(Alkyl)(monocyclopentadienyl)niobium and -tantalum Complexes in Insertion Processes

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Dedicated to Professor Pascual Royo on the ocassion of his 65th birthday

Keywords: Niobium / Tantalum / Cyclopentadienyl ligands / Insertions

Alkyl high-valent early transition metal compounds are important organometallic species, particularly because their reactions with unsaturated molecules, such as carbon monoxide and organic isocyanides, are relevant to several industrial stoichiometric and catalytic processes. Recently, we have reported several studies concerning (alkyl)(monocyclopentadienyl) derivatives of group-5 metals, including both synthetic aspects and chemical behaviour in insertion reactions. This Microreview is an account of this work, covering syntheses, structure, spectroscopic, and reactivity details that have been reported by us together with the most significant contributions from other authors.

Introduction

The transfer of alkyl groups from transition metal atoms to coordinated unsaturated molecules,[1] such as carbon monoxide and isocyanides, is an important organometallic reaction that has been the subject of relevant synthetic, mechanistic and theoretical studies.[2] Further, the resulting η^2-acyl− and η^2-iminoacyl−metal functionalities constitute a powerful strategy for C−C bond formation under mild reaction conditions and are versatile reactive intermediates in many transition-metal-promoted stoichiometric and catalytic organometallic transformations.[3]

Compared with the η^2-acyl moiety, the reactivity of the η^2-iminoacyl group is even more versatile because it can be transformed into metallacyclic imines,[2d,2f,2h,2k] azaallyl complexes,[3i,3j,3k] and aminocarbyne derivatives[3f] or may participate in alkyne coupling processes[3g] and double[3e,3i,3j,3k] or multiple[3e,3i,3j,3k] isocyanide insertion reactions. It may also be transformed into azametallacyclopropane species, which give imido complexes[2e] by thermal decomposition. These reactions[2c,2d,2j,3g] are profoundly dependent on both the metal and the nature of its substituents, particularly on the number of metal-bound alkyl groups that can participate in the reaction. In this context, a systematic study[4] of isocyanide insertion reactions into methyl−tantalum bonds of different chloro(methyl)(pentamethylcyclopentadienyl) derivatives ($TaCp^*Cl_{4-x}Me_x$) led us to isolate a series of (η^2-iminoacyl)- ($x = 1$) and dichloroazatantalacyclopropane ($x = 2$) as well as chloro- and (methyl)(alkenylamido)(imido) ($x = 3, 4$) complexes.

This Microreview aims to systematically overview the synthetic methods of producing different alkyl(monocyclopentadienyl)niobium- and -tantalum(v) derivatives and also their behaviour in insertion reactions, as well as provid-

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Manuel Gómez was born in Cieza (Murcia, Spain) in 1954. He received his Diploma in Chemistry at the University of Murcia in 1976 and his Ph.D. in 1981 from the University of Alcalá de Henares working in the field of coordination and organometallic chemistry with Professor Pascual Royo. He was a postdoctoral fellow at the University of Sheffield in 1982−1983 under the supervision of Professor Peter M. Maitlis. He subsequently joined the Inorganic Chemistry Department at the University of Alcalá de Henares where he is Professor of Inorganic Chemistry, a position he has held since 1985. His main research interests are in the field of organometallic chemistry, with an emphasis on synthesis, reactivity and applications of mono(cyclopentadienyl)niobium and -tantalum complexes.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

ing some data on intra- or intermolecular rearrangement processes of the insertion products.

Results and Discussion

Synthesis of Dichloro Complexes

The studies described here start with dichloro(imido)-, dialkyldichloro-, (alkyne)dichloro-, and (diazabutadiene)dichloro(monocyclopentadienyl)niobium and -tantalum complexes. Recent years have witnessed an extensive development of imido group-5 metal chemistry containing monofunctional,[5] tetradentate triamidoamine,[6] and cyclopentadienyl ligands in mono-[7] and dicyclopentadienyl-type[8] complexes. Protonated lithium amides[7b] have been extensively used to generate the imido ligand, but other synthetic strategies have been based on the deprotonation of cyclopentadiene by metal amides,[7e,8c] β-hydrogen elimination of amides and amines coordinated to metal(III) compounds[8a,8b] and oxidation of metal(III) complexes with azides.[8b] Related alkoxyimido and hydrazido(2−) derivatives have been reported[9] more recently.

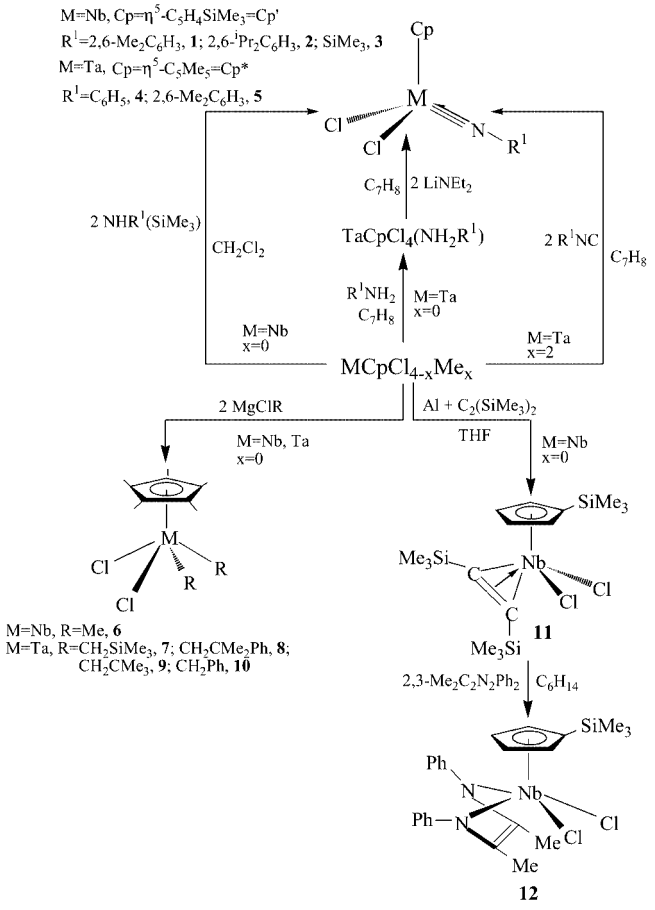
Pseudo-tetrahedral dichloro(imido) compounds **$MCpCl_2(NR^1)$** (M = Nb,[10] Cp = η^5-$C_5H_4SiMe_3$ = Cp′, R^1 = 2,6-$Me_2C_6H_3$, **1**; 2,6-*i*$Pr_2C_6H_3$, **2**; $SiMe_3$, **3**; M = Ta, Cp = η^5-C_5Me_5 = Cp*, R^1 = C_6H_5, **4**;[11] 2,6-$Me_2C_6H_3$, **5**[4]) can be easily obtained from the corresponding tetrachloro derivative $MCpCl_4$ (Scheme 1). Complex **5** was prepared by reacting $TaCp^*Cl_2Me_2$[12] with 2 equiv. of 2,6-$Me_2C_6H_3NC$ in toluene as described previously.[4c]

Dialkyldichloro complexes **$MCp^*Cl_2R_2$** (M = Nb, R = Me, **6**;[13c] M = Ta, R = CH_2SiMe_3, **7**;[13d] CH_2CMe_2Ph **8**;[13d] CH_2CMe_3, **9**;[13a,13b] CH_2Ph, **10**[13a,13b]) have been obtained by treating *n*-hexane suspensions of the MCp^*Cl_4 complex with stoichiometric amounts of the Grignard reagents MgClR (R = Me, CH_2SiMe_3, CH_2CMe_2Ph, CH_2Ph) or $Mg(CH_2CMe_3)_2(THF)_2$ under rigorously anhydrous conditions at room temperature (Scheme 1).

The (alkyne)dichloro complex **$NbCp'Cl_2(Me_3SiCCSiMe_3)$**, **11**[14] has been synthesized in high yield by treating $NbCp'Cl_4$ with an excess of aluminium powder and mercury(II) chloride in the presence of 1 equiv. of bis(trimethylsilyl)acetylene. Additionally, the reaction of **11** with 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph-DAD) in hexane leads to the (diazabutadiene)dichloro complex **$NbCp'Cl_2$(Me,Ph-DAD)**, **12**[15] with elimination of $C_2(SiMe_3)_2$ (Scheme 1). Related DAD complexes[16] have been, essentially, isolated by treatment of the corresponding half-sandwich complexes $NbCpCl_4$ (Cp = η^5-C_5H_5, η^5-C_5Me_5) with a dilithium salt of the different DAD ligands.

Synthesis of Alkyl Complexes

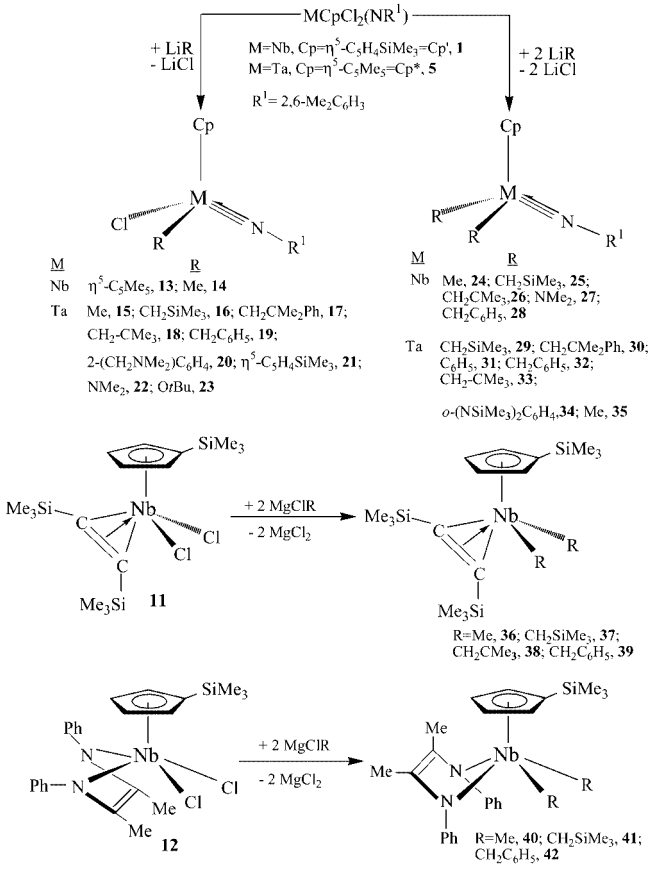
Although the imido ligand has been employed as an ancillary group to support high-oxidation state metal centres,[17] these complexes can be made highly reactive in terms of synthesizing coordinatively unsaturated derivatives containing multiple π-bonded ligands. Further, an increasing number of complexes having reactive imido ligands have been shown to participate in C−H activation[18] and cycloaddition reactions.[19] Conversely, reactions based on carbon−carbon bond formation have led to many important synthetic applications of organo group-5 metal complexes by migration of methyl substituents to unsaturated isocyanide[4,20] and carbonyl[20a] ligands through the intermediate formation of (iminoacyl)- and (acyl)metal compounds, respectively. Whereas the chemistry of (cyclopentadienyl)(halo)(imido)niobium and -tantalum complexes is well defined, the alkyl derivatives are less well known although a great number of related amido and alkoxide complexes have been reported recently. Following our preliminary work on the dichloro- and chloro(methyl)(imido) derivatives[4b,20a] we reported a systematic study on the reactivity of (arylimido)(monocyclopentadienyl)niobium and -tantalum complexes towards alkylating reagents.



