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Sandwich and half-sandwich niobium imido complexes: X-ray crystal structure of [Nb(=NAr)Cp'_2Cl] ($Cp' = \eta^5$-$C_5H_4SiMe_3$, Ar = C_6H_4OMe-4)

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Abstract

The imido niobium complexes [Nb(=NAr)Cl_3(dme)] (Ar = C_6H_4Me-4 (**1**), C_6H_4OMe-4 (**2**)) have been prepared and characterised. The half-sandwich complex [Nb(=NBu^t)CpCl_2] (**3**) (Cp = η^5-C_5H_5) has been synthesised by a new method via the reaction of NaCp and [Nb(=NBu^t)Cl_3(py)$_2$] and in a similar manner the novel complex [Nb(=NC_6H_4Me-4)CpCl_2] (**4**) was prepared by the reaction of NaCp with **1**. The preparation of [Nb(=NBu^t)Cp′Cl_2] (**5**) ($Cp' = \eta^5$-$C_5H_4SiMe_3$) yielded an essentially inseparable mixture of **5** and [Nb(=NBu^t)Cp'_2Cl] (**6**). The imido niobocene(V) complex **6** was prepared and isolated as the unique product by a new synthetic pathway via the reaction of two equivalents of LiCp′ and [Nb(=NBu^t)Cl_3(py)$_2$] and in a similar manner the novel complexes [Nb(=NAr)Cp'_2Cl] (Ar = C_6H_4Me-4 (**7**), C_6H_4OMe-4 (**8**)) were prepared. The molecular structure of **8** has been determined by X-ray diffraction studies. The mixed metallocene complex [Nb(=NBu^t)CpCp′Cl] (**9**) was prepared by the reaction of Li($C_5H_4SiMe_3$) and **3**. The alkylation of **6**–**8** by $ClMgCH_2CH$=CH_2 yielded the η^1-allyl complexes [Nb(=NR)Cp'_2(CH_2CH=CH_2)] (R = Bu^t (**10**), C_6H_4Me-4 (**11**), C_6H_4OMe-4 (**12**)).

Keywords: Niobium; Imido; Allyl; Niobocene; Half-sandwich

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1. Introduction

Half-sandwich complexes are well known in niobium imido chemistry [1]. The principle synthetic route is the reaction of [Nb(η^5-C_5R_5)Cl_4] with the appropriate amine, H_2NR', or NR′($SiMe_3$)$_2$ to yield [Nb(=NR′)(η^5-C_5R_5)Cl_2]. Bent imido metallocene complexes of niobium to date have not been widely studied and have generally been prepared by various methods. [Nb(=NPh)Cp'_2Cl] ($Cp' = \eta^5$-$C_5H_4SiMe_3$) was synthesised by either the reaction of [{Cp'_2NbCl}$_2$] with the amine or by heating a toluene solution of [NbCp'_2(PhNCO)Cl] [2]. [Nb(=NBu^t)Cp_2Cl] was prepared by the reaction of NaCp with the half-sandwich complex Nb(=NBu^t)CpCl_2 (Cp = η^5-C_5H_5) [3]. The hydrazido complexes [Nb(=$NNMe_2$)(η^5-C_5H_4R)$_2$Cl] (R = H, Me) were prepared in a similar manner from their half-sandwich analogue [4]. Mixed cyclopentadienyl (Cp) niobocene imide complexes have been reported in two cases, namely [Nb(=$NNMe_2$)Cp(η^5-C_5H_4Me)Cl] [4] and [Nb(=NBu^t)Cp(η^5-C_5Me_5)Cl] [3b]. *Ansa*-complexes of the type [Nb(=NR)Cp{(η^5-C_5H_4)CMe_2(η^1-C_5H_4)}] have also been reported [4,5]. This paper will focus on the synthesis and structural details of new families of half-sandwich and sandwich niobium imido complexes.

