Sandwich and Half-Sandwich (Imido)niobium Complexes

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This review discusses the study we have carried out towards the synthesis, structure and reactivity of (imido)niobium complexes, which contain at least one cyclopentadienyl ligand. The following families of niobium complexes are described: (i) half-sandwich imido complexes; (ii) metallocene imido compounds; (iii) imido complexes containing *ansa*-cyclopentadienyl ligands; (iv) dinuclear imido complexes such as $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\}_2(\mu\text{-}1,3\text{-}N_2C_6H_4)]$. In addition we describe spectroscopic and structural features of the (imido)niobium complexes.

1. Introduction

The interest arising from the use of imido groups as ligands in the organometallic chemistry of the group 5 elements has experienced a rapid increase in the past decade. Half-sandwich complexes are well known in (imido)niobium chemistry.[1−25] Their metallocene counterparts have also been studied but to a lesser degree.[24−30]

The attention dedicated to imido-containing niobium complexes can be attributed firstly to the isoelectronic relationship that this ligand shares with the cyclopentadienyl moiety. Thus, the half-sandwich imido fragment Nb(=NR)Cp is isoelectronic with MCp_2 (M = Ti, Zr, Hf). Secondly, the imido group can also be bound to the metal atom in differing fashions acting either as a two- or four-electron donor.

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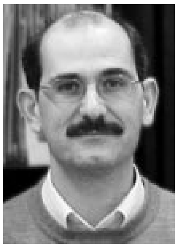


Antonio Antiñolo (top, left) was born in Cartagena, Spain in 1956. He obtained his graduate degree in 1978 from the University of Murcia and his Doctorate in 1982 with Prof. Pascual Royo at the University of Alcalá de Henares. After his postdoctoral appointment with Prof. Michael F. Lappert in 1984 at the University of Sussex, Antonio Antiñolo took up a lectureship position at the University of Alcalá de Henares in 1984. In 1990 he moved to the University of Castilla-La Mancha and became a Full Professor in 1999. His current research interests are centred on metallocene and ansa-metallocene derivatives of early transition metals as possible stereoselective catalysts in olefin polymerization and the activation of small molecules in polyhydride chemistry.

Mariano Fajardo (top, right) was born in Cartagena, Spain in 1956. He obtained his graduate degree in 1978 from the University of Murcia and his Doctorate in 1982 with Prof. Pascual Royo at the University of Alcalá de Henares. From 1982 to 1984 he worked as a postdoc with Prof. Jack Lewis at the University of Cambridge. On his return to Spain he took up a lectureship post at the University of Alcalá de Henares. In the year 2000 he was appointed Full Professor at the University Rey Juan Carlos in Madrid. His current research interests are centred on complexes of early transition metals as possible stereoselective catalysts in olefin polymerization and epoxidation processes and the role of metal complexes in environmental chemistry.

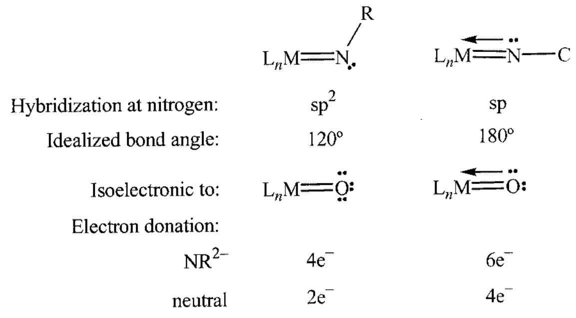
Antonio Otero (bottom, left) was born in Minglanilla (Cuenca), Spain in 1949. He obtained his graduate degree in 1973 from the University of Murcia and his Doctorate in 1976 with Prof. Pascual Royo. From 1978−1979, he worked as a postdoctoral fellow at the University of Oxford with Prof. Malcolm Green researching C−H bond activation processes from cyclopentadienylmolybdenum and -tungsten organometallic complexes. From 1979 to 1989 he was a lecturer at the University of Alcalá. In December 1989, he was appointed Full Professor in Inorganic Chemistry at the University of Castilla-La Mancha. He has authored more than 130 publications in reviewed journals. His current research interests include organometallic chemistry of early transition metals, particularly of group 4 and 5 elements, homogeneous catalytic processes of olefin polymerization with group 4 metallocene catalysts, and heterogeneization of homogeneous catalysts on different inorganic supports.

Sanjiv Prashar (bottom, right) was born in London, United Kingdom in 1966. He obtained his B.Sc. in 1987 and his D.Phil. in 1992 with Prof. Michael F. Lappert from the University of Sussex. His first postdoctoral appointment took him to Spain where he worked with Prof. Pascual Royo at the University of Alcalá de Henares. In 1995 he moved to Ciudad Real in the Spanish Mancha and for more than 6 years he worked at the University of Castilla-La Mancha in collaboration with Professors Antonio Antiñolo and Antonio Otero. It was here that the majority of this study of (imido)niobium compounds was carried out. In October 2001 he took up a lectureship position at the University Rey Juan Carlos in Madrid where his current research interests are centred on ansa-metallocene derivatives of early transition metals as possible stereoselective catalysts in olefin polymerization.

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

Imido ligands, are common ligands in high-oxidation-state transition-metal chemistry. An (imido)metal complex has the general form M=NR where there is a double bond between the metal centre and the nitrogen atom. In addition, the lone pair on the nitrogen atom usually donates electron density to the metal centre, providing a triple-bond interaction with the metal atom.

In high-valent complexes the imido unit is usually considered to be RN^{2-} whereas in low-valent complexes it tends to be considered as a neutral ligand. When specifying how many electrons an imido ligand donates it is therefore necessary to state which electron formalism one is using and to consider how the nitrogen atom is participating in the bonding (Scheme 1). It should be noted that the imido and oxo ligands are isoelectronic.



Scheme 1. Hybridization and electron counting in imido compounds

The M−N−R bond angle can, in most cases be regarded as an indicator of the degree of π-donation from the nitrogen atom. Imido ligands are very good π-donors and thus the overwhelming majority of imido complexes are linear or near-linear (bond angles from 150 to 180°).

The imido ligand can act as a spectator ligand similar to the role played by cyclopentadienyl or can directly participate in the reactivity namely in protonation processes. Imido ligands are of interest not only for their role as ancillary ("spectator") ligands, but for the potential group transfer of the imido unit to an organic moiety.

2. Discussion

2.1 (Imido)niobium Precursors

The complexes [Nb(=NAr)Cl_3(DME)] [Ar = C_6H_4Me-4 (**1**), C_6H_4OMe-4 (**2**)][31] [Equation (1)] were prepared by a modification of the synthetic methods reported for other (imido)niobium halide complexes.[32,33] The synthesis of [Nb(=N*t*Bu)$Cl_3(py)_2$] was reported by Sundermeyer et al.[34] These complexes have been employed in the synthesis of the cyclopentadienyl-containing niobium complexes discussed hereafter.

$$NbCl_5 + ArNH_2 + DME + 2py + 2ZnCl_2 \xrightarrow{CH_2Cl_2} [Nb(=NAr)Cl_3(DME)] + 2[pyH][ZnCl_3] \quad (1)$$

$$Ar = C_6H_4Me\text{-}4\ (\mathbf{1}),\ C_6H_4OMe\text{-}4\ (\mathbf{2})$$

The ^1H NMR spectra of **1** and **2** show clearly the inequivalence of the methyl and methylene groups of the DME adduct suggesting, for an octahedral disposition, that this ligand is bonded to the metal centre by two Nb−O links in which one oxygen atom is located *cis* to the imide group and the other oxygen atom *trans*. This has been confirmed by X-ray crystal diffraction studies (Figure 1).[35]