Scheme 1. Synthesis of dichloro complexes

Thus, the reactions of the dichloro complexes **1** and **5** with a stoichiometric amount of the alkylating reagent gave solutions from which the alkyl(chloro)imido complexes **$MCpClR(NR^1)$** [R^1 = 2,6-$Me_2C_6H_3$; M = Nb,[10] Cp = Cp′, R = Cp*, **13**; Me, **14**; M = Ta, Cp = Cp*, R = Me, **15**;[10] CH_2SiMe_3, **16**;[21] CH_2CMe_2Ph, **17**;[21] CH_2CMe_3, **18**;[21] $CH_2C_6H_5$, **19**;[21] 2-$(CH_2NMe_2)C_6H_4$, **20**;[21] Cp′,

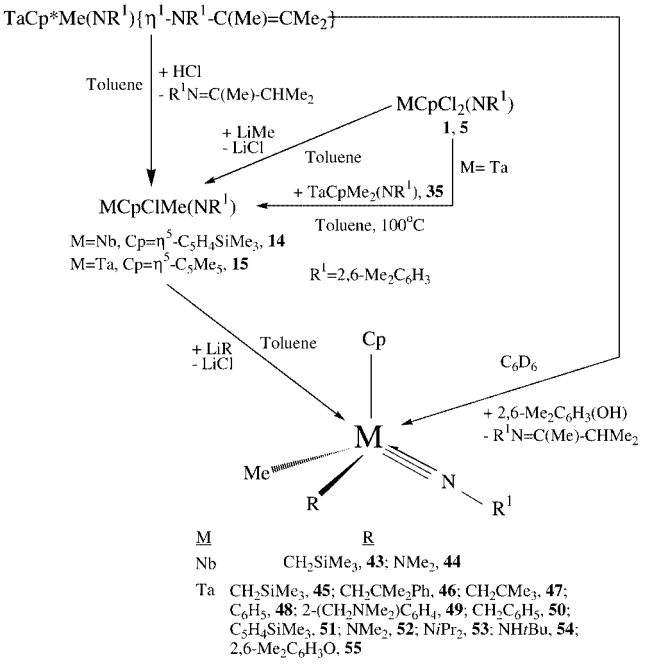
21;[21] NMe_2, **22**;[10] O*t*Bu, **23**[10]] and dialkyl(imido) complexes **$MCpR_2(NR^1)$** [R^1 = 2,6-$Me_2C_6H_3$; M = Nb,[10] Cp = Cp′, R = Me, **24**; CH_2SiMe_3, **25**; CH_2CMe_3, **26**; NMe_2, **27**; $CH_2C_6H_5$, **28**; M = Ta, Cp = Cp*, R = CH_2SiMe_3, **29**;[21] CH_2CMe_2Ph, **30**;[21] C_6H_5, **31**;[21] $CH_2C_6H_5$, **32**;[21] CH_2CMe_3, **33**;[21] *o*-$(NSiMe_3)_2C_6H_4$, **34**;[10] Me, **35**[20a]] were isolated. Alternatively, the chloro(methyl)(imido)tantalum derivative **15** can be prepared[21] by treating the (alkenylamido)imido(methyl) complex [TaCp*Me(NR^1){η^1-NR^1-C(Me)=CMe_2}] (R^1 = 2,6-$Me_2C_6H_3$)[4c] with HCl or by a redistribution[21] reaction between the corresponding dichloro- (**5**)[4c] and dimethyl- (**35**)[20a] (imido)tantalum derivatives (Scheme 2).



Scheme 2. Synthesis of alkyl(chloro) and dialkyl complexes

Conversely, dialkyl(alkyne) derivative **$NbCp'R_2(Me_3Si$-$CCSiMe_3)$**[14] (R = Me, **36**; CH_2SiMe_3, **37**; CH_2CMe_3, **38**; $CH_2C_6H_5$, **39**) and dialkyl(diazabutadiene) derivative **$NbCp'R_2(\eta^2$-$Ph_2N_2C_2Me_2$-2,3)**[15] (R = Me, **40**; CH_2SiMe_3, **41**; $CH_2C_6H_5$, **42**) were, respectively, isolated in good yields by alkylation of the dichloro complexes **11** and **12** with Grignard reagents in a 1:2 molar ratio (Scheme 2).

As shown in Scheme 3, the mixed alkylated imido compounds **MCpRMe(NR^1)** [R^1 = 2,6-$Me_2C_6H_3$; M = Nb,[10] Cp = Cp′, R = CH_2SiMe_3, **43**; NMe_2, **44**; M = Ta, Cp = Cp*, R = CH_2SiMe_3, **45**,[21] CH_2CMe_2Ph, **46**;[21] CH_2CMe_3, **47**;[21] C_6H_5, **48**;[21] 2-$(CH_2NMe_2)C_6H_4$, **49**;[21] $CH_2C_6H_5$, **50**;[21] Cp′, **51**;[21] NMe_2, **52**;[10] N*i*Pr_2, **53**;[10] NH*t*Bu, **54**;[10] 2,6-$Me_2C_6H_3O$, **55**[10]] were obtained from the starting chloro(methyl)imido complexes **14** and **15** by reactions with the corresponding alkylating reagent, except for the methyl(imido) phenoxide complex **55** which was synthesized by treating the alkenylamido(imido)methyltantalum derivative [TaCp*Me(NR^1){η^1-NR^1-C(Me)=CMe_2}] (R^1 = 2,6-$Me_2C_6H_3$)[4c] with 2,6-$Me_2C_6H_3$(OH). Related alkyl, amido, and imido alkoxide derivatives of different stoichiometries such as *monoalkyl compounds* MCpClR(NR^1) [M = Nb, Cp = η^5-C_5H_5, R = Me, R^1 = *t*Bu;[7c] 2,6-$Me_2C_6H_3$;[22d] 2,6-*i*$Pr_2C_6H_3$;[7c,22d] R = CH_2Ph, NH*t*Bu, R^1 = 2,6-*i*$Pr_2C_6H_3$;[22a,22d] R = NHR^1,[22d] R^1 = *t*Bu; 2,6-$Me_2C_6H_3$; R = NEt_2, R^1 = *t*Bu;[22d] R = $CH_2CH=CH_2$, $CH_2C(Me)=CH_2$, R^1 = *t*Bu;[22b] Cp = η^5-$C_5H_4SiClMe_2$;[7h,22c] η^5-$C_5H_4SiClMePh$,[7c] R = CH_2Ph, R^1 = *t*Bu; Cp = η^5-$C_5H_4SiMe_2NH$*t*Bu,[7h] R = CH_2Ph, NH*t*Bu, R^1 = *t*Bu; M = Ta,[22f] Cp = η^5-C_5Me_5, R = Me, NH*t*Bu, R^1 = *t*Bu], *dialkyl compounds* $MCpR_2(NR^1)$ (M = Nb, Cp = η^5-C_5H_5, R = NHR^1, R^1 = 2,6-$Me_2C_6H_3$;[22e] R = Ph, R^1 = 2,6-*i*$Pr_2C_6H_3$;[22a] R = *t*BuO; 2,6-Me_2-C_6H_3O, R^1 = Me;[7a] R = 2,6-*i*$Pr_2C_6H_3O$; 2,6-$Ph_2C_6H_3O$, R^1 = *t*Bu;[7a] Cp = η^5-C_5Me_5, R = Me,[7c] CH_2Ph,[22a] R^1 = 2,6-*i*$Pr_2C_6H_3$; Cp = η^5-$C_5H_4CMe_2C_9H_7$, R = NEt_2, R^1 = 2,6-*i*$Pr_2C_6H_3$;[22e] Cp = η^5-$C_5H_4SiMeXY$, X = Cl, CH_2Ph, Y = Me,Ph; X = Me, Y = NH*t*Bu; R = CH_2Ph, R^1 = *t*Bu;[7h] M = Ta, Cp = η^5-C_5Me_5, R^1 = *t*Bu;[2d] 2,6-*i*$Pr_2C_6H_3$[7c]) and *mixed alkyl* compounds $MCpRR'(NR^1)$ [M = Nb, Cp = η^5-C_5H_5, R = Me, R′ = NH*t*Bu, R^1 = 2,6-*i*$Pr_2C_6H_3$;[22d] R = NH*t*Bu, R′ = *n*Bu, NEt_2, σ-C_5H_5, R^1 = *t*Bu;[22d] R = Me, R′ = NHR^1, R^1 = 2,6-Me_2-C_6H_3;[22e] M = Ta, Cp = η^5-C_5Me_5, R = Me, R′ = NMe_2, NHMe, $OOCNMe_2$, OOCNH*t*Bu, R^1 = *t*Bu;[22g] R = Me, R′ = OMe, O*t*Bu, NH*t*Bu, R^1 = *t*Bu;[22f] R = Me, R′ = NPh_2, $N(SiMe_3)_2$ [22h]] have been reported.



Scheme 3. Synthesis of alkyl(methyl)imido complexes

Complexes **1**−**55** are air- and moisture-sensitive and soluble in most organic solvents, including saturated hydrocarbons, except that dichloro(diazabutadiene) complex **12** is insoluble in hexane.

Imido complexes **1**−**5**, **13**−**35**, and **43**−**55** are monomers, pseudotetrahedral, and isostructural with other half-sandwich imido group-5 metal derivatives.[7a,23] The formulation as dichloro- **1**−**5**, (alkyl)chloro- **13**−**23**, dialkyl- **24**−**35**, and alkyl(methyl)- **43**−**55** -(imido) complexes is supported by analytical and spectroscopic data (IR, and ^{1}H and ^{13}C{^{1}H} NMR) that show the expected behaviour for such prochiral, chiral, prochiral and chiral species, respectively. Further, the molecular structure of **21** (Figure 1) shows a typical bent-metallocene moiety with the chlorine atom and the imido group lying in the equatorial plane. Although the two Cp rings differ, the distance from the tantalum atom to both centroids is the same, the angles between the equatorial plane and the mean Cp planes are also equivalent, and the bonding of both Cp rings to the metal centre is very similar. The Ta1−N1 distance of 1.803(4) Å is very similar to those of the closely related complexes [TaCp*$_2$X(NPh)] [X = Cl: 1.799(4) Å;[8a] X = H: 1.831(10) Å[9c]] and the Ta1−N1−C41 angle, 174.6(3)°, is almost linear. These data are consistent with a Ta−N bond order of about 2, in an 18-electron configuration at the metal centre,[24] and an sp nitrogen atom with a lone pair of electrons involved in bonding with the phenyl substituent centred on it.