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2. Results and discussion

The preparation of the niobium imido complexes [Nb(=NAr)Cl_3(dme)] (Ar = C_6H_4Me-4 (**1**), C_6H_4OMe-4 (**2**)) was carried out by a modification of the method reported for the synthesis of other niobium and tantalum halide imido compounds [6]. In this reaction (Eq. (1)) the pyridine acts as a base, dme as a donating ligand and $ZnCl_2$ abstracting halide and forming an insoluble salt, in CH_2Cl_2, with HPy^+ thus facilitating its removal. The complexes **1** and **2** were isolated as red air-sensitive solids and were characterised by spectroscopic methods. Their ^1H-NMR spectra showed clearly the inequivalence of the methyl and methylene groups of the dme adduct (see Section 3) 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* (Fig. 1). This has previously been observed in other complexes of this type [6,7].

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

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

The half-sandwich niobium imido complex [Nb(=NBu^t)CpCl_2] (**3**) was prepared by the reaction of [Nb(=NBu^t)$Cl_3$$(py)_2$] [8] and NaCp in THF (Eq. (2)) and isolated in yields of 80%. This complex was previously prepared by the addition of NH(Bu^t)($SiMe_3$) to [NbCpCl_4] and the subsequent elimination of $SiMe_3Cl$ and HCl [1a]. The reaction depicted in Eq. (2) offers an alternative and more facile route to **3** as both starting components, NaCp and [Nb(=NBu^t)$Cl_3$$(py)_2$], are easily prepared.

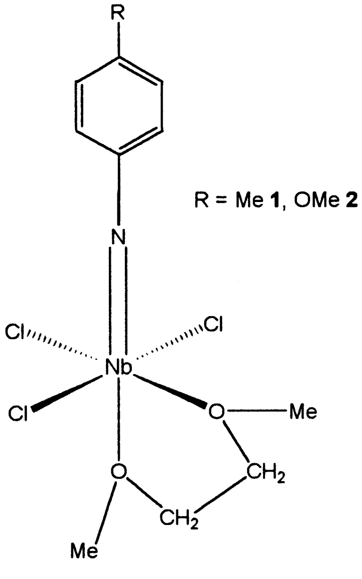
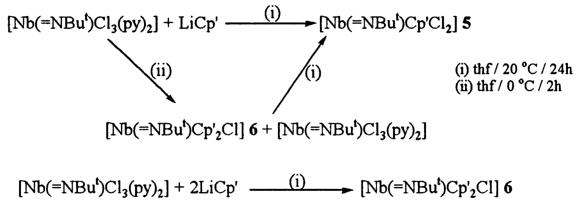
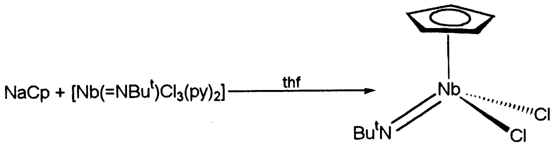


Fig. 1. Proposed structure of [Nb(=NAr)Cl_3(dme)] (Ar = C_6H_4Me-4 (**1**), C_6H_4OMe-4 (**2**)).

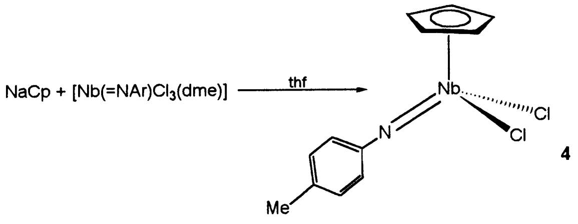


Scheme 1.



(2)

Using this same method the half-sandwich imido complex [Nb(=NC_6H_4Me-4)CpCl_2] (**4**) was prepared (Eq. (3)). Complex **4** was characterised by spectroscopic methods. In the ^1H spectrum of **4** two singlets at 2.12 and 5.75 ppm corresponding to the methyl protons of *p*-tolyl and the Cp protons, respectively and two doublets at 6.46 and 6.88 ppm associated with the phenylic protons of the *p*-tolyl group were observed. The integrals of these signals are in agreement with the monosubstitution of the Cp ligand (see Section 3).



