[TaC($CH_2CHCH\mathbf{C}H_3$)NAr], 18.6(Ta-$CH_2CHCH\mathbf{C}H_3$), 16.2, 16 [TaC($CH_2CHCHCH_3$)$NC_6H_3\mathbf{Me}_2$], not observed ($TaCH_2\mathbf{C}HCHCH_3$), not observed($TaCH_2CH\mathbf{C}HCH_3$). ^{15}N gHMBC NMR (C_6D_6): δ = 3.85(**N**CMe_3), –91 [TaC(CH_2-CMeCH_2)**N**Ar]. Anal. Calcd. for $C_{34}H_{48}N_3Ta$: C, 60.11; H, 7.06; N, 6.18. Found: C, 60.08; H, 6.96; N, 6.16%.

Reaction of **5** with 1 equiv of xilylisocyanide.

A C_6D_6 (0.75 mL) solution of **5** (12 mg, 0.03 mmol) was placed into a 5 mm valved NMR tube, and under rigorously anhydrous conditions, a 1.01 mM solution of 2,6-$Me_2C_6H_3NC$ (35 μL, 0.03 mmol) in C_6D_6 solution was added in small portions. The reaction was monitored by ^1H NMR spectroscopy and the spectrum showed the presence of a mixture of the three following components: a new complex **[TaR$_2$(N*t*Bu){C(R)NAr-κ^1*C*}]** (R = CH_2CMeCH_2; Ar = 2,6-$Me_2C_6H_3$ **9**) (monoinsertion product), **7** (diinsertion product) and a small amount of starting material **5**. Formation of **9** was confirmed by NMR spectroscopy, however, repeated attempts to obtain **9** as a unitary product by preparative scale were unsuccessful.

^1H NMR (C_6D_6): δ = 6.90[m, 3H, TaC(CH_2CMeCH_2)-$NC_6\mathbf{H}_3Me_2$], 4.60[br, 2H, TaC($CH_2CMeC\mathbf{H}_2$)NAr], 3.20[br, 2H, TaC(C$\mathbf{H}_2$CMeCH_2)NAr], 3.18[br, 8H, Ta(C$\mathbf{H}_2$CMeC$\mathbf{H}_2$)$_2$], 2.04[s, 6H, Ta($CH_2C\mathbf{Me}CH_2$)$_2$], 1.99[s, 3H, TaC($CH_2C\mathbf{Me}CH_2$)NAr], 1.74[s, 6H, TaC(CH_2CMeCH_2)$NC_6H_3\mathbf{Me}_2$], 1.11(s, 9H, NC$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 252.6[Ta**C**(CH_2CMeCH_2)NAr], 150.9[Ta($CH_2\mathbf{C}MeCH_2$)$_2$], 142, 128.2, 124.4[several phenyl, TaC(CH_2CMeCH_2)N**C**$_6H_3Me_2$], 141.8[TaC($CH_2\mathbf{C}MeCH_2$)NAr], 114.8[TaC(CH_2CMeCH_2)NAr], 77.05[Ta(**C**H_2CMeCH_2)$_2$], 68-(N**C**Me_3), 46.7[TaC(**C**H_2CMeCH_2)NAr], 32.8(NC$\mathbf{Me}_3$), 26.3[Ta($CH_2C\mathbf{Me}CH_2$)$_2$], 23.5[TaC($CH_2C\mathbf{Me}CH_2$)NAr], 19.6-[TaC(CH_2CMeCH_2)$NC_6H_3\mathbf{Me}_2$], not observed[TaC($CH_2\mathbf{C}$Me-CH_2)NAr]. ^{15}N gHMBC NMR (C_6D_6): δ = 9.0(**N**CMe_3), –96.7[TaC(CH_2CMeCH_2)**N**Ar].

Synthesis of [Ta(OCPh$_2$R)$_3$(N*t*Bu)] (R = CH_2CMeCH_2 10)

At room temperature, a 0.87 mM solution of $COPh_2$ (72 μL, 0.06 mmol) in C_6D_6 was added to a C_6D_6 (0.75 mL) solution of **5** (0.01 g, 0.02 mmol) placed in a NMR valved tube. The color of the mixture quickly changed from dark red to orange and the reaction was checked by ^1H NMR spectroscopy until no further change was observed. After 1 h the spectrum showed the presence of **10** in quantitative yield.

^1H NMR (C_6D_6): δ = 7.46[12H, H_o, TaOC($C_6\mathbf{H}_5$)$_2$R], 7.12[12H, H_m, TaOC($C_6\mathbf{H}_5$)$_2$R], 7.04[6H, H_p, TaOC($C_6\mathbf{H}_5$)$_2$R], 4.91(3H), 4.84[AB, 3H, TaOCPh$_2$($CH_2CMeC\mathbf{H}_2$)], 3.20[s, 6H, TaOCPh$_2$(C$\mathbf{H}_2$CMeCH_2)], 1.47[s, 9H, TaOCPh$_2$($CH_2C\mathbf{Me}$-CH_2)], 0.99(s, 9H, NC$\mathbf{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 148.1(C_i), 129.0(C_o), 127.4(C_m), 126.9(C_p, TaOC(**C**$_6H_5$)$_2$R], 141.6[TaOCPh$_2$($CH_2\mathbf{C}MeCH_2$)], 116.6[TaOCPh$_2$(CH_2CMe-**C**H_2)], 88.1[Ta**O**CPh$_2$(CH_2CMeCH_2)], 65.2(N**C**Me_3), 50.6[TaO-CPh$_2$(**C**H_2CMeCH_2)], 34.1(NC$\mathbf{Me}_3$), 24.9[TaOCPh$_2$($CH_2C\mathbf{Me}$-CH_2)]. ^{15}N gHMBC NMR (C_6D_6): δ = –30.3(**N**CMe_3).

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14 NMR data for MgCl($CH_2CHCHCH_3$): ^{1}H NMR (C_6D_6): δ = 6.6(s, 1H), 5.02(s, 1H, CH_2**C**H**C**HCH_3), 2.0(s, 3H, CH_2CHCHC**H**$_3$), 1.44(s, 2H, C**H**$_2CHCHCH_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 140.8(CH_2**C**$HCHCH_3$), 101.2(CH_2CH**C**HCH_3), 17.6(**C**$H_2CHCHCH_3$), 15.0(CH_2CHCH**C**H_3).

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