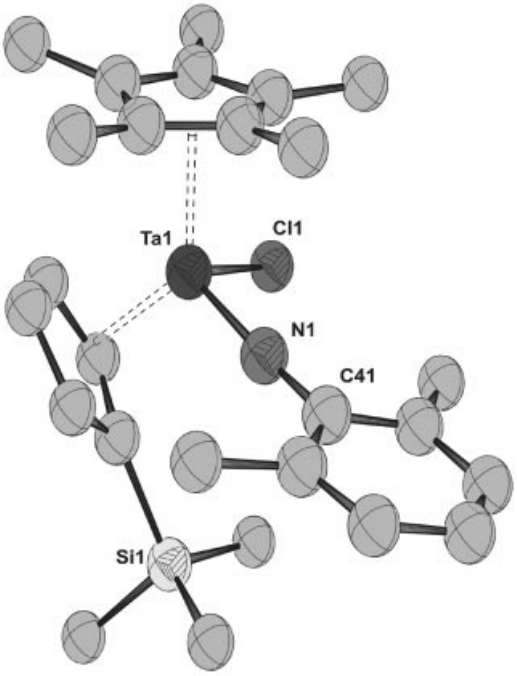


Figure 1. Molecular structure and atom labelling scheme for **[TaCp*Cp′Cl(NR^1)]** (Cp* = η^5-C_5Me_5; Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$, **21**)

The dichloro- **11** and dialkyl- **36**−**39** -(alkyne) complexes are monomers with a C_s symmetry and spectroscopic properties that are basically similar to those reported for metallacyclopropene derivatives[25,26] in which the alkyne ligand acts as a four-electron donor. The IR spectra show an absorption band for the stretching vibration $\nu_{(C=C)}$ ($\tilde{\nu} \approx$ 1582 cm^{-1}) in accordance with the hybridization change of the carbon atoms in the alkyne ligand,[26,27] whereas ^{13}C{^{1}H} NMR chemical shifts for the acetylenic carbon atoms appear to be $\delta \approx 244$.[28] Complex **37** (Figure 2) can be described as a monomer with a typical three-legged piano-stool environment for the niobium atom, assuming that the centroid of the alkyne ligand occupies a single coordination site. Notable are the perpendicular disposition of the alkyne ligand with respect to the $C_5H_4SiMe_3$ ring and the plane formed by the alkyl substituents at the niobium centre. The average Nb−C_{alkyne} distance is 2.090(6) Å and C41−C51 is 1.323(7) Å, values just within the range expected for a four-electron-donor alkyne ligand,[26,29] in which the C−C bond order is less than 3. Conversely, the DFT theoretical data[14] corresponding to the dichloro- and dimethyl(acetylene) compounds $NbCpR_2(HCCH)$ (R = Cl, Me) agree with a preferential disposition of the alkyne ligand lying perpendicular to the Cp plane, such as that observed for complex **37**.

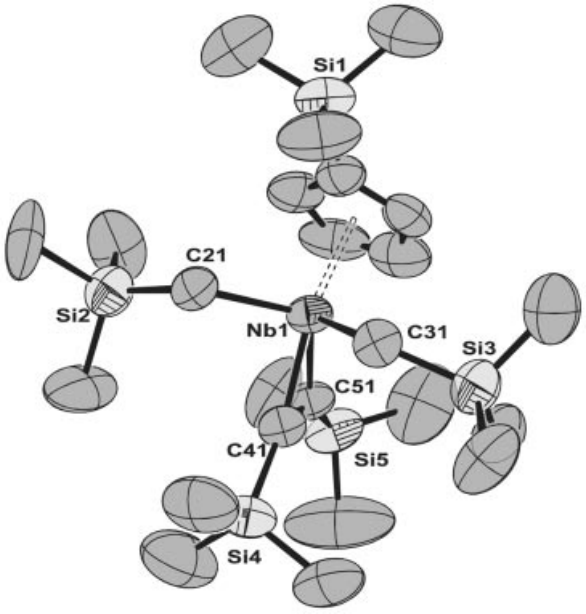


Figure 2. Molecular structure and atom labelling scheme for **[NbCp′R$_2$(Me$_3$SiCCSiMe$_3$]** (Cp′ = η^5-$C_5H_4SiMe_3$; R = CH_2SiMe_3, **37**)

The NMR spectroscopic data of complex **12** suggest that the (ene)diamido ligand adopts a *supine* conformation with respect to the (trimethylsilyl)cyclopentadienyl ring (Scheme 2), which accords with studies by Mashima et al.[30] on the geometric preferences of 1,4-diazadiene ligands in half-sandwich metallocene complexes of early transition metals. Furthermore, detailed DFT analysis of the fragment orbital interactions in the model complex $NbCpCl_2(HNCHCHNH)$ provides no evidence for positive overlap between the niobium centre and the inner carbon atoms of the DAD ligand.[15] The ^{1}H NMR spectrum of **40**

displays a singlet at δ = 0.15 due to the Nb−Me, and shows an AB spin system for the diastereotopic α-CH_2 protons of alkyl groups in complexes **41** and **42**. The singlet δ = 1.75 due to the methyl substituents of the (ene)diamido ligand is at higher field than the δ = 1.84 ppm of the starting dichloro complex **12**. The ^{13}C resonances of the inner carbon atoms also show a high field displacement. These data, along with the preferential orientation discussed by Mashima et al.[30] in related complexes, suggest that the alkylation reactions of the dichloro complex involve an orientation change in the (ene)diamido ligand from the *supine* conformation in **12** to the *prone* form in the dialkyl derivatives **40**−**42**.[16d]

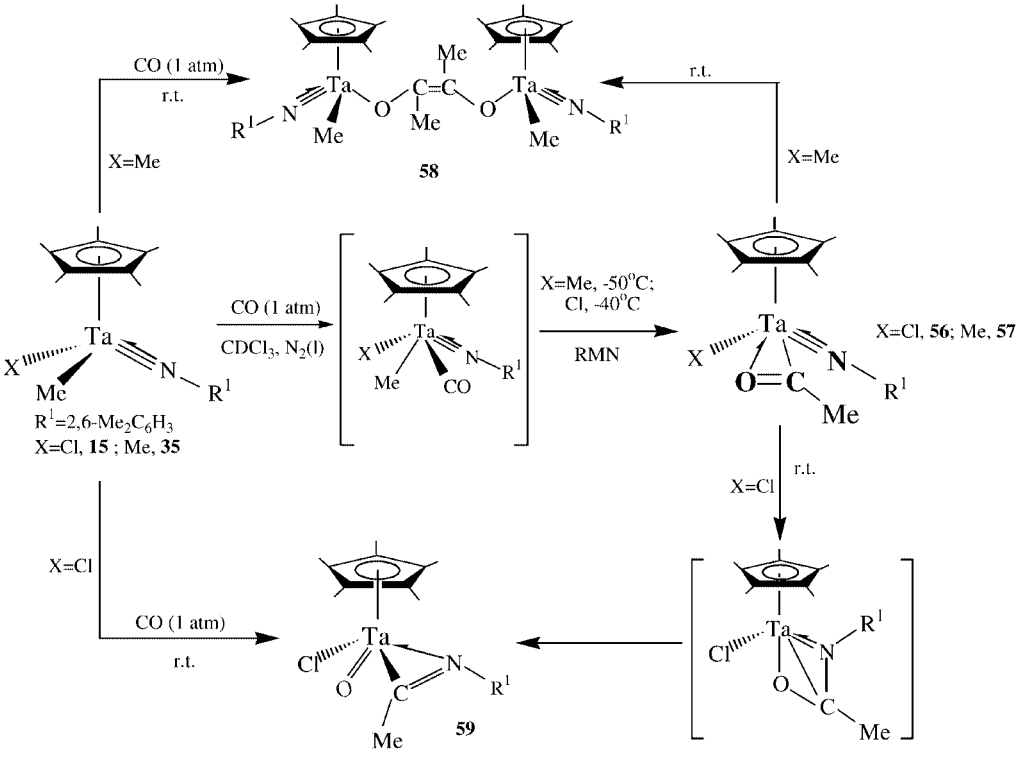
Insertion Processes

Reactions with Carbon Monoxide

Dimethyl(imido) complex **35** reacts with carbon monoxide (1 atm) at room temperature in toluene to give the dinuclear μ-enediolate complex **[{TaCp*Me(NR^1)}$_2${μ-η^2-OC(Me)=C(Me)O}]** (R^1 = 2,6-$Me_2C_6H_3$, **58**)[20a] in good yield. This takes place by intermolecular coupling between two acyl carbon atoms of the intermediate η^2-acyl(methyl)imido derivative **[TaCp*Me(NR^1){η^2-C(Me)=O}]** (R^1 = 2,6-$Me_2C_6H_3$, **57**),[20a] (Scheme 4) whose formation can be observed in situ by NMR spectroscopy[31] at low temperatures. Complex **57** is quantitatively transformed into the enediolate species **58** on heating to room temperature, preventing its isolation as a solid.

With the chloro(methyl)imido complex **15** as starting material the expected η^2-acyl(imido) derivative was not obtained, since it was spontaneously converted into the chloro(η^2-methyliminoacyl)oxo complex **[TaCp*Cl(O){η^2-C(Me)=NR^1}]** (R^1 = 2,6-$Me_2C_6H_3$, **59**).[20a] The formation of **59** can be explained (Scheme 4) by assuming the initial coordination of CO, followed by migration of the methyl group bonded to the metal atom to the electrophilic carbonyl carbon atom to give the scarcely stable intermediate η^2-acyl(chloro)imido complex **[TaCp*Cl(NR^1){η^2-C(Me)=O}]** (R^1 = 2,6-$Me_2C_6H_3$, **56**),[20a] which was identified in solution by NMR spectroscopy[31] at −40 °C. Nucleophilic attack of the imido nitrogen atom at the electrophilic acyl carbon atom leads to an unidentified intermediate species that spontaneously rearranges, breaking the C−O bond with simultaneous formation of M−C single and M=O double bonds to give the final chloro(η^2-methyliminoacyl)oxo compound **59**. Complex **59** is chiral and its structure (Figure 3) shows the tantalum centre in a three-legged piano-stool environment, assuming that the centroid of the Cp* ring and the centroid of the iminoacyl group is taken as occupying a single coordination site. The η^2-iminoacyl group is coordinated in a similar mode to that in related complexes[4c] with Ta−C1 and Ta−N1 distances of 2.133(9) and 2.132(7) Å, respectively, corresponding to single bonds, and a C1−N1 distance of 1.276(11) Å, which implies double-bond character. The oxygen ligand−tantalum atom bond of 1.731(7) Å is in the range reported for Ta=O double bonds.[32]

As well as alkyl (methyl) groups, the alkyl(chloro)- (**17**, **18**, **22**), dialkyl- (**29**−**33**), and alkyl(methyl)- (**46**, **47**, **49**) -imidotantalum complexes [TaCp*XR(NR^1)] (R^1 = 2,6-$Me_2C_6H_3$) also react with carbon monoxide (1 atm) at



Scheme 4. Insertion reactions of carbon monoxide

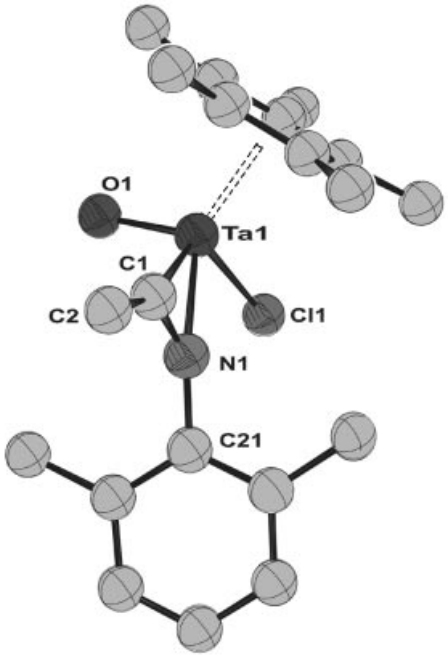


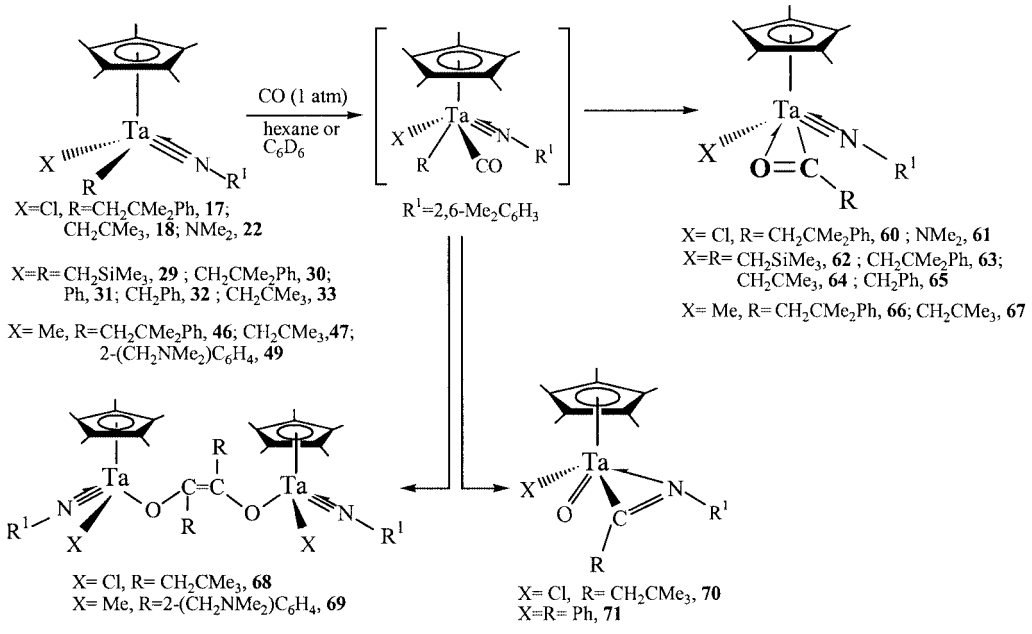
Figure 3. Molecular structure and atom labelling scheme for **[TaCp*Cl(O){η²-C(Me)=NR¹}]** (Cp′ = η⁵-C_5Me_5; R^1 = 2,6-$Me_2C_6H_3$, **59**)