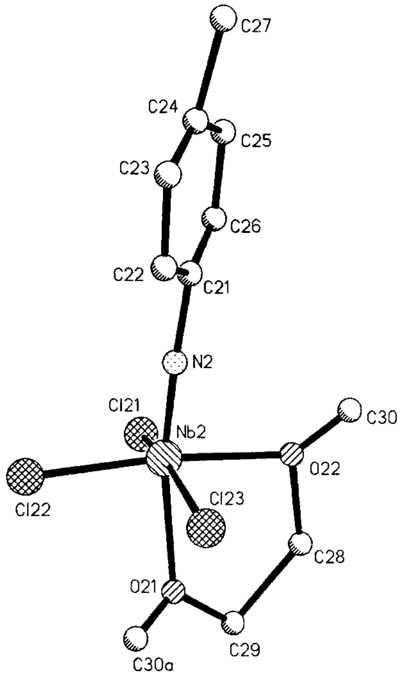
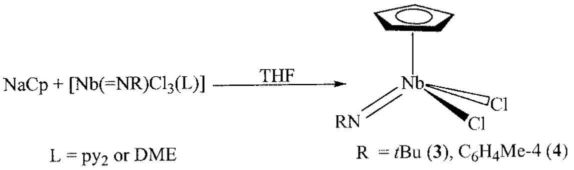


Figure 1. Molecular structure of [Nb(=NC_6H_4Me-4)Cl_3(DME)] (**1**)

2.2 Half-Sandwich (Imido)niobium Complexes

2.2.1 Synthesis

The principal synthetic routes, reported previously in the literature, for the preparation of half-sandwich (imido)niobium complexes involved the reaction of [Nb(η^5-C_5R_5)Cl_4] with the appropriate amine H_2NR' or $NR'(SiMe_3)_2$.[20,23] However, [Nb(=N*t*Bu)CpCl_2] (**3**) and [Nb(=NC_6H_4Me-4)CpCl_2] (**4**) were prepared by the straightforward reaction of 1 mol-equiv. of NaCp with [Nb(=N*t*Bu)$Cl_3(py)_2$] or **1**, respectively [Equation (2)].[31]



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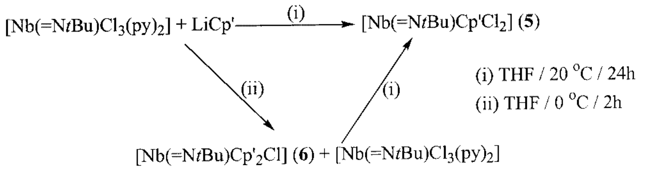
When the same reaction was carried out between [Nb(=N*t*Bu)$Cl_3(py)_2$] and LiCp′ (Cp′ = η^5-$C_5H_4SiMe_3$) both the monosubstituted [Nb(=N*t*Bu)Cp′Cl_2] (**5**) and disubstituted [Nb(=N*t*Bu)Cp′$_2$Cl] (**6**) complexes were shown to be present (Scheme 2).[31]

2.2.2 Structural Characterization

Complexes containing the unsubstituted cyclopentadienyl ligand show a unique signal in their ^1H NMR

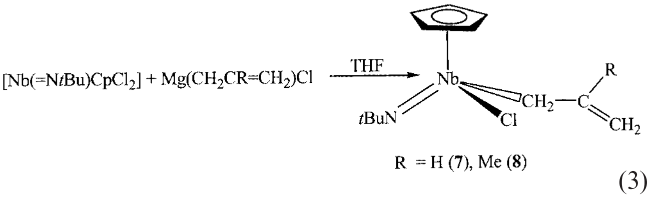


Scheme 2

spectra regardless of the surrounding symmetry for this moiety. However, when a substituent is introduced in the cyclopentadienyl ring, the resulting ring protons give signals directly related to the symmetry of the complex. Thus for **5**, an AA′BB′ system for the ring protons is observed in the ^1H NMR spectrum.

2.2.3 Reactivity with Allyl Grignard Reagents

The allyl(imido)niobium complexes [Nb(=N*t*Bu)Cp(η^1-$CH_2C(R)CH_2$]Cl] [R = H (**7**), Me (**8**)] were prepared by the reaction of **3** with the corresponding allylmagnesium chloride [Equation (3)].[36] In the ^1H NMR spectrum for **7** and **8** the signals associated with η^1-allyl systems, namely three signals corresponding to the CH_2 moiety bonded to the metal centre, the central group C(R) and the olefinic protons for the terminal CH_2, were observed. The values of the coupling constants and those of other η^1-allyl complexes discussed in this review are given in Table 1.



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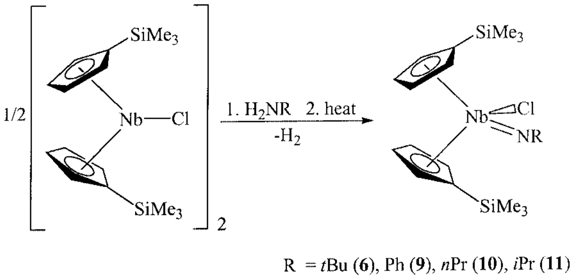
2.3 (Imido)niobocene Complexes

2.3.1 Synthesis

Although the chemistry of monocyclopentadienyl(imido) complexes of niobium is well documented[1−25] far fewer examples of bent (imido)niobocene complexes can be found in the literature.[24−30] Our initial studies in this field led to the synthesis of [Nb(=NR)Cp′$_2$Cl] [R = *t*Bu (**6**), Ph (**9**), *n*Pr (**10**), *i*Pr (**11**)] along two distinctive preparative routes.[37,38] The first involved the reaction of RNH_2 with [{NbCp′$_2$Cl}$_2$] in accordance with a sequence involving initial oxidative addition of the amine, giving rise presumably to an amido intermediate which on subsequent thermolytic expulsion of H_2 affords the imido derivative [Equation (4)].[37] The second route consisted of the thermal treatment of [NbCp′$_2$(RNCO)Cl] to give the desired imido complex [see Equation (5)].[37,38]



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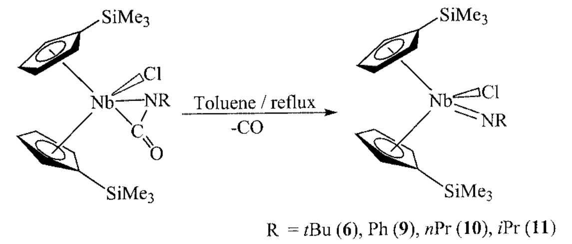

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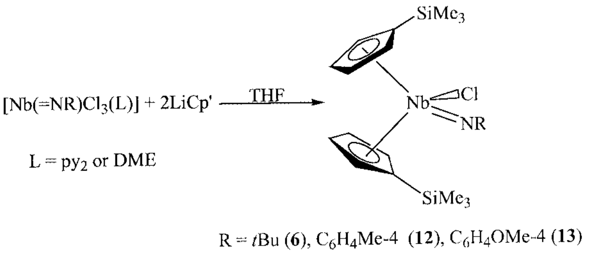
A more straightforward preparative method, by the reaction of 2 equiv. of LiCp′ with the corresponding (imido)niobium halide precursor [Equation (6)], was used in the synthesis of [Nb(=NR)Cp′$_2$Cl] [R = *t*Bu (**6**), C_6H_4Me-4 (**12**), C_6H_4OMe-4 (**13**)].[31] In a similar manner the imido complex [Nb(=NC_6H_4Me-4)Cp_2Cl] (**14**) was synthesized.[39] The mixed sandwich complex [Nb(=N*t*Bu)-CpCp′Cl] (**15**) was prepared by the addition of LiCp′ to a THF solution of [Nb(=N*t*Bu)$CpCl_2$] (**3**) [Equation (7)].[31]



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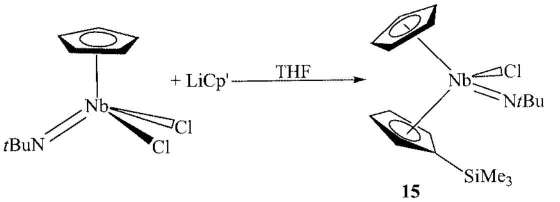

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Table 1. Coupling constants for the η^1-allyl complexes