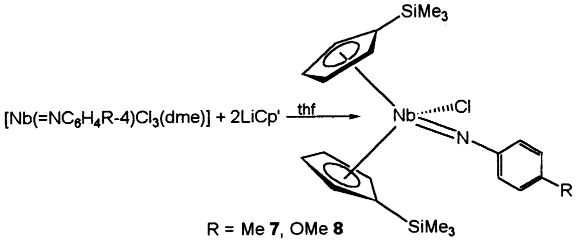
(3)

In order to prepare the half-sandwich complex [Nb(=NBu^t)Cp′Cl_2] (**5**) using the trimethylsilyl substituted Cp ligand, the reaction of one equivalent of LiCp′ with [Nb(=NBu^t)$Cl_3$$(py)_2$] was carried out. When this reaction mixture in THF was stirred at room temperature (r.t.) for 24 h, a yellow oil was isolated which, by ^1H-NMR spectroscopy, was shown to be a mixture, in proportion ca. 1:1, of **5** and the disubstituted analogue [Nb(=NBu^t)Cp'_2Cl] (**6**). The reaction was repeated at low temperature and only stirred for 2 h. After appropriate work up the only product isolated was that of **6**. With this observation we propose that the reaction initially commences with the rapid formation of the bis-Cp complex **6**. This is then followed by the slow reaction of **6** with [Nb(=NBu^t)$Cl_3$$(py)_2$], which yields the half-sandwich complex **5**. The direct reaction of **6** with [Nb(=NBu^t)$Cl_3$$(py)_2$], stirred in THF for 24 h at r.t. yielded **5** and endorses the proposed mechanism (Scheme 1).

Complex **5** was characterised by spectroscopic methods. ^1H-NMR spectroscopy showed that only one Cp′

ligand was incorporated in **5** and this was confirmed by the AA′BB′ system observed for the Cp′ ring protons, two multiplets at 6.11 and 6.35 ppm. The symmetry of **5** means that for the Cp′ ring protons that H2 and H5, and H3 and H4 become equivalent. In the case of the bis-Cp′ complex **6** an ABCD system is observed due to the inequivalency of the Cp′ ring protons although a plane of symmetry makes the two Cp′ rings equivalent, thus giving four multiplets for the eight ring protons.

Complex **6** can be synthesised directly by the reaction of two equivalents of LiCp′ with $[Nb(=NBu^t)Cl_3(py)_2]$ in yields of ca. 80%. ^{1}H-NMR spectroscopy shows **6** to be the unique product isolated after work up. This compound was previously prepared by either the reaction of $[\{NbCp'_2Cl\}_2]$ with the amine or by heating a toluene solution of $[NbCp'_2(Bu^tNCO)Cl]$ [2]. The niobocene(V) imido complexes $[Nb(=NAr)Cp'_2Cl]$ (Ar = C_6H_4Me-4 (**7**), C_6H_4OMe-4 (**8**)) were synthesised in a similar manner (Eq. (4)) and characterised by spectroscopic methods. Their ^{1}H-NMR spectra showed them to be unique complexes and were similar to the spectrum recorded for **6**, namely four multiplets for the Cp′ ring protons and a singlet corresponding to the $SiMe_3$ groups. In addition the expected signals for the aryl-imido group were observed.



(4)

The molecular structure of **8** was established by X-ray crystal studies. The molecular structure and atomic numbering scheme are shown in Fig. 2. Selected bond lengths and angles are given in Table 1.

Suitable X-ray-quality crystals of **8** were obtained by the slow evaporation of a toluene solution. The compound crystallises in the $P2_1/n$ space group, monoclinic and with four molecules in the unit cell. The structure consists of a typical bent metallocene with distances between the metal atom and the centroids of the Cp rings of 2.189(1) and 2.1880(5) Å and the angle Cent(1)–Nb(1)–Cent(2) 125.23(2)°. The orientation of the Cp rings is between eclipsed and staggered as indicated by the value of the torsion angle Si(3)–Cent(1)–Cent(2)–Si(4) of 24°.