room temperature in hexane or [D_6]benzene (NMR tube scale) to give η²-acyl(chloro)- (X = Cl, R = CH_2CMe_2Ph, **60**), (η²-carbamoyl)chloro- (X = Cl, R = NMe_2, **61**), (η²-acyl)alkyl- (X = R = CH_2SiMe_3, **62**; CH_2CMe_2Ph, **63**; CH_2CMe_3, **64**; CH_2Ph, **65**), and (η²-acyl)methyl- (X = Me, R = CH_2CMe_2Ph, **66**; CH_2CMe_3, **67**) -imido complexes **[TaCp*X(NR¹){η²-C(R)=O}]** (**60**−**67**)[33] (Scheme 5), as result of migration of the alkyl group bonded to the metal atom to the electrophilic carbonyl atom of the previously coordinated CO ligand. The regioselective synthesis of the (η²-acyl)methyl complexes **66** and **67** reflects the preferential migration of CH_2CMe_2Ph and CH_2CMe_3 groups with respect to the methyl group, which accords with the sequence established for the isocyanide insertion process.[33]

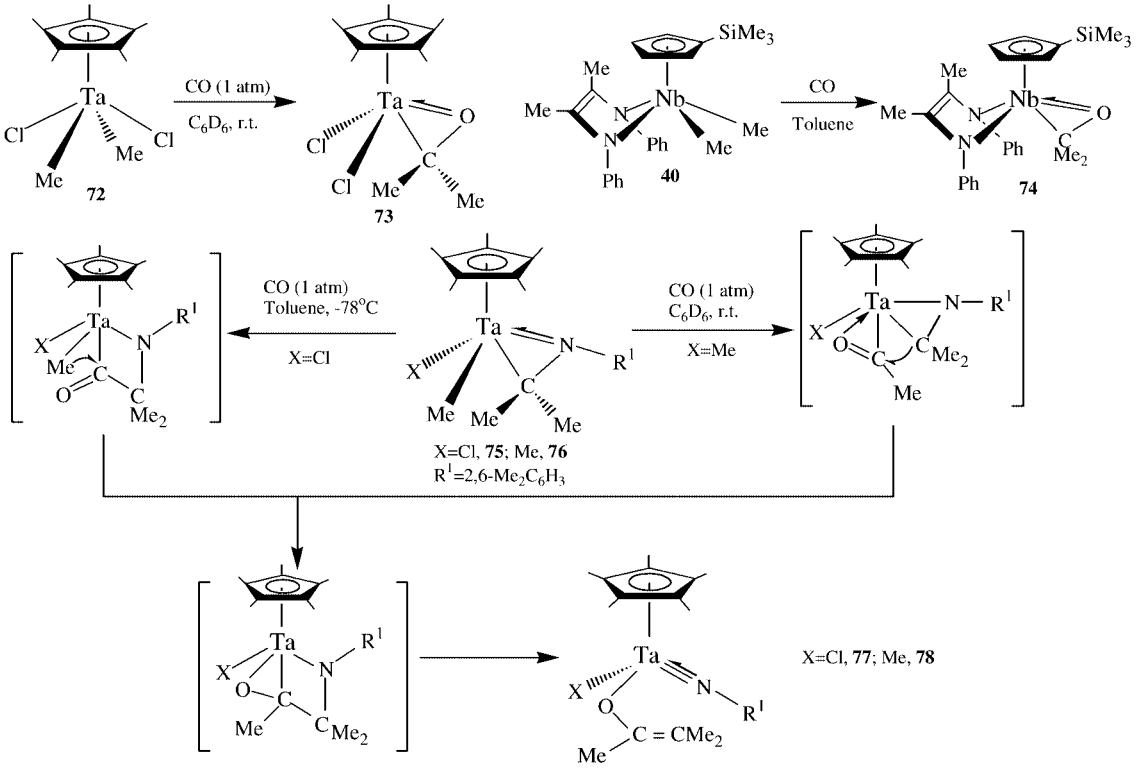
When X = Cl, R = CH_2CMe_3 (**18**) and X = Me, R = 2-(CH_2NMe_2)C_6H_4 (**49**) the η²-acyl derivatives can neither be isolated nor detected by ^{1}H NMR spectroscopy due to their very low stability; however, the dinuclear μ-enediolate complexes **[{TaCp*X(NR¹)}₂{μ-η²-OC(R)=C(R)O}]** [R^1 = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3, **68**; X = Me, R = 2-(CH_2NMe_2)C_6H_4, **69**] are easily obtained when the corresponding chloro- or methyl(alkyl)imido complex reacts with CO under the same conditions (Scheme 5), probably by intermolecular coupling between two acyl carbon atoms of the unstable intermediate η²-acyl complexes "[TaCp*X(NAr){η²-C(R)=O}]", which could not be observed in situ by ^{1}H NMR spectroscopy.[20a] The same reaction with CO but using [TaCp*XR(NR^1)] (R^1 = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3, **18**; X = R = Ph, **31**) as starting materials failed to give the expected (η²-acyl)imido derivatives as they were spontaneously converted into the (η²-iminoacyl)oxo complexes **[TaCp*X(O){η²-C(R)=NR¹}]** after 35 d (X = Cl, R = CH_2CMe_3, **70**) and 12 h (X = R = Ph, **71**), respectively (Scheme 5); the formation of these products can be explained as with the analogous chloro(methyl)imidotantalum derivatives.[20a]

When X = Cl and R = CH_2SiMe_3, **16**; CH_2Ph, **19**; and X = Me and R = CH_2SiMe_3, **45**; Ph, **48**; CH_2Ph, **50** the reaction with CO leads to an unidentified mixture of products, whereas for X = Cl, R = 2-(CH_2NMe_2)C_6H_4, **20** there is no reaction, even on heating at 100 °C.

The dimethyl complexes [TaCp*Cl_2Me_2] (**72**)[12] and [NbCp′Me_2(Me,Ph-DAD)] (**40**) react with carbon monoxide (1 atm) at room temperature in [D_6]benzene and toluene



Scheme 5. Insertion reactions of carbon monoxide



Scheme 6. Insertion reactions of carbon monoxide

to give the oxametallacyclopropane complexes **[TaCp*Cl_2(η^2-CMe_2-O)]** (**73**)[20a] and **[NbCp′(η^2-CMe_2-O)(Me,Ph-DAD)]** (**74**),[15] respectively, by double migration of two methyl groups, first to the electrophilic carbon atom of the coordinated CO ligand and then to the related η^2-acyl intermediate, which could not be detected (Scheme 6). The oxametallacyclopropane moiety, which is not further transformed, is analogous to that reported for the (acetone)tantalum complex [TaCp*Me_2(η^2-CMe_2-O)].[2d,34]

Conversely, the azatantalacyclopropane complexes [TaCp*XMe(η^2-CMe_2NR^1)] (R^1 = 2,6-$Me_2C_6H_3$; X = Cl, **75**; Me, **76**)[4b] react with 1 equiv. of CO, leading to the pseudotetrahedral enolate derivatives **[TaCp*X(NR^1){η^1-OC(Me)=CMe_2}]** (X = Cl, **77**; Me, **78**)[20a] (Scheme 6), probably by formation of intermediate species that could not be detected in situ by ^{1}H NMR spectroscopy.

All spectroscopic data for compounds **56**−**78** are consistent with their formulation. The (η^2-acyl)imido complexes **56**, **57** and **60**−**67** show $\nu_{Ta=N}$[7a,35] and $\nu_{C(R)=O}$[1d,36] at $\tilde{\nu} \approx$ 1327 and 1589 cm^{-1}, respectively. The C=O stretching vibration in η^2-acyl compounds ranges from 1453 to 1625 cm^{-1} and the lowest stretching frequencies occur for η^2-acyl complexes containing high-valent metal atoms (as we also found). This has been attributed to the participation of a "carbene-like" resonance form[37] or to the contribution of a "carbenium-ion-like" acceptor orbital on the undistorted η^2-acyl structure.[38] The η^2-acyl[39] and η^2-carbamoyl[40] (**61**) carbon resonances appear at $\delta \approx$ 317 and 228 ppm, respectively, in the typical ranges for both types of complexes. The η^2-acyl(methyl)imido complex **66** (Figure 4) is a monomer with a chiral tantalum atom in a typical four-legged piano-stool environment. The imido ligand is bonded to the metal centre in an almost linear disposition[4a,20a] with a Ta1−N1 bond length and a Ta1−N1−C21 bond angle of 1.815(11) Å and 172.2(10)°, respectively. The bonding system between the η^2-acyl moiety and the metal centre is similar to that of the trichloro derivative [TaCp*Cl_3\{η^2-C(CH_2CMe_3)=O\}],[41] but in our case the Ta1−C31 [2.126(14) Å] and Ta1−O1 [2.214(11) Å] bond lengths are slightly longer due to the different donor capacities and the *trans* influence of the chloride and imido ligands.

The μ-enediolates **58**, **68**−**69**, the (η^2-iminoacyl)oxo compounds **59**, **70**−**71**, the oxametallacyclopropanes **73** and **74**, and the enolate complexes **77** and **78** show the expected structural behaviour according to IR and NMR spectroscopy.

Reactions with 2,6-Dimethylphenyl Isocyanide

Several years ago we reported a systematic study[4] on the insertion of isocyanides into Ta−C(methyl) bonds of various chloro methyl derivatives, TaCp*$Cl_{4-x}Me_x$. When x = 2 azatantalacyclopropane species are formed in which the imine linkage typically binds strongly to the metal centre in an η^2-CN fashion.[2,42] These complexes have been postulated as intermediates in organometallic transformations[2a,2g,2i,20a] but few have been isolated and fully characterized.[4b,13d,43] Because of such high reactivity,[2b,4,42a,42d,44] we decided to extend our study to bulky alkyltantalum derivatives.