	$^3J(^1H-^1H)$	$^2J_{gem}(^1H-^1H)$	$^3J_{cis}(^1H-^1H)$	$^3J_{trans}(^1H-^1H)$
[Nb(=N*t*Bu)Cp(η^1-CH_2CHCH_2)Cl] (**7**)	8.1 Hz	2.6 Hz	9.9 Hz	16.8 Hz
[Nb(=N*t*Bu)Cp[η^1-$CH_2C(Me)CH_2$]Cl] (**8**)		3.0 Hz		
[Nb(=NC_6H_4Me-4)Cp_2(η^1-CH_2CHCH_2)] (**25**)	8.3 Hz	2.5 Hz	9.9 Hz	16.8 Hz
[Nb(=N*t*Bu)Cp′$_2$(η^1-CH_2CHCH_2)] (**26**)	8.5 Hz	2.5 Hz	9.9 Hz	16.9 Hz
[Nb(=NC_6H_4Me-4)Cp′$_2$(η^1-CH_2CHCH_2)] (**27**)	8.1 Hz	2.5 Hz	9.9 Hz	16.8 Hz
[Nb(=NC_6H_4OMe-4)Cp′$_2$(η^1-CH_2CHCH_2)] (**28**)	8.3 Hz	2.4 Hz	10.0 Hz	16.8 Hz
[Nb(=N*t*Bu){Me_2Si(η^5-C_5H_4)$_2$}(η^1-CH_2CHCH_2)] (**55**)	8.5 Hz	2.6 Hz	9.9 Hz	16.8 Hz

2.3.2 Structural Characterization

The ^{1}H NMR spectra of the (Cp′)$_2$(imido) complexes **6**, **9−13** all give similar signal patterns reflecting the C_s symmetry of the molecules. Thus, there is inequivalency between the cyclopentadienyl ring protons in the same system but equivalency between the two rings. An ABCD system is therefore observed.

The molecular structures of **9** and **13**, determined by single-crystal X-ray diffraction studies are depicted in Figures 2 and 3.

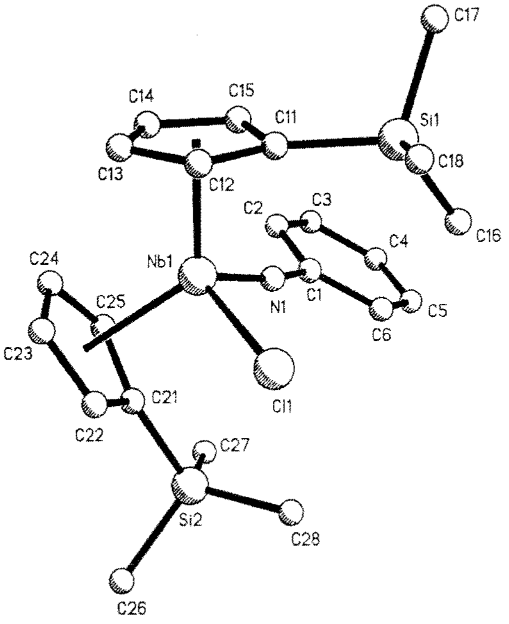


Figure 2. Molecular structure of [Nb(=NPh)Cp′$_2$Cl] (**9**)

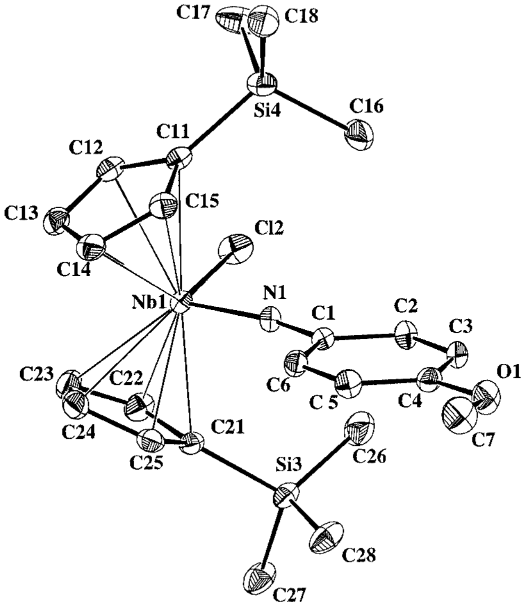


Figure 3. Molecular structure of [Nb(=NC$_6$H$_4$OMe-4)Cp′$_2$Cl] (**13**)

The structural features of **9** and **13** are nearly identical and thus for reasons of simplicity, reference is only made to the former complex.

Compound **9** is a monomer in the solid state and shows a typical bent-metallocene structure. Interestingly, the chlorine atom and the phenyl group lie practically in the equatorial plane, in a similar disposition to that found previously for [Ta(=NPh)(η^5-C$_5$Me$_5$)$_2$H] and [Ta(=NH)(η^5-C$_5$Me$_5$)$_2$Cl].[40,41] Using a frontier-orbital approach Jørgensen[42] explained why the phenyl group in this type of complexes lies in the equatorial plane and not perpendicular to it in an alternative arrangement. The Nb−N bond length is 1.792(2) Å, indicating that probably a bond order halfway between two (Nb=N) and three (Nb≡N) is present. However, the interesting structural parameter is the value of 165.1(2)° found for the Nb−N−C$_{ipso}$ moiety. In the structures reported linear M−N−C geometries are observed for virtually all metallocene complexes (see Table 4). However, for **9** a deviation in this angle of about 15° is observed. The bent arrangement may indicate that the imido nitrogen atom is sp^2-hybridized, but in such a case the phenyl substituent should be orientated out of the equatorial plane towards one of the cyclopentadienyl ligands.[40] Therefore, in spite of the low angle for Nb−N−C$_{ipso}$, we propose that the nitrogen atom is sp-(not sp^2-)hybridized and that the two limiting descriptions, Nb≡N−R and Nb=N−R, proposed by Bercaw and co-workers for (η^5-C$_5$Me$_5$)$_2$Ta(=NPh)(H) may explain the true bonding situation.[40]

In order to gain more insight into the nature of the Nb−N bond, extended-Hückel molecular-orbital calculations have been performed.[43−46] Figure 4 shows an interaction diagram for the frontier orbitals of [Nb(=NPh)Cp$_2$Cl] from [NbCp$_2$Cl]$^{2+}$ to the left and NPh^{2-} to the right.[37] The results are in agreement with those found previously by Jørgensen[42] for [Ta(=NPh)(η^5-C$_5$Me$_5$)$_2$H].

A Walsh diagram for five of the frontier orbitals for bending of the phenyl group in the equatorial plane between 180 and 120° is illustrated in Figure 5, and shows that the highest occupied molecular orbital (HOMO) is unaffected by this bending in contrast to the bending out of the equatorial plane where an increase in energy similar to that described for [Ta(=NPh)(η^5-C$_5$Me$_5$)$_2$H] is observed.[37] However, the Walsh diagram shows that the second and third HOMO increase in energy upon bending the phenyl group (θ = 140°) and a change in total energy from −1717.63 eV for θ = 180° to 1714.54 eV for θ = 120° is observed. However, no significant changes in energy between θ = 180 and 140° are observed, indicating that in complex **9**, with Nb−N−C$_{ipso}$ of 165°, electronic effects are not responsible for this deviation from linear. The Nb−N and N−C$_{ipso}$ overlap populations decrease as a result of the bending and the charge at the niobium atom decreases as the charge at the nitrogen atom increases (see Table 2). The phenyl substituent arranges itself so as to maximize the overlap with the nitrogen p-orbital, but slight modifications of this overlap are observed in the range θ = 180−160°. We have established that the imido bond angles for "linear imide" in this class of complexes can vary to 140° with little effect on the M−N bonding.[37]

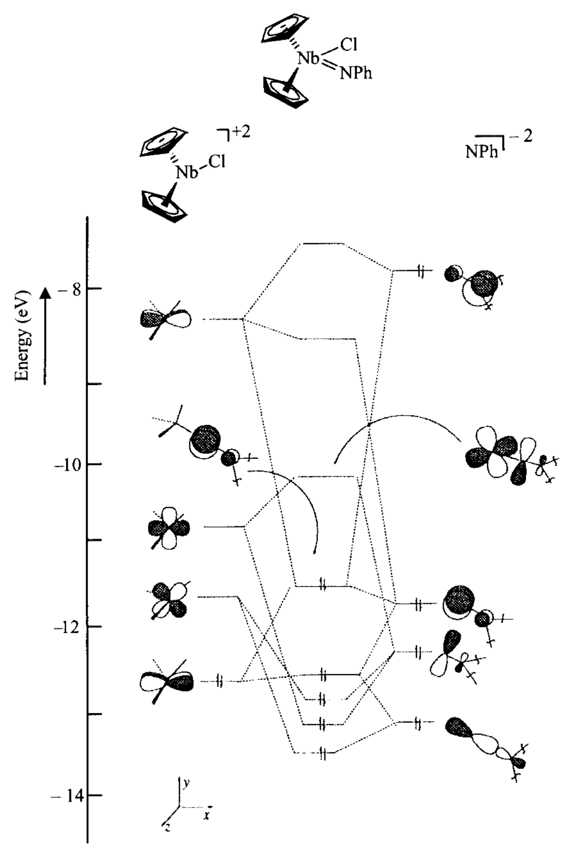


Figure 4. Interaction diagram for the formation of $[Nb(=NPh)Cp_2Cl]$ from $[NbCp_2Cl]^{2+}$ to the left and NPh^{2-} to the right; some of the frontier orbitals are shown in the centre

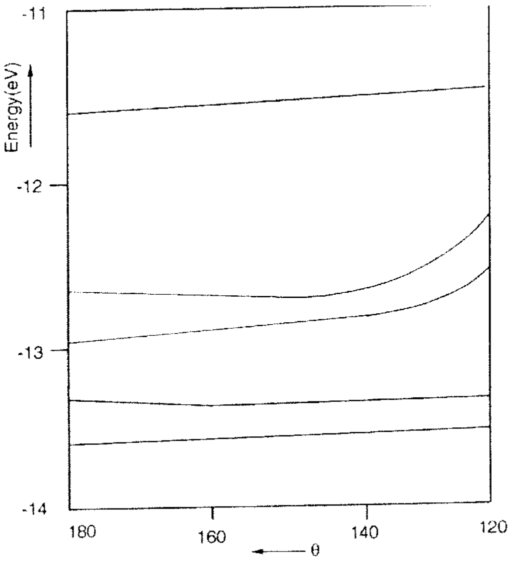


Figure 5. Walsh diagram for the bending of the phenyl group in the equatorial plane

Table 3. Comparison of Nb−Cent distances in selected Cp′-containing niobocene complexes (Cp′ = η^5-$C_5H_4SiMe_3$; Cent = the centroid of the C_5 ring)

Compound	Average Nb−Cent [Å]	Ref.
$[Nb(=NC_6H_4OMe\text{-}4)Cp'_2Cl]$ (**13**)	2.189	[31]
$[\{NbCp'_2Cl\}_2(\mu\text{-}1,3\text{-}N_2C_6H_4)]$ (**61**)	2.188	[53]
$[Nb(=O)Cp'_2Me]$	2.181	[54]
$[Nb(=NPh)Cp'_2(C{\equiv}CPh)]]$ (**37**)	2.180	[55]
$[Nb(=NPh)Cp'_2Cl]$ (**9**)	2.180	[37]
$[NbCp'_2Cl(\eta^2\text{-}N,C\text{-}OCNPh)]$	2.121	[53]
$[NbCp'_2Cl_2]$	2.079	[54,56]
$[\{NbCp'_2Cl\}_2]$	2.07	[37]
$[NbCp'_2(C_6F_5)(CO)]$	2.04	[54]

The formal electron count of **9** is 20 electrons with the excess 2 electrons probably being located in a nonbonding orbital similar to that proposed by Green et al. for $[Mo(=N\textit{t}Bu)(\eta^5\text{-}C_5H_5)_2]$.[47] Similar "20-electron" (imido)niobocene complexes $[Nb(=NR)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ have shown a lengthening of the Nb−centroid distances in comparison with their 18- and 17-electron analogues and this too occurs in **9** (see Table 3). Indeed, such lengthening has also been observed in (imido)metallocene complexes of titanium[48] and molybdenum.[47] The bonding in the "19-electron" vanadium complex $[V(=NC_6H_3Me_2\text{-}2,6)(\eta^5\text{-}C_5Me_5)_2]$ has previously been studied by molecular orbital calculations and led to the proposal that the surplus electrons in these "high-electron" complexes are located in essentially ligand-based orbitals and thus the 18-electron rule is not violated.[49−51] Similar calculations have been carried out for "20-electron" osmium complexes $[Os(NR)_3]$.[52]

A comparison of selected structural data of (imido)niobocene complexes is given in Table 4.

2.3.3 Alkyl Derivatives

Despite the broad scope of imido group 5 metal chemistry only a handful of alkyl-containing (imido)niobocene complexes have previously been reported.[24,25,30] We have expanded this field by the preparation of the following new

Table 2. Values for the overlap populations of the N−C and Nb−N bonds and charges (N, Nb) as a function of the bending angle Nb−N−C(Ph) in the equatorial plane

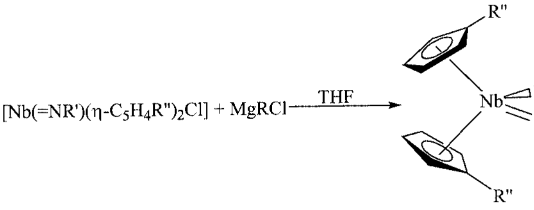
Angle θ (in the plane) [°]	120	140	160	180
Energy [eV]	−1714.54	−1716.84	−1717.50	−1717.63
Overlap population (N−C bond)	797	836	857	862
Charge on N	−1.091	−0.894	−0.806	−0.786
Charge on Nb	0.840	0.623	0.531	0.512
Overlap population (Nb−N bond)	895	978	1017	1030

Table 4. Selected structural data for (imido)niobocene complexes

	Cp−Nb−Cp [°]	Nb−N−C [°]	Nb−N [Å]	Ref.
(*S*) [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}Cl] (**58**)	122.7	168.0(4)	1.790(5)	[57]
(*R*) [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}Cl] (**58**)	122.3	167.5(4)	1.782(5)	[57]
[Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3$*i*Pr)}Cl] (**59**)	122.1	172.3(2)	1.772(2)	[57]
[Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5H_4)_2$}Cl]	121.21	178.8(2)	1.756(3)	[58]
[Nb(=$NSiMe_3$){$Me_2C(\eta^5-C_5H_4)_2$}Cl]	114.2	167.71(7)	1.777(1)	[59]
[Nb(=N*t*Bu){$Me_2C(\eta^5-C_5H_4)_2$}Cl]	113.3	178.4(3)	1.762(3)	[59]
[Nb(=N*t*Bu){$Me_2C(\eta^5-C_5H_4)_2$}Br]	113.4	178.3(2)	1.765(2)	[59]
[Nb(=N*t*Bu){$Me_2C(\eta^5-C_5H_4)_2$}I]	114.2	171.8(2)	1.770(2)	[59]
[Nb(=NAr){$Me_2C(\eta^5-C_5H_4)_2$}Cl][a]	114.4	167.5(1)	1.798(2)	[60]
[Nb(=NAr){$Me_2C(\eta^5-C_5H_4)_2$}(NMe_2)][$B(C_6H_5)_4$][a]	114.0	166.8(1)	1.803(2)	[60]
[Nb(=N*t*Bu)($\eta^5-C_5H_5)_2$Cl][b]	122.7	173.6(4)	1.789(4)	[30]
	124.0	179.4(5)	1.737(6)	
[Nb(=$NC_6H_5)(\eta^5-C_5H_4SiMe_3)_2$NbCl] (**9**)	124.9	165.1(2)	1.792(2)	[37]
[Nb(=NC_6H_4OMe-4)($\eta^5-C_5H_4SiMe_3)_2$Cl] (**13**)	125.23	163.0(2)	1.787(3)	[31]
[Nb(=NPh)Cp'_2(C≡CPh)]] (**37**)	128.2	167.9(6)	1.804(5)	[55]
[{$NbCp'_2Cl$}$_2$(μ-1,3-$N_2C_6H_4$)] (**61**)	124.5	167.4(14)	1.754(20)	[53]
	125.6	168.4(15)	1.763(18)	

[a] Two independent molecules exist in the unit cell.

(imido)niobocene complexes containing alkyl ligands: [Nb(=N*t*Bu)Cp_2R] [R = Et (**16**), CH_2SiMe_3 (**17**)],[39] [Nb(=NC_6H_4Me-4)Cp_2R] [R = Me (**18**), Et (**19**), CH_2Ph (**20**) CH_2SiMe_3 (**21**)][39] and [Nb(=NPh)Cp'_2R] [R = Me (**22**), Et (**23**), *i*Pr (**24**)].[53] The synthetic pathway to these complexes is determined by the reaction of the appropriate magnesium reagent MgRCl with the corresponding metallocene complex [Equation (8)].