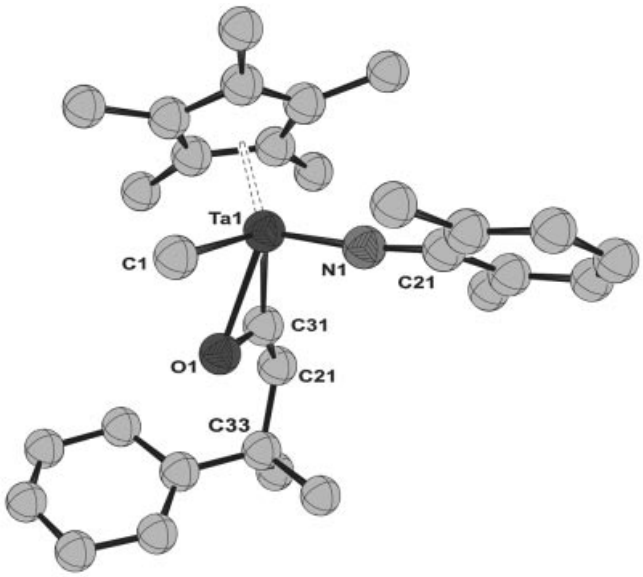
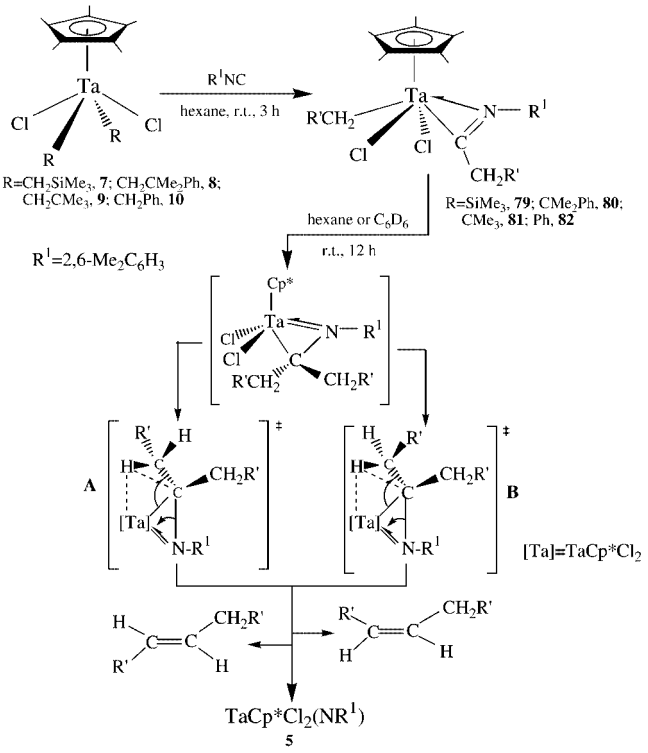


Figure 4. Molecular structure and atom labelling scheme for **[TaCp*Me(NR^1){η^2-C(CH$_2$CMe$_2$Ph)=O}]** (Cp′ = η^5-C$_5$Me$_5$; R^1 = 2,6-Me$_2$C$_6$H$_3$, **66**)

The complexes TaCp*Cl$_2$R$_2$ (R = CH$_2$SiMe$_3$, **7**;[13d] CH$_2$CMe$_2$Ph **8**;[13d] CH$_2$CMe$_3$, **9**;[13a,13b] CH$_2$Ph, **10**[13a,13b]) react with 1 equiv. of 2,6-Me$_2$C$_6$H$_3$NC in hexane under a rigorously dry inert gas to give reddish solutions, from which, after workup, the alkyldichloro(η^2-iminoacyl)tantalum complexes **[TaCp*Cl$_2$R{η^2-C(R)=NR^1}]** (R^1 = 2,6-Me$_2$C$_6$H$_3$; R = CH$_2$SiMe$_3$, **79**; CH$_2$CMe$_2$Ph, **80**; CH$_2$CMe$_3$, **81**; CH$_2$Ph, **82**)[13d] could be recovered (Scheme 7). This behaviour contrasts with that observed[4b] for the [TaCp*Cl$_2$Me$_2$] derivative, which with 1 equiv. of isocyanide gives a dichloroazatantalacyclopropane complex by a migration of the second methyl group to the electrophilic iminoacyl carbon atom of the dichloro(methyl)(η^2-iminoacyl) intermediate. In the present case, the remaining bulkier alkyl substituent does not migrate. Furthermore, the same η^2-iminoacyl complexes (**79**−**82**) are obtained by treating [D$_6$]benzene solutions of the starting dialkyldichloro compounds with 2 equiv. of isocyanide at room temperature, and no bis(η^2-iminoacyl) species are formed.

On the other hand, the η^2-iminoacyl complexes **79**−**82** slowly decompose at room temperature in [D$_6$]benzene or hexane solutions to give the dichloro(imido)tantalum compound **TaCp*Cl$_2$(NR^1)** (R^1 = 2,6-Me$_2$C$_6$H$_3$, **5**) together with a mixture of *cis* and *trans* olefins **R′-CH$_2$-CH=CH-R′** (R′ = SiMe$_3$, **79**o; CMe$_2$Ph, **80**o; CMe$_3$, **81**o; Ph, **82**o),[13d] probably via intermediate dialkylazatantalacyclopropane complexes (Scheme 7), which cannot be detected in situ by ^{1}H NMR spectroscopy. However, the azatantalacyclopropane 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 and back-rearrangements give the imido complex with elimination of the corresponding olefins.



R′	trans%	Olefin
SiMe$_3$	90	1,3-bistrimethylsilyl-propene, **79**o
CMe$_2$Ph	80	2,6-dimethyl-2,6-diphenyl-3-heptene, **80**o
CMe$_3$	66	2,2,6,6-tetramethyl-3-heptene, **81**o
Ph	100	1,2-diphenyl-propene, **82**o

Scheme 7. Insertion reactions of isocyanide

The spectroscopic data (IR and ^{1}H and ^{13}C{^{1}H} NMR) are consistent with the expected pseudooctahedral geometries of these η^2-iminoacyl complexes. Compound **80** (Figure 5) has a tantalum atom in a pseudooctahedral environment, with the centroid of the Cp* ring and the carbon atom of the iminoacyl ligand occupying the axial positions. The tantalum atom is 0.61(1) Å above the plane

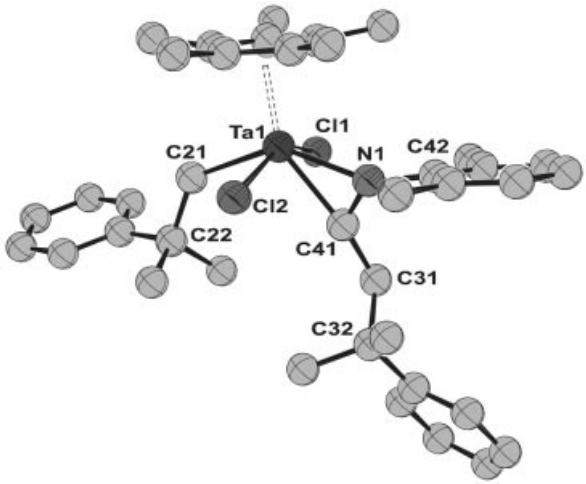
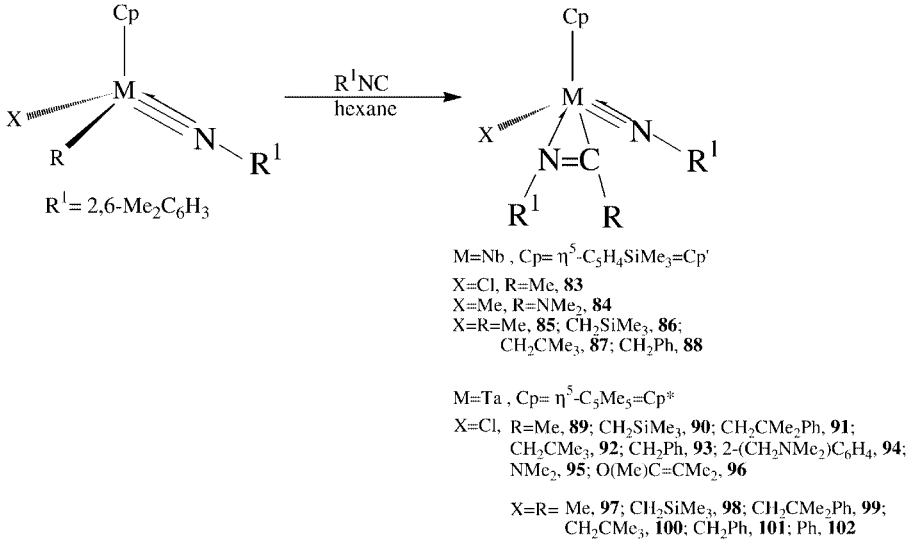


Figure 5. Molecular structure and atom labelling scheme for **[TaCp*Cl$_2$R{η^2-C(R)=NR^1}]** (Cp′ = η^5-C$_5$Me$_5$; R = CH$_2$CMe$_2$Ph; R^1 = 2,6-Me$_2$C$_6$H$_3$, **80**)

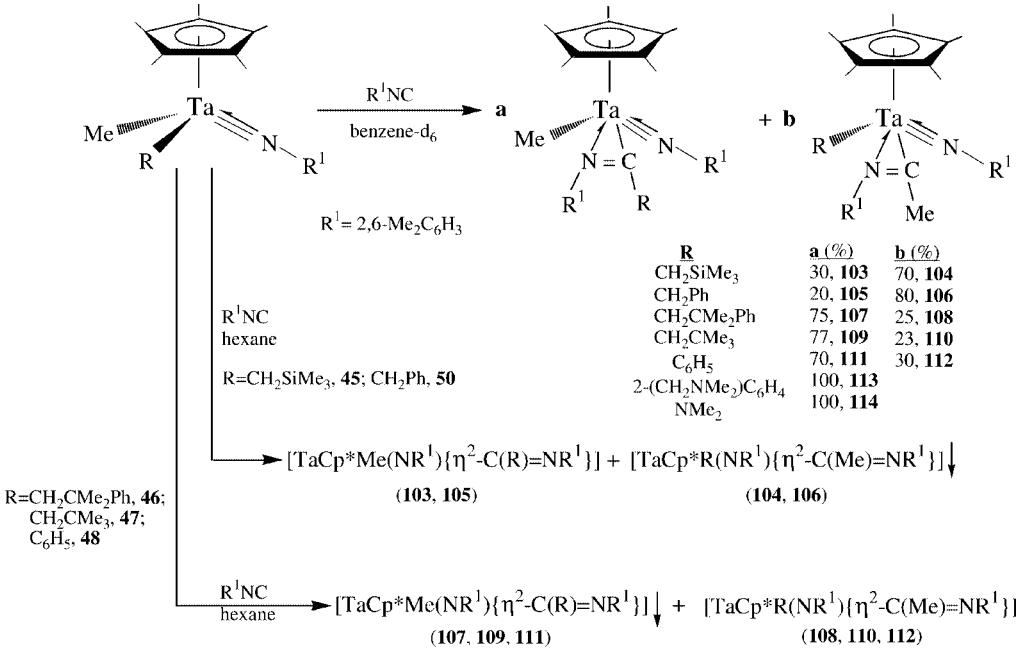


Scheme 8. Insertion reactions of isocyanide

formed by C21, Cl1, Cl2, and N1[45] and the C=N bond of the iminoacyl group is almost perpendicular to this plane.