(8)

R = Et, R' = *t*Bu, R" = H (**16**);
R = CH_2SiMe_3, R' = *t*Bu, R" = H (**17**);
R = Me, R' = C_6H_4Me-4, R" = H (**18**);
R = Et, R' = C_6H_4Me-4, R" = H (**19**);
R = CH_2Ph, R' = C_6H_4Me-4, R" = H (**20**);
R = CH_2SiMe_3, R' = C_6H_4Me-4, R" = H (**21**);
R = Me, R' = Ph, R" = $SiMe_3$ (**22**);
R = Et, R' = Ph, R" = $SiMe_3$ (**23**);
R = *i*Pr, R' = Ph, R" = $SiMe_3$ (**24**).

In the ^1H NMR spectra of the ethyl complexes **16** and **19** (Figure 6) the ethyl group displays an A_3BC pattern with typical values of J_{AB} = 7.0, J_{AC} = 7.5, J_{BC} = 14.0 Hz, similar to those reported previously in two ethyl complexes of niobium.[61,62] This observation indicates the inequivalency of the methylene protons due to either H-bonding interactions C−H···N between the alkyl and imido groups, which restrict rotation about the Nb−C bond or the presence of an unusually weak agostic interaction between an α-hydrogen atom of the ethyl group and the metal centre. The latter explication is favoured because in complexes that do not contain electronegative ligands, e.g. [$NbCp_2$(Et)(RC≡CR)], the same phenomena of possible agostic interactions is observed in the NMR spectra.[62]

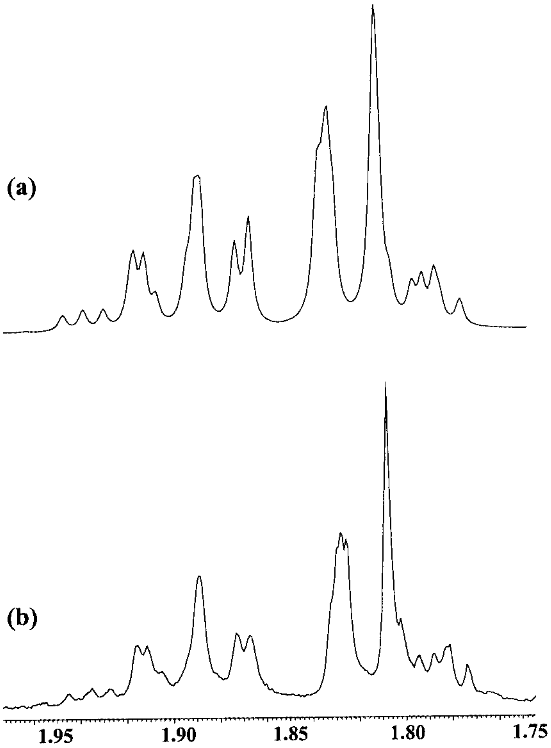
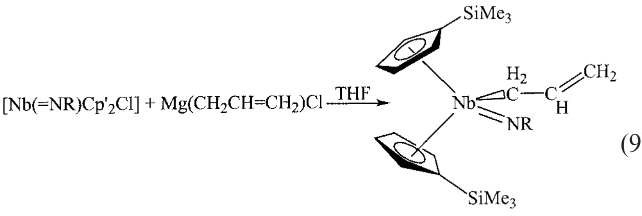


Figure 6. ^1H NMR spectra of [Nb(=NC_6H_4Me-4)Cp_2Et] (**19**) in the ethyl region: (a) simulated; (b) experimental

2.3.4 Allyl Derivatives

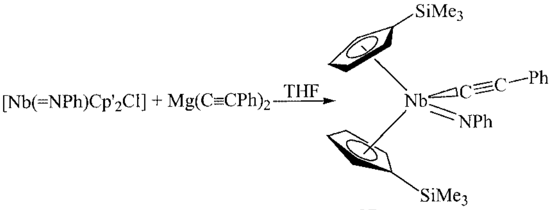
In a similar manner the η^1-allyl(imido)niobocene complexes, [Nb(=NC_6H_4Me-4)$Cp_2(\eta^1-CH_2CHCH_2)$] (**25**)[39] and [Nb(=NR)$Cp'_2(\eta^1-CH_2CHCH_2)$] [R = *t*Bu (**26**), C_6H_4Me-4 (**27**), C_6H_4OMe-4 (**28**)][31] have been synthesized [Equation (9)]. The ^1H NMR spectra for the η^1-allyl complexes were similar to that recorded for **7**. Couplings constants are given in Table 1.



(9)

R = *t*Bu (**26**), C_6H_4Me-4 (**27**), C_6H_4OMe-4 (**28**)

Recently, we reported the preparation of first alkynyl-containing niobocene complexes[63] and by a natural extension of this work the alkynyl(imido)niobium complexes [Nb(=N*t*Bu)(η^5-C_5H_5)$_2$(C≡CR)] [R = Me (**29**), $SiMe_3$ (**30**), *t*Bu (**31**), CH_2Ph (**32**)], [Nb(=NC_6H_4Me-4)(η^5-C_5H_5)$_2$(C≡CR)] [R = $SiMe_3$ (**33**), *t*Bu (**34**)], [Nb(=N*t*Bu)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] [R = $SiMe_3$ (**35**), *t*Bu (**36**)], [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] (R = Ph (**37**), *t*Bu (**38**)], [Nb(=NC_6H_4Me-4)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] [R = $SiMe_3$ (**39**), *t*Bu (**40**)], [Nb(=NC_6H_4OMe-4)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] [R = $SiMe_3$ (**41**), *t*Bu (**42**)], were synthesized.[55] The general synthetic method involved the reaction of dialkynylmagnesium reagents and the corresponding (imido)niobocene halide derivative. An example is given in Equation (10).



(10)

37

The molecular structure of **37**, determined by single-crystal X-ray diffraction studies is depicted in Figure 7. Complex **37** presents a typical bent-metallocene structure with two additional ligands. Both cyclopentadienyl rings are η^5-bonded to the metal atom with a Cent−Nb−Cent angle of 128.2°. The alkynyl ligand is σ-bonded to the metal atom as indicated by the C(1)−C(2) distance of 1.20(1) Å which is typical for a C−C triple bond and the Nb−C(1)−C(2) angle of 177.9(6)° whose linear nature confirms that the C(1) and C(2) atoms are sp-hybridized. The Nb−N bond length of 1.804(5) Å, is at the upper limit for those observed for (imido)niobium complexes (1.73−1.80 Å) (see Table 4) and is indicative of an Nb−N triple bond. As in complexes **9** and **13**, the formal electron count is 20.

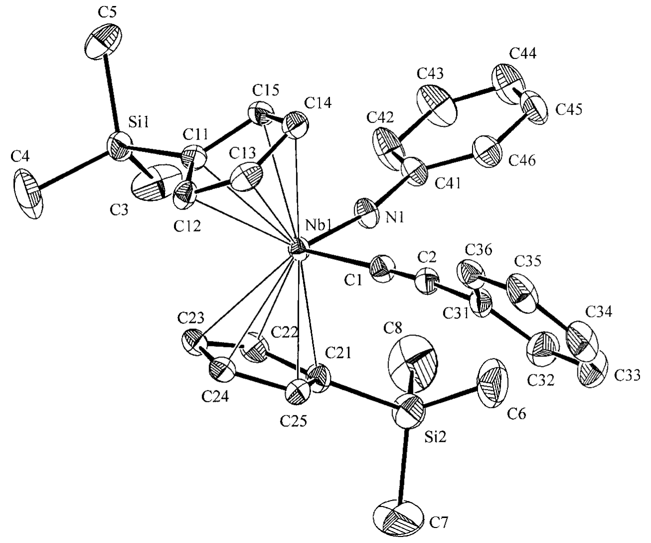
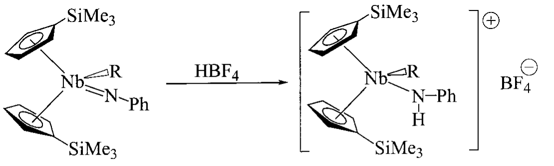


Figure 7. Molecular structure of [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$-(C≡CPh)] (**37**)

2.3.5 Reactivity

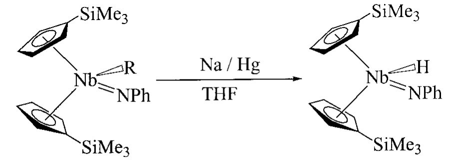
The cationic niobium species, [Nb(NHPh)Cp'_2R]$^+$ (R = Cl (**43**), Me (**44**), Et (**45**), *i*Pr (**46**)], were obtained by the reaction of the neutral (imido)niobocene complexes **9** and **22−24** with HBF_4.[53] Protonation took place at the nitrogen atom to give the corresponding amido derivative [Equation (11)].



(11)

R = Cl (**43**), Me (**44**), Et (**45**), *i*Pr (**46**)

The hydride complex [Nb(=NPh)Cp'_2H] (**47**)[53] was prepared by initially reducing the (imido)niobocene(V) complexes **9** and **22−24** and their subsequent oxidation by hydrogen abstraction from the solvent to give the corresponding niobium(V) hydride derivative [Equation (12)].

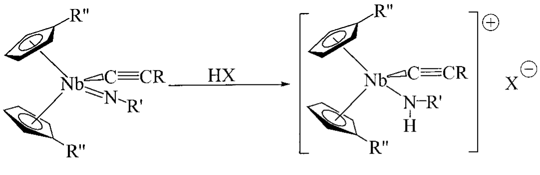


(12)

R = Cl, Me, Et, *i*Pr

47

The reactivity of the alkynyl(imido) complexes **30** and **37** with the protic reagents CF_3COOH and HBF_4 was studied.[55] Protonation of these complexes may occur at the alkynyl and/or the imido moiety as observed previously in niobocene complexes containing only one of these ligands.[53,63] In the reactions of **30** and **37** with CF_3COOH and HBF_4, respectively, the protonated compounds were isolated [Equation (13)]. It was found that in these alkynyl-(imido) complexes protonation takes place preferentially at the nitrogen atom of the imido group leading to the formation of the cationic amide species [Nb(NH*t*Bu)(η^5-C_5H_5)$_2$(C≡$CSiMe_3$)]$^+$ (**48**) and [Nb(NHPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)]$^+$ (**49**).[55]

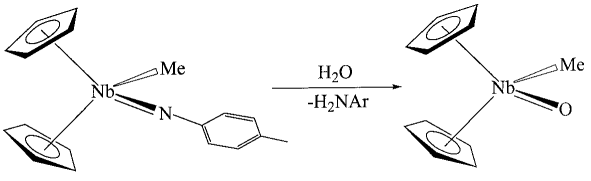


(13)

R = $SiMe_3$, R' = *t*Bu, R" = H, X = CF_3COO (**48**);
R = Ph, R' = Ph, R" = $SiMe_3$, X = BF_4 (**49**).

The normally greater Brønsted basicity of the imido ligand relative to the alkynyl ligand may explain the selective nature of the protonation reaction of these alkynyl(imido)niobocene complexes.

It was found that when [Nb(=NC$_6$H$_4$Me-4)Cp$_2$Me] (**18**) was treated with H$_2$O, the reaction took place at the Nb−N and not the Nb−C bond of the alkyl group. The alkyl(oxo) complex [Nb(=O)Cp$_2$Me] (**50**) was isolated by recrystallization from a hexane solution.[39] The amine H$_2$NC$_6$H$_4$Me-4 was identified by ^{1}H NMR spectroscopy to be the by-product of this reaction [Equation (14)].



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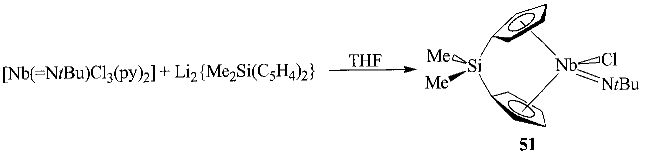
(14)

2.4 *ansa*-(Imido)niobocene Complexes

In 1996 we reported the first *ansa*-niobocene complexes in which both cyclopentadienyl rings are bound only in an η^5-mode to the niobium atom[64] and following from this work we prepared the *ansa*-(imido)niobocene complex [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] (**51**) [Equation (15)].[58] The ^{1}H NMR spectrum reveals the presence of a system similar to that obtained for its non-*ansa* analogues. The C_s symmetry of the molecule is such that there is only one plane of symmetry and the two methyl groups of SiMe$_2$ become inequivalent, as do the cyclopentadienyl protons, thus giving two singlets for the former and four multiplets for the latter. The molecular structure of **51**, determined by single-crystal X-ray diffraction studies, is depicted in Figure 8. The following *ansa*-(imido)niobocene complexes have also been reported by other authors: [Nb(=NR){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Cl] (R = *t*Bu, SiMe$_3$),[59] [Nb(=NC$_6$H$_3$*i*Pr$_2$-2,6){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Cl].[60]



51

(15)

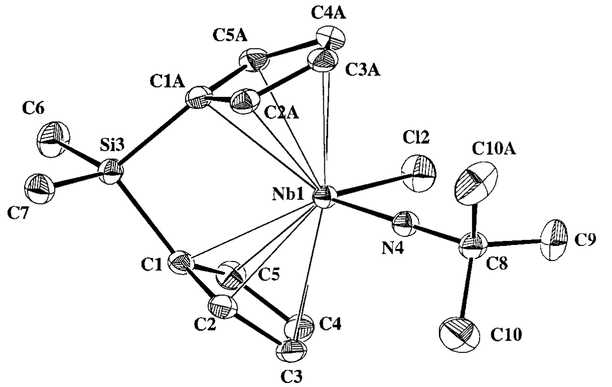


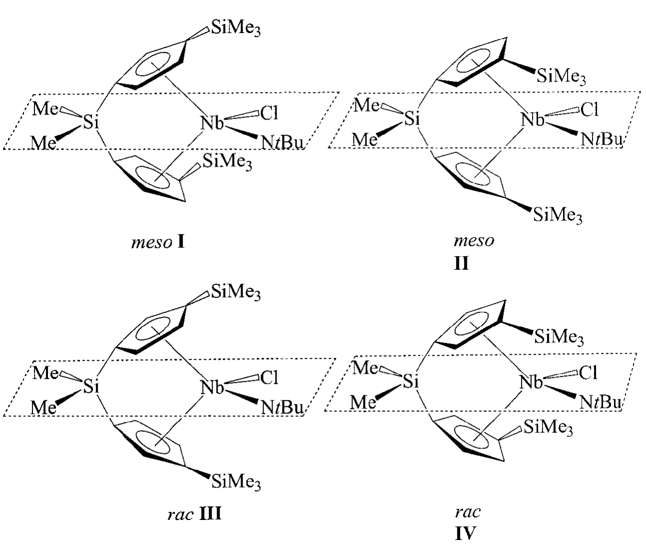
Figure 8. Molecular structure of [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] (**51**)

2.4.1 Alkyl, Allyl and Alkynyl Derivatives

The alkyl derivatives [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}R] [R = Me (**52**), Et (**53**), CH$_2$Ph (**54**)] were synthesized from **51** and the corresponding Grignard reagent.[58] The allyl and alkynyl products [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}(η^1-CH$_2$CHCH$_2$)] (**55**)[58] and [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}(C≡CR)] [R = SiMe$_3$ (**56**), *t*Bu (**57**)][55] were prepared in a similar manner. The ^{1}H NMR spectrum of the ethyl complex **53** showed the same characteristics as those observed for **16** and **19**. The η^1-allyl complex **55** was identical in nature to those already discussed.