When R^1NC is added to hexane solutions of the alkyl(chloro)- or dialkyl(imido) complexes $MCpXR(NR^1)$ (R^1 = 2,6-$Me_2C_6H_3$; M = Nb, Cp = η^5-$C_5H_4SiMe_3$=Cp′; M = Ta, Cp = η^5-C_5Me_5 = Cp*) in a 1:1 molar ratio an instantaneous insertion reaction gives the stable 18-electron chloro imido(η^2-iminoacyl) [M = Nb, Cp = Cp′, X = Cl, R = Me, **83**;[33] M = Ta, Cp = Cp*, X = Cl, R = Me, **89**;[20a] CH_2SiMe_3, **90**;[33] CH_2CMe_2Ph, **91**;[33] CH_2CMe_3, **92**;[33] $CH_2C_6H_5$, **93**;[33] 2-$(CH_2NMe_2)C_6H_4$, **94**;[33] O(Me)C=CMe_2, **96**[20]], alkyl(imido)η^2-iminoacyl (M = Nb, Cp = Cp′, X = R = Me, **85**;[33] CH_2SiMe_3, **86**;[33] CH_2CMe_3, **87**;[33] CH_2Ph, **88**;[33] M = Ta, Cp = Cp*, X = R = Me, **97**;[20a] CH_2SiMe_3, **98**;[33] CH_2CMe_2Ph, **99**;[33] CH_2CMe_3, **100**;[33] $CH_2C_6H_5$, **101**;[33] C_6H_5, **102**[33]], methyl- and chloro(imido)(η^2-iminocarbamoyl) (M = Nb, Cp = Cp′, X = Me, R = NMe_2, **84**;[33] M = Ta, Cp = Cp*, X = Cl, R = NMe_2, **95**[33]) derivatives **[MCpX(NR¹){η²-C(R)=NR¹}]** (R^1 = 2,6-$Me_2C_6H_3$, **83**−**102**) (Scheme 8).

For dialkyl derivatives (X = R = alkyl) the migration of the second alkyl group observed for $[TaCp^*Cl_2Me_2]$[4b] does not occur and an excess of isocyanide does not produce a second insertion reaction in the M−C(alkyl) or M−C(iminoacyl) bonds.[1d,3d,3i,3j] However, when X = OC(Me)=CMe_2 and R = Me the methyl group bound to



Scheme 9. Insertion reactions of isocyanide

the tantalum atom migrates to the electrophilic carbon atom of the isocyanide ligand, which does not attack the terminal olefinic carbon atom of the enolate ligand, in contrast to when (alkenylamido)imido complexes[4c] are used.

The addition of 1 equiv. of 2,6-$Me_2C_6H_3NC$ to [D_6]benzene solutions of the alkyl(methyl)imido complexes [TaCp* RMe(NR^1)] under rigorously anhydrous conditions gives a mixture of (η^2-alkyliminoacyl)imido(methyl) **[TaCp* Me(NR^1){η^2-C(R)=NR^1}]** (R^1 = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **103**; CH_2Ph, **105**; CH_2CMe_2Ph, **107**; CH_2CMe_3, **109**; C_6H_5, **111**; 2-(CH_2NMe_2)C_6H_4, **113**; NMe_2, **114**)[33] and alkyl(η^2-methyliminoacyl)imido **[TaCp* R(NR^1){η^2-C(Me)=NR^1}]** (R^1 = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **104**; CH_2Ph, **106**; CH_2CMe_2Ph, **108**; CH_2CMe_3, **110**; C_6H_5, **112**)[33] complexes, in ratios determined from ^{1}H NMR spectra (Scheme 9).

The same reaction at room temperature using *n*-hexane as solvent in a dry box affords the insoluble microcrystalline (alkyl)imido(η^2-methyliminoacyl) (R = CH_2SiMe_3, **104**; CH_2Ph, **106**) and (η^2-alkyliminoacyl)methyl(imido) (R = CH_2CMe_2Ph, **107**; CH_2CMe_3, **109**. C_6H_5, **111**) complexes as solids, which are major components in the above-mentioned mixture. Further, when the resulting suspension of the above experiment is concentrated to dryness, the ^{1}H NMR spectrum in [D_6]benzene of the crude residue gave the same result. The yields reflect the relative ease of migration[46] of the various alkyl groups, such as 2-(CH_2NMe_2)C_6H_4 ≈ NMe_2 > CH_2CMe_2Ph ≈ CH_2CMe_3 > C_6H_5 > ***Me*** > CH_2SiMe_3 > CH_2Ph as compared with the methyl group. Our particular contribution also establishes the regioselective migration of the 2-[(dimethylamino)methyl]phenyl (**113**) and dimethylamido groups (**114**). The preferential migration of the NMe_2 moiety, for starting amido(methyl)niobium and -tantalum derivatives that give (η^2-iminocarbamoyl)methyl complexes **84** and **114**, is quite unusual because in similar alkyl- or methyl(amido)titanium,[47] -zirconium,[48] -tungsten[49] and -uranium[50] complexes the insertion occurs preferentially at the M−C_{alkyl} bond. More recent reports[22h] found similar behaviour in an almost instantaneous reaction of the amido(imido)methyl complexes [TaCp*MeX(N*t*Bu)] (X = NMe_2, NHMe) with 1 equiv. of R^1NC to give the corresponding η^2-iminocarbamoyl compounds [TaCp*Me(N*t*Bu){η^2-C(X)=NR^1}] (R^1 = 2,6-$Me_2C_6H_3$; X = NMe_2, NHMe). The authors justify, by DFT calculations, that coordination of the isocyanide ligand followed by nucleophilic attack initiates the insertion reaction, neither into Ta−NR_2 nor Ta−Me bonds, and is governed by kinetic factors. However, insertion into the Ta−Me bond is preferred for amido(imido)methyl [TaCp* Me(NR_2)(N*t*Bu)] (R = Ph, $SiMe_3$) complexes to give (amido)imido(η^1-iminoacyl) derivatives [TaCp*(NR_2)(N*t*Bu)-{η^1-C(Me)=NR^1}], whereas stereoselective insertion into the Ta−NR_2 bond occurs for related amido(methyl) derivatives, leading to (methyl)imido(η^2-iminocarbamoyl) complexes [TaCp*Me(N*t*Bu){η^2-C(X)=NR^1}] (X = NMe_2, NHMe).

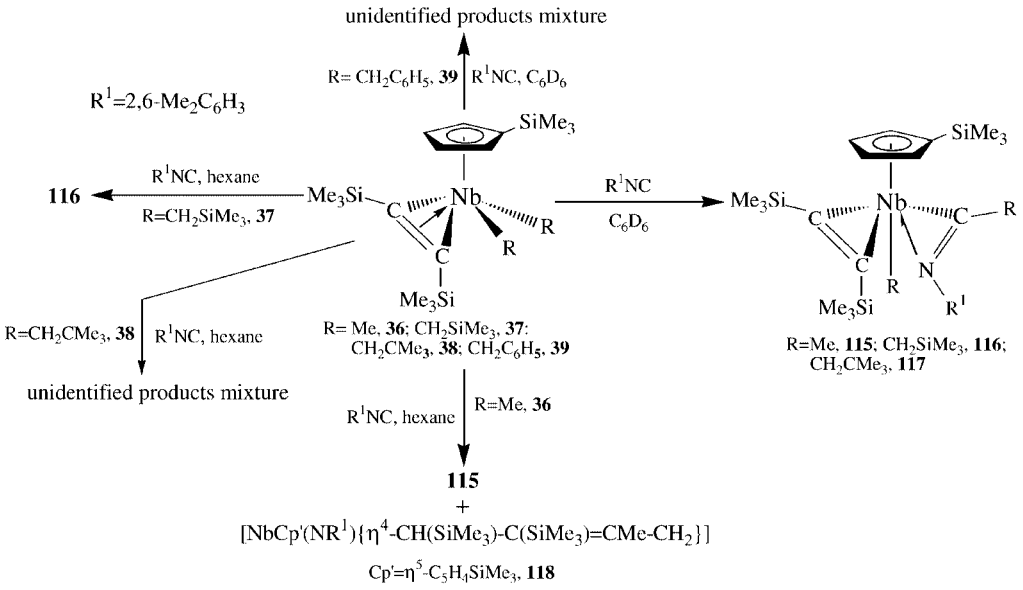
The reaction of the starting mixed alkyl(imido)methyl derivatives with 2 equiv. of the isocyanide ligand in [D_6]benzene solutions at room temperature affords the same η^2-iminoacyl complexes **103**−**114**, and bis(η^2-iminoacyl) derivatives cannot be detected by ^{1}H NMR spectroscopy.

Structural studies[33] of the imido(η^2-iminoacyl) (**83**, **85**−**113**) and imido(η^2-iminocarbamoyl) (**84**, **95**, **114**) complexes agree with the expected pseudo-square-pyramidal geometry found for similar chiral niobium and tantalum derivatives.[20]

Early transition metal complexes[2f,42a,51] constitute a powerful component in carbon−carbon bond formation strategies in organic synthesis[52] and catalytic polymerization.[53] In particular, (alkyne)niobium and -tantalum complexes have provided convenient routes to carbonylic derivatives[54] and nitrile[55] coupling reactions via metallacyclic intermediates. Furthermore, (alkyne)niobium- and -tantalum(III) derivatives react with nitriles to give azatantalacyclopentene complexes that may participate in an intermolecular tautomerization process to enamines,[42c] and are also efficient catalysts for the oligomerization and polymerization of internal alkynes.[53]

In accord with this background, we recently reported a novel study[14] of the chemical behaviour of the (alkyl)alkyne[(trimethylsilyl)cyclopentadienyl]niobium complexes [NbCp′R_2($Me_3SiCCSiMe_3$)][14] (Cp′ = η^5-$C_5H_4SiMe_3$; R = Me, **36**; CH_2SiMe_3, **37**; CH_2CMe_3, **38**; $CH_2C_6H_5$, **39**) in insertion processes. Thus, when 1 equiv. of the isocyanide 2,6-$Me_2C_6H_3NC$ was added to [D_6]benzene solutions of the dialkyl(alkyne) derivatives **36**−**39**, under a rigorously dry inert gas in a sealed NMR tube, reddish solutions corresponding to (alkyl)alkyne(η^2-iminoacyl) complexes **[NbCp′R{η^2-C(R)=NR^1}($Me_3SiCCSiMe_3$)]**[14] (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$; R = Me, **115**; CH_2SiMe_3, **116**; CH_2CMe_3, **117**) as the unique reaction products were obtained (Scheme 10). The insertion process is instantaneous and after coordination of the isocyanide ligand the migration of one alkyl group to the electrophilic isocyanide carbon atom produces an η^2-iminoacyl complex. With (alkyne)dibenzyl complex **39** the reaction takes place but, probably, the η^2-iminoacyl derivative is very unstable and decomposes to an unidentified product mixture. In the same reactions carried out in a Schlenk tube using hexane as solvent, only complex **116**, as a crystalline red solid, could be isolated. Both **115** and **117** are unstable at room temperature, and while **115** is partially transformed into an imidoniobacyclopent-3-ene complex (**118**) the alkyne(η^2-iminoacyl)neopentyl derivative **117** decomposes into an unidentified products mixture.