2.4.2 Substituted ansa-(Imido)niobocene Complexes

We prepared the first niobocene complex containing a substituted *ansa* ligand [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$}Cl] (**56**) [Equation (16)].[58] The synthesis of substituted *ansa*-ligand complexes of niobium can lead to a variety of isomers (Figure 9) depending on the configuration of the cyclopentadienyl rings. These include two *meso*-(*R*,*S*) forms **I** and **II** and the enantiomers *rac*-(*R*,*R*) (**III**) and *rac*-(*S*,*S*) (**IV**). For this complex ^{1}H NMR spectroscopy will show clearly the existence of the *meso* and *rac* isomers. Complex **56** was isolated uniquely as the *meso* isomer as was revealed by ^{1}H NMR spectroscopy. The *meso* isomer contains a plane of symmetry (C_s), which makes the cyclopentadienyl rings of the *ansa* ligand equivalent, and hence only three signals for the ring protons are observed in its ^{1}H NMR spectrum, which in addition gave the expected signals for the *t*Bu and the SiMe$_3$ groups and two for SiMe$_2$. The cyclopentadienyl rings of the *ansa* ligand, however, will be inequivalent in the *rac* complex due to the lack of symmetry (C_1). In the case of **56**, the *rac* isomer is probably disfavoured due to steric effects and for this same reason in the *meso* complex the SiMe$_3$ groups should be pointing away from the bulky imido group.



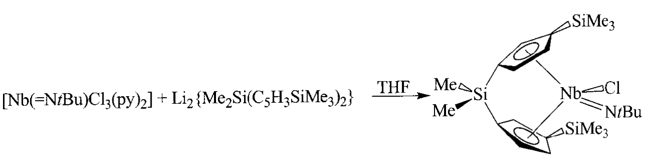
meso **I**

meso **II**

rac **III**

rac **IV**

Figure 9. Possible isomers for [Nb(=N*t*Bu){Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$}Cl] (**56**)

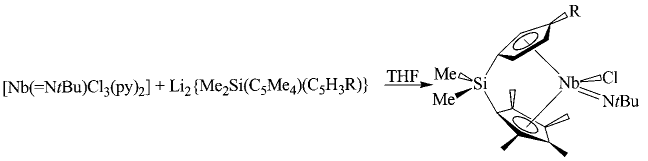


56

(16)

2.4.3 Asymmetric ansa-(Imido)niobocene Complexes

We have prepared the first (imido)niobocene complexes incorporating asymmetric *ansa* ligands. The complexes [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3R)$}Cl] [R = H (**57**), Me (**58**), *i*Pr (**59**), $SiMe_3$ (**60**)] were synthesized by the reaction of [Nb(=N*t*Bu)$Cl_3(py)_2$] with Li_2{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3R)$} [Equation (17)].[57]



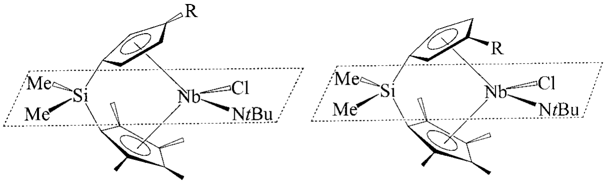
R = H (**57**); Me (**58**); *i*Pr (**59**); $SiMe_3$ (**60**)

(17)

2.4.4 Structural Characterization

The ^1H NMR spectrum of **57** shows the lack of symmetry in this chiral complex, with the four methyl groups attached to the cyclopentadienyl ring being inequivalent as are the methyl groups of the $SiMe_2$ bridge and the four protons of the unsubstituted cyclopentadienyl moiety.

In the case of complexes **58**−**60** the monosubstitution of one of the cyclopentadienyl rings of the *ansa* ligands gives rise to the possibility of two different isomers (**I**) and (**II**) (Figure 10) depending on the configuration of the cyclopentadienyl rings in which the substituent R can be orientated towards or away from the imido group. The niobium atom is chiral and thus in both cases **I** and **II** should exist as pairs of enantiomers.



I

II

Figure 10. Possible isomers for complexes [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3R)$}Cl] [R = Me (**58**), *i*Pr (**59**), $SiMe_3$ (**60**)]

The ^1H spectra of **58**−**60** are similar to that observed in **57** and in addition show the existence exclusively of only one of the possible isomers. It is assumed that this corresponds to isomer **I**, i.e., that the substituent R is pointing away from the bulky imido group. The isomer **II** is probably heavily disfavoured due to steric effects.

The molecular structures of **58** and **59** were established by X-ray crystal structure studies; they are shown in Figures 11 and 12, respectively.[57]

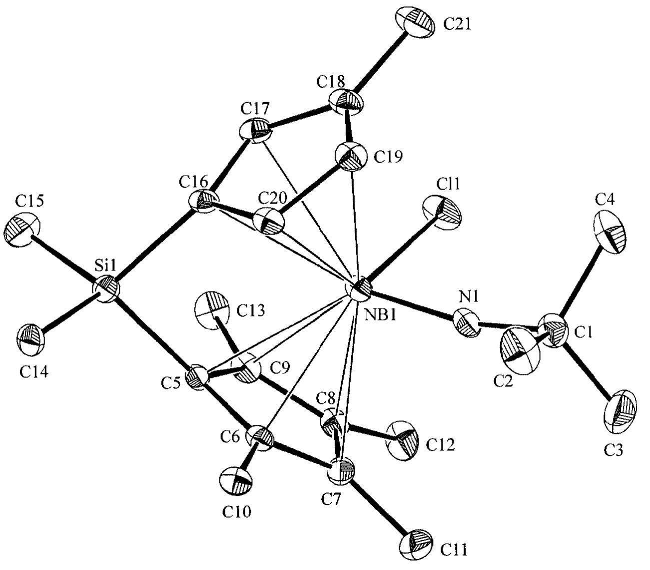


Figure 11. Molecular structure of [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}Cl] (**58**)

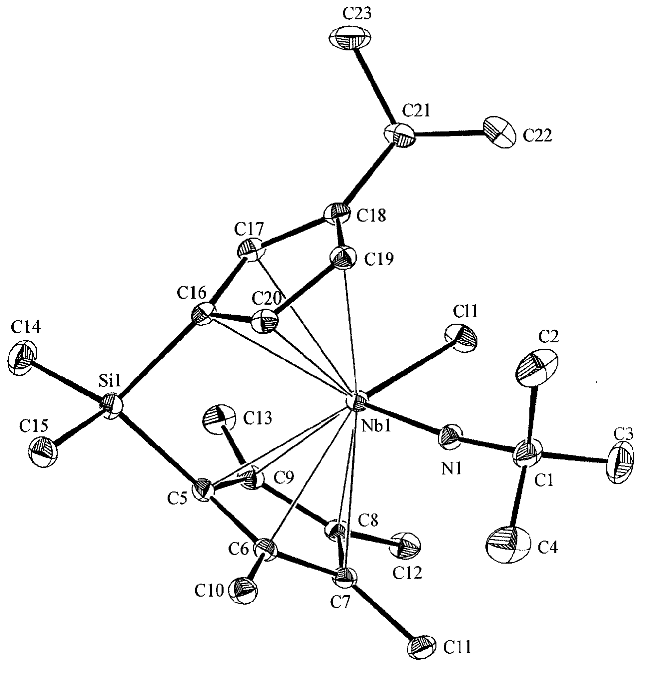
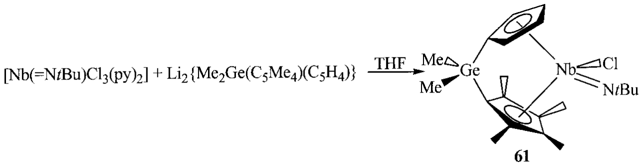


Figure 12. Molecular structure of [Nb(=N*t*Bu){$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3iPr)$}Cl] (**59**)

The niobium atoms in both **58** and **59** show a geometry that is typical for pseudo-tetrahedral (imido)niobocene(V) derivatives. The $Me_2Si(C_5Me_4)(C_5H_3R)$ *ansa* ligand chelates the niobium centre, and both cyclopentadienyl rings are bound to the metal atom in an η^5-mode adopting the typical bent-metallocene conformation. The environment of the niobium atom is completed by a chlorine atom and the imido group bonded through the nitrogen atom to the niobium atom. The structure also reveals that the alkyl group in the monosubstituted C_5 ring is oriented away from the imido group. The Cent−Nb−Cent angles (122.7 and 122.3° in **58**; 122.1° in **59**) are similar to those reported for other *ansa*-niobocene complexes containing the $SiMe_2$-bridged *ansa* ligand (see Table 2). The formal electron count for **58** and **59** is 20.