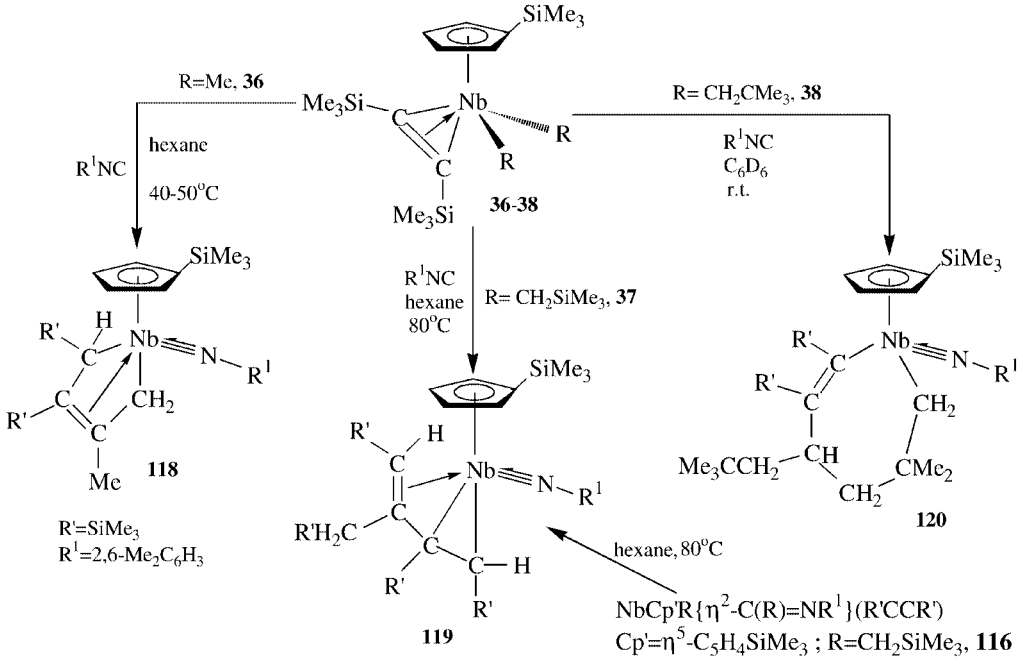
Alternatively, the imidoniobacyclopent-3-ene complex **[NbCp′(NR^1){η^4-CH($SiMe_3$)-C($SiMe_3$)=C(Me)-CH_2}]**[14] (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$, **118**) can be prepared when the (alkyne)dimethyl derivative **36** is treated with 1 equiv. of isocyanide in hexane at 40−50 °C for 12 h (Scheme 11). Conversely, if the alkyne(trimethylsilylmethyl)-(η^2-iminoacyl) complex **116** is heated to 80 °C in hexane for 12 h it can be isolated as an imido(vinyl)niobacyclopropane derivative **[NbCp′(NR^1){η^4-CH($SiMe_3$)C($SiMe_3$)-C(CH_2SiMe_3)=CH($SiMe_3$)}]**[14] (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$, **119**), a crystalline red solid, the struc-



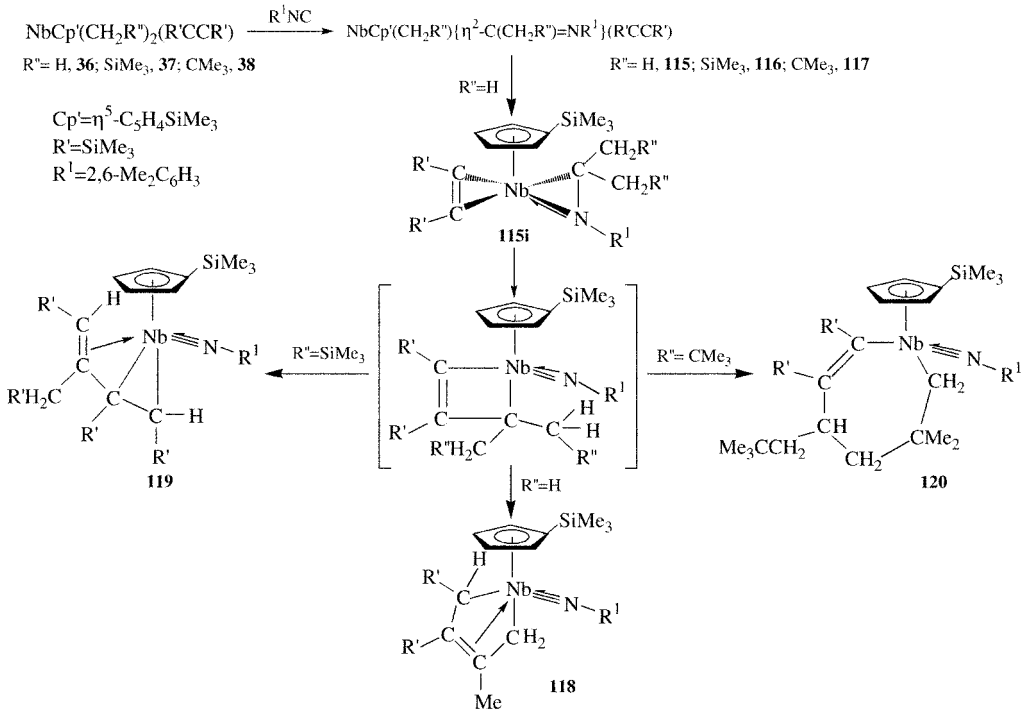
Scheme 10. Insertion reactions of isocyanide

ture of which was determined by X-ray diffraction methods. Identical results are obtained by thermally treating a mixture of **37** and 2,6-$Me_2C_6H_3NC$ (1:1 molar ratio). In contrast, the reaction between the (alkyne)bis(neopentyl) complex **39** and 2,6-$Me_2C_6H_3NC$ leads, in a first step, to an alkyne(η^2-iminoacyl)neopentyl complex (**117**) that is gradually transformed into the imidoniobacyclohept-2-ene complex **[NbCp′(NR¹){η²-$CH_2CMe_2CH_2CH(CH_2CMe_3)$C-($SiMe_3$)=C($SiMe_3$)}]**[14] (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$, **120**), the structure of which may be proposed on the basis of NMR spectroscopic data.

On monitoring the formation processes of complexes **118**−**120** by ^{1}H NMR spectroscopy, only complex **118** was found to give an intermediate (alkyne)azaniobacyclopropane derivative, **[NbCp′{η²-C(CH_2R'')-NR¹}(Me_3SiCC-$SiMe_3$)]**[14] (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$; R′′ = $SiMe_3$, **115i**). This transformation can be rationalized by migration of the second metal-bonded methyl group to the iminoacyl carbon center to give the intermediate **115i** (Scheme 12). Similar azametallacyclopropane species have been proposed and isolated by us in the reactions of dichlorodimethyl(pentamethylcyclopentadienyl)niobium[13d] and



Scheme 11. Insertion reactions of isocyanide



Scheme 12. Insertion reactions of isocyanide

-tantalum[4b] complexes and isocyanides and their structures confirmed by X-ray diffraction methods. Rearrangement of the intermediate **115i** is followed by migration of the hydrogen atom, and back-rearrangement gives the imidoniobacyclopent-3-ene complex **118**. Complexes **119** and **120** could be formed via imidoniobacyclobutene intermediates; when R′′ = $SiMe_3$, migration of the hydrogen atom and subsequent rearrangement leads to **119**, which is a niobacyclopropane complex with an η^2-coordinated vinyl substituent at the metal center. However, a different pathway may be proposed by the formation of azaniobacyclopentatriene species[3b,3g,56] as result of the intramolecular coupling between both alkyne and iminoacyl ligands. When R′′ = CMe_3, C−H activation of a methyl group of the *tert*-butyl fragment and back-rearrangement leads to the imidoniobacyclohept-2-ene complex **120**. This is probably due to the steric and electronic differences between $SiMe_3$ and CMe_3 groups. Thus, the lesser steric hindrance of the *tert*-butyl group permits a closer approach to the metal atom and the activation of a C−H bond gives the complex **120**.

Structural studies (IR, ^1H and $^{13}C\{^1H\}$ NMR)[14] of complexes **115**−**120** agree with the proposed structures. The pseudooctahedral complexes **115**−**117**, due to the chiral character of the metal center, show in their ^1H and $^{13}C\{^1H\}$ NMR spectra an ABCD spin system and five resonances, respectively, for the $C_5H_4SiMe_3$ moiety and, also, two inequivalent methyl groups for the 2,6-$Me_2C_6H_3$ ring, in accordance with the slow rotation of the aryl substituent around the N−C_{ipso}(aryl) bond. Complex **118** exhibits NMR behaviour that is consistent with a diene ligand in an *s-cis* conformation, as has been observed in other diene group-5 metal derivatives.[57] The unusual conformation of the diene ligand in complex **119** was deduced from detailed analysis of the NMR spectroscopic and X-ray diffraction data, which strongly suggest that the diene ligand is bonded

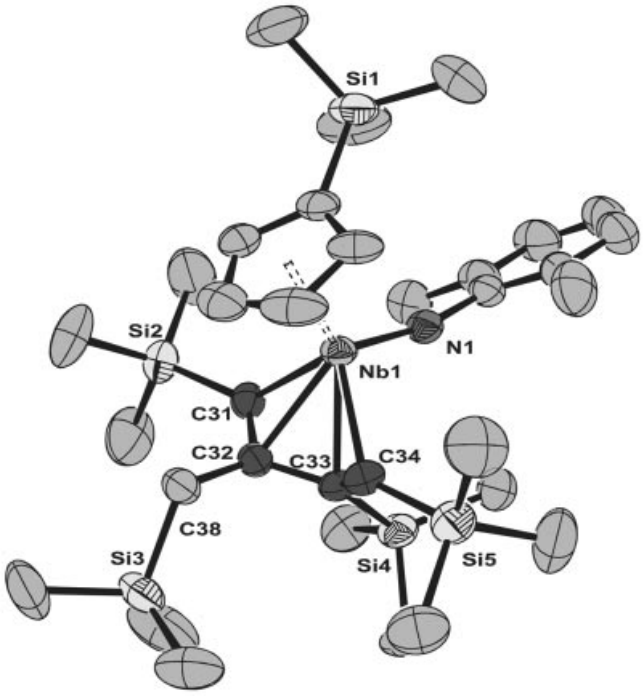
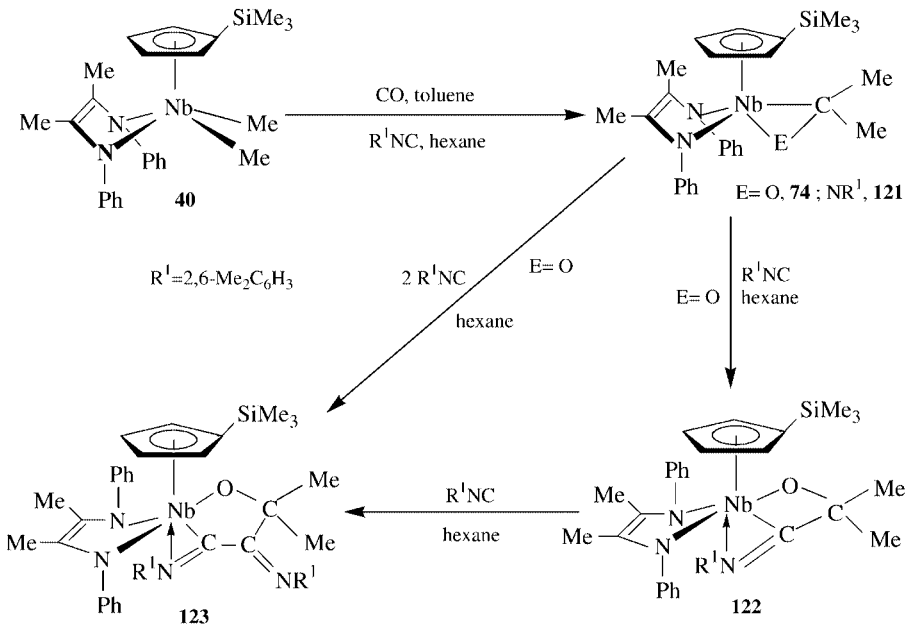


Figure 6. Molecular structure and atom labelling scheme for **[NbCp′(NR1){η4-CH(SiMe3)C(SiMe3)C(CH2SiMe3)=CH(SiMe3)}]** (Cp′ = η^5-$C_5H_4SiMe_3$; R^1 = 2,6-$Me_2C_6H_3$, **119**)



Scheme 13. Insertion reactions of carbon monoxide and isocyanide

in an η^2-niobacyclopropane fashion with a vinyl substituent η^2-coordinated to the metal center. This is the most relevant detail of the molecular structure (Figure 6) because, frequently, in diene mono(cyclopentadienyl)niobium and -tantalum complexes[57a,57d,58] the diene ligand forms a metallacyclopent-3-ene system with a preferred *supino* conformation, although there are examples with a *prono* conformation. Furthermore, the diene ligand can adopt an *s-trans* conformation, as observed in bis(cyclopentadienyl)zirconium,[59] mono(cyclopentadienyl)tantalum[60] and cationic bis(cyclopentadienyl)tantalum[61] complexes. In our case, the crystallographic data do not correspond to the same bonding system and, therefore, we propose a moiety consisting of a "diene" C31−C32−C33−C34 fragment linked to the metal atom through the C33−C34 atoms, forming a niobacyclopropane ring, and the donor vinyl substituent C31−C32.