2.4.5 Asymmetric Complexes with Germanium-Bridged ansa Ligands

The reaction of $Li_2\{Me_2Ge(C_5Me_4)(C_5H_4)\}$ with $[Nb(=N\mathit{t}Bu)Cl_3(py)_2]$ gave the niobium derivative $[Nb(=N\mathit{t}Bu)\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]$ (**61**) [Equation (18)].[65] This is the first example of a niobocene complex incorporating a germanium-bridged *ansa* ligand.



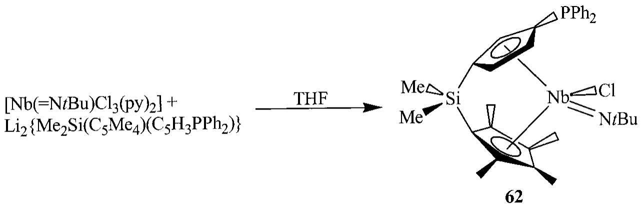
61

(18)

2.5 (Imido)niobocene Complexes with Phosphane-Substituted Cyclopentadienyl Ligands

The use of phosphane-substituted cyclopentadienyl ligands in the chemistry of group 5 elements has been restricted to one reference concerning the tantalum complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_4PPh_2)Cl_2]$ and its reactivity.[66] To the best of our knowledge there have been no reports of this type of compounds in the chemistry of niobium.

By the reaction of the lithium derivative $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ with $[Nb(=N\mathit{t}Bu)Cl_3(py)_2]$ we have prepared the *ansa*-phosphane(imido)niobocene complex $[Nb(=N\mathit{t}Bu)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl]$ (**62**) [Equation (19)].[67] The complex $[Nb(=N\mathit{t}Bu)(\eta^5\text{-}C_5H_4PPh_2)_2Cl]$ (**63**), was prepared in a similar way by reaction of 2 equiv. of $Li(C_5H_4PPh_2)$ with $[Nb(=N\mathit{t}Bu)Cl_3(py)_2]$.[67]



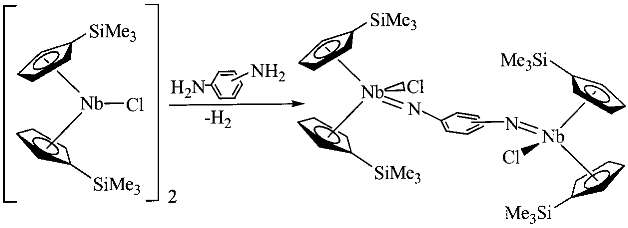
62

(19)

2.6 Dinuclear (Imido)niobocene Complexes

2.6.1 Synthesis

The [bis(imido)]diniobocene complexes were prepared in a similar manner to their mononuclear analogues. Thus, the complexes $[\{NbCp'_2Cl\}_2(\mu\text{-}1,3\text{-}N_2C_6H_4)]$ (**64**) and $[\{NbCp'_2Cl\}_2(\mu\text{-}1,4\text{-}N_2C_6H_4)]$ (**65**) were prepared by two distinct synthetic routes; firstly by oxidative addition of the bis(amine) and subsequent loss of H_2 [Equation (20)], alternatively by thermal treatment of $[\{NbCp'_2Cl\}_2(OCNC_6H_4NCO)]$ and elimination of CO [Equation (21)].[53]



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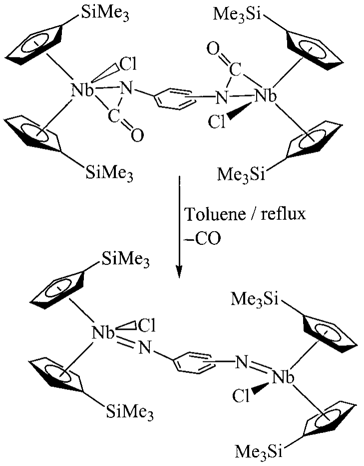


(21)

2.6.2 Characterization

Complexes **64** and **65** were characterized by ^1H NMR spectroscopy which revealed spectra similar to those obtained for other (imido)niobocene complexes. The molecular structure of **64**, determined by single-crystal X-ray diffraction studies, is illustrated in Figure 13.[53]

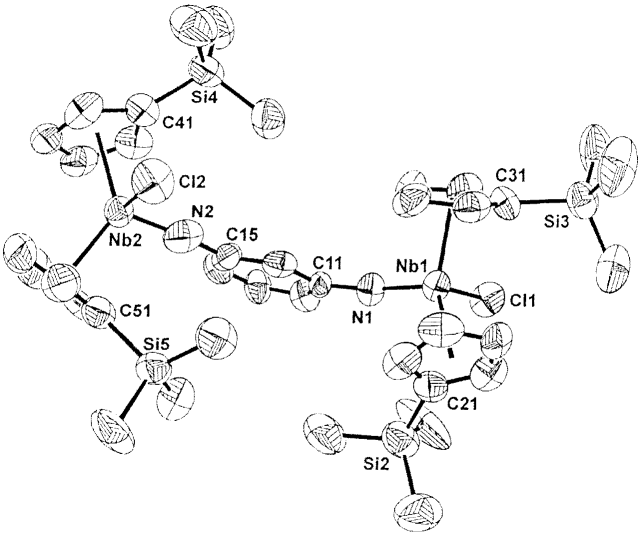


Figure 13. Molecular structure of $[\{NbCp'_2Cl\}_2(\mu\text{-}1,3\text{-}N_2C_6H_4)]$ (**64**)

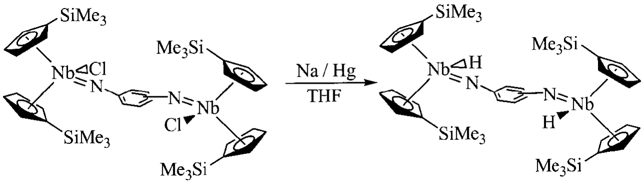
The complex shows two bent niobocene units linked to a phenylenebis(imido) ligand and is to date the only known example of this type reported in the chemistry of metallocene compounds. The formal electron count is 20 at both niobium centres and the structural parameters are similar to those previously discussed for other niobium complexes (see Table 4).[53]

2.6.3 Alkyl Derivatives

The alkyl derivatives [{NbCp′$_2$R}$_2$(μ-1,3-$N_2C_6H_4$)] [R = Me (**66**), Et (**67**), *i*Pr (**68**)] and [{NbCp′$_2$R}$_2$(μ-1,4-$N_2C_6H_4$)] [R = Me (**69**), Et (**70**), *i*Pr (**71**)] were prepared by the reaction of the chloro precursor with the corresponding Grignard reagent.[53]

2.6.4 Hydride Derivatives

The hydride derivatives [{NbCp′$_2$H}$_2$(μ-1,3-$N_2C_6H_4$)] (**72**) and [{NbCp′$_2$H}$_2$(μ-1,4-$N_2C_6H_4$)] (**73**) were prepared according to Equation (22).[53]



(22)

Conclusion

This review gives an insight into our work in the field of (imido)niobium complexes containing at least one cyclopentadienyl ligand. Amongst the compounds described are the first examples of: (a) symmetrically and asymmetrically substituted *ansa*-(imido)niobocene complexes, (b) germanium-bridged *ansa* ligands, (c) (imido)niobocene and *ansa*-(mido)niobocene complexes incorporating phosphane-substituted ligands. (d) [bis(imido)]diniobocene complexes.

The molecular structures for many of the niobocene complexes have been determined and show the linear or near linear nature of the imido group. This indicates that the imido group is acting as a four-electron donor. Thus, the formal electron count is 20 with surplus electrons probably being located in ligand-based orbitals. In addition we have observed in these compounds a lengthening of the niobium−cyclopentadienyl distance compared with their 18-electron analogues.

In symmetrically and asymmetrically substituted *ansa*-(imido)niobocene complexes we have observed that steric conditions are the governing factor in the final orientation of the ligands in the complexes.

Alkyl, allyl and alkynyl derivatives have been readily synthesized by reaction of the initial (imido)niobium chloride precursor with the corresponding magnesium reagent. It was found that protonation and hydrolysis take place preferentially at the imido group and not at the Nb−C σ-bond.

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