Finally, when 2,6-$Me_2C_6H_3NC$ (1 equiv.) is added to a hexane solution of the dimethyl complex $NbCp'Me_2$(Me,Ph-DAD) (Cp′ = η^5-$C_5H_4SiMe_3$, **40**) under rigorously anhydrous conditions an orange solution is obtained, which after evaporation of the solvent produces the azaniobacyclopropane complex **[NbCp′(η²-CMe₂NR¹)(Me,Ph-DAD)]** (R^1 = 2,6-$Me_2C_6H_3$, **121**),[15] as the result of two consecutive steps (Scheme 13). The first step involves migration of one methyl group to the electrophilic isocyanide carbon atom to form an η^2-iminoacyl intermediate,[1d,2f,2h,2i,2j,2k,62] which could not be detected by ^1H NMR spectroscopy. Subsequent migration of the second methyl group to the iminoacyl carbon centre yields an azaniobacyclopropane.[2b,2c,4b,13d,63]

Dialkyl complexes **41** (R = CH_2SiMe_3) and **42** (R = $CH_2C_6H_5$) do not react with isocyanide at room temperature; when the solution is heated the reaction probably takes place simultaneously with the decomposition of the organometallic complex formed, leading to an unidentified product mixture. When **40** is treated with 2 equiv. of isocyanide the result is the same, in contrast to the behaviour of the azatantalacyclopropane derivatives [$TaCp^*Cl_2(\eta^2$-$CMe_2NR^1)$][4b] (R^1 = 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$), which in the presence of isocyanides give the corresponding dichloro(imido) complex [$TaCp^*Cl_2(NR^1)$] with elimination of the arylimine ketene $ArN{=}C{=}CMe_2$. However, the oxaniobacyclopropane [$NbCp'Cl_2(\eta^2$-CMe_2-O)(Me,Ph-DAD)] (**74**),[15] reacts with 1 or 2 equiv. of 2,6-$Me_2C_6H_3NC$ to give the expected insertion products **[NbCp′Cl₂{η²-OCMe₂(CNR¹)ₓ}(Me,Ph-DAD)]** (R^1 = 2,6-$Me_2C_6H_3$; x = 1, **122**; x = 2, **123**).[15] Complex **122** can be transformed into **123** by a simple isocyanide insertion reaction.

Conclusions

The review shows that direct alkylation of the corresponding chloro derivatives can afford dialkyldichloro [$MCp^*Cl_2R_2$] (**6**−**10**), alkyl(chloro)imido [$MCpClR(NR^1)$] (**13**−**23**), dialkyl(imido) [$MCpR_2(NR^1)$] (**24**−**35**), alkyl(methyl)imido [$MCpRMe(NR^1)$] (**43**−**55**), dialkyl(alkyne) [$NbCp'R_2(Me_3SiCCSiMe_3)$] (**36**−**39**), and dialkyl(diazabutadiene) complexes [$NbCp'R_2$(Me,Ph-DAD)] (**40**−**42**), whose reactivity has been studied in carbon monoxide and isocyanide insertion processes.

Imido(methyl) complexes [$TaCp^*MeX(NR^1)$] (R^1 = 2,6-$Me_2C_6H_3$; X = Cl, **15**; Me, **25**) react with carbon monoxide via the expected η^2-acyl derivatives [$TaCp^*X(NR^1)\{\eta^2$-C(Me)=O}] (X = Cl, **56**; Me, **57**) but lead to different products that depend on X. The higher carbenoid character of the η^2-acyl ligand when X = Me affords dinuclear μ-enedi-

olate complex **58**, whereas imido nitrogen attack at the more electrophilic acyl carbon atom when X = Cl gives the chloro (η^2-iminoacyl)oxo complex **59**.

Alkyl groups, other than methyl, as in alkyl(chloro)- (**17**, **18**, **22**) dialkyl- (**29**−**33**) and alkyl(methyl)- (**46**, **47**, **49**) -imidotantalum complexes react with CO (1 atm) to give (η^2-acyl)chloro (X = Cl, R = CH_2CMe_2Ph, **60**), (η^2-carbamoyl)chloro (X = Cl, R = NMe_2, **61**), (η^2-acyl)alkyl (X = R = CH_2SiMe_3, **62**; CH_2CMe_2Ph, **63**; CH_2CMe_3, **64**; $CH_2C_6H_5$, **65**), and (η^2-acyl)methyl (X = Me, R = CH_2CMe_2Ph, **66**; CH_2CMe_3, **67**) -imido derivatives [TaCp*X(NR^1){η^2-C(R)=O}] (R^1 = 2,6-$Me_2C_6H_3$) as result of a simple insertion process. The preferential migration of neophyl and neopentyl groups with respect to the methyl group determines the regioselective synthesis of complexes **66** and **67**, but when X = Cl, R = CH_2CMe_3 (**18**) and X = Me, R = 2-$(CH_2NMe_2)C_6H_4$ (**49**) the dinuclear μ-enediolate complexes **68** and **69** are formed through intermolecular coupling between two acyl carbon atoms of the unstable intermediate η^2-acyl complexes. For **18** and X = R = Ph (**31**) insertion of CO furnishes (η^2-iminoacyl)oxo complexes **70** and **71** by a mechanism similar to that proposed for the chloro(methyl)imidotantalum derivative **15**. However, the related dichlorodimethyl complex TaCp*Cl_2Me_2 (**72**) reacts with CO to give the oxametallacyclopropane derivative TaCp*Cl_2(η^2-CMe_2-O) (**73**) as result of a double migration of both methyl groups, whereas the azatantalacyclopropane complexes [TaCp*XMe(η^2-CMe_2NR^1)] (X = Cl, **75**; Me, **76**) lead to the pseudotetrahedral enolate derivatives [TaCp*X(NR^1){η^1-OC(Me)=CMe_2}] (R^1 = 2,6-$Me_2C_6H_3$; X = Cl, **77**; Me, **78**) by formation of unidentified intermediate species.

Dialkyldichloro complexes **7**−**10** react with R^1NC (1 equiv.) to give (alkyl)dichloro(η^2-iminoacyl) derivatives [TaCp*Cl_2R{η^2-C(R)=NR^1}] (R^1 = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **79**; CH_2CMe_2Ph, **80**; CH_2CMe_3, **81**; $CH_2C_6H_5$, **82**) in contrast to the related dichlorodimethyl compounds (M = Nb, **6**: Ta, **72**) which, under the same conditions, give a dichloroazametallacyclopropane system by migration of the second methyl substituent to the electrophilic iminoacyl carbon atom of the dichloro(η^2-iminoacyl)methyl intermediate species. Here, the remaining bulkier alkyl group does not migrate and no bis(η^2-iminoacyl) complexes are formed by treating the starting dialkyldichloro compounds with 2 equiv. of isocyanide. The η^2-iminoacyl complexes **79**−**82** slowly decompose at room temperature in [D_6]benzene solutions to give [TaCp*Cl_2(NR^1)] and a mixture of *cis*/*trans* olefins R′CH_2CH=CHR′ (**79**o−**82**o), probably via unidentified intermediate azatantalacyclopropane species.

Stable 18-electron η^2-iminoacyl derivatives, [MCpX(NR^1){η^2-C(R)=NR^1}] (**83**−**102**), are obtained by inserting 1 equiv. of R^1NC into the M−C(alkyl) bonds of alkyl(chloro) or dialkyl(imido) complexes. In contrast, alkyl(methyl)imidotantalum complexes react by migration of alkyl or methyl substituent to give a mixture of (η^2-alkyliminoacyl)methyl(imido) [TaCpMe(NR^1){η^2-C(R)=NR^1}] (**103**, **105**, **107**, **109**, **111**, **113**, **114**) and (alkyl)imido(η^2-methyliminoacyl) derivatives [TaCpR(NR^1){η^2-C(Me)=NR^1}] (**104**, **106**, **108**, **110**, **112**), respectively. When starting with {2-[(dimethylamino)methyl]phenyl}methyl and (dimethylamido)imido(methyl) complexes, insertion takes place with regioselective migration of 2-[(dimethylamino)-methyl]phenyl and dimethylamido groups.

The reaction of dialkyl(alkyne) derivatives **36**−**38** with 2,6-$Me_2C_6H_3NC$ (1 equiv.) occurs through initial formation of the (alkyl)alkyne(η^2-iminoacyl) compounds [NbCp′R-{η^2-C(R)=NR^1}($Me_3SiCCSiMe_3$)] (R^1 = 2,6-$Me_2C_6H_3$; R = Me, **115**; CH_2SiMe_3, **116**; CH_2CMe_3, **117**) but leads to different coupling products depending on R. When hexane solutions of **36** or **37** were treated with isocyanide (1 equiv.) at 40−50 °C (**36**) and 80 °C (**37**), respectively, imidoniobacyclopent-3-ene [NbCp′(NR^1){η^4-$CH(SiMe_3)C(SiMe_3)$=C(Me)CH_2}] (**118**) and imido(vinyl)niobacyclopropane [NbCp′(NR^1){η^4-$CH(SiMe_3)C(SiMe_3)C(CH_2SiMe_3)$=CH-$(SiMe_3)$}] (**119**) complexes are obtained, probably via azaniobacyclopropane intermediates. If R = CH_2CMe_3, after the initial formation of a non-stable η^2-iminoacyl complex (**117**), spontaneous conversion into the imidoniobacylohept-2-ene complex [NbCp′(NR^1){η^2-$CH_2CMe_2CH_2CH$-$(CH_2CMe_3)C(SiMe_3)$=$C(SiMe_3)$}] (**120**) occurs, but the intermediate species could not be observed by ^1H NMR spectroscopy. The NMR spectroscopic data of the coupling products confirmed an *s*-*cis* conformation for the diene ligand in complex **118**, while in complex **119** such a ligand presents an unusual coordination mode and forms, with the metal center, a niobacylopropane system with an η^2-vinyl substituent.

The dimethyl(diazabutadiene) complex **40** reacts with carbon monoxide and isocyanide to give oxa- and azaniobacyclopropane derivatives [NbCp′(η^2-CMe_2E)(Me,Ph-DAD)] (E = O, **74**; NR^1, **121**) due to migration of both methyl groups and, probably, via undetected η^2-acyl and η^2-iminoacyl intermediates. Successive isocyanide insertion reactions into the Nb−C bond take place in the oxaniobacyclopropane complex **74**, leading to insertion products **122** and **123**.

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