The imide ligand is able to act as either a two or four electron donor. In the first case the nitrogen atom would be sp^2-hybridised and therefore results in the bending back of the imide substituent. In the second case the nitrogen would be sp-hybridised and the metal–nitrogen-substituent angle linear. In the structures previously reported for niobocene imido complexes, linear Nb–N–C_{ipso} geometries are observed (see Table 2). However, in **8**, the angle Nb(1)–N(1)–C(1), 163.0(2)° deviates from linear. The bent arrangement could indicate that the imido nitrogen is sp^2-hybridised, but in such a case the anisole substituent would be orientated out of the equatorial plane towards one of the Cp ligands [9]. However, the phenyl substituent of the imido group is situated practically in the equatorial plane. The phenyl plane forms an angle of 175.81(9)° with the equatorial plane defined by the atoms Cl(2)–Nb(1)–N(1) similar to that observed in $[Nb(=NPh)Cp'_2Cl]$ [2] and $[Ta(=NPh)(\eta^5\text{-}C_5Me_5)_2H]$ [9]. Deviation from linear of the Nb–N–C_{ipso} angles has been reported for some niobocene imido complexes and is normally in the range of 12–15° (see Table 2). These complexes in general contain aryl-imido and/or sterically demanding ligands. In the case of $[Nb(=NPh)Cp'_2Cl]$ extended-Hückel MO calculations established that the imido bond angles for 'linear imide' in this class of complexes can vary until 140° with little effect on the Nb–N bonding [2]. Therefore we propose that in **8** the nitrogen atom is sp-hybridised and that the two limiting descriptions proposed by Bercaw and coworkers [9a], for $[Ta(=NPh)(\eta^5\text{-}C_5Me_5)_2H]$ may explain the true bonding situation.

The Nb(1)–N(1) bond distance of 1.787(3) Å is at the upper limit for those observed for niobium imido complexes (1.73–1.80 Å) (see Table 2) and is indicative of a Nb–N triple bond. The formal electron count is 20

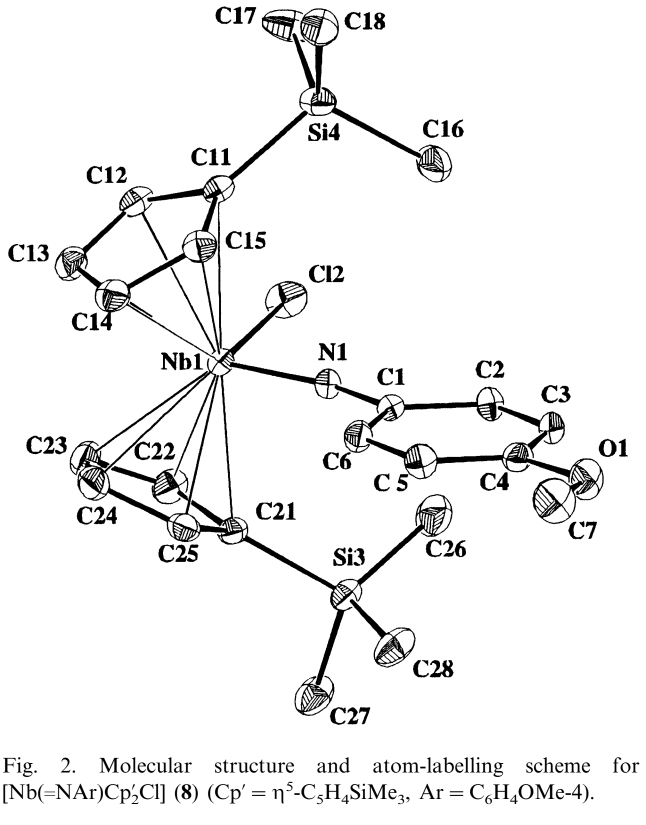


Fig. 2. Molecular structure and atom-labelling scheme for $[Nb(=NAr)Cp'_2Cl]$ (**8**) (Cp′ = $\eta^5\text{-}C_5H_4SiMe_3$, Ar = C_6H_4OMe-4).

Table 1
Selected bond lengths (Å) and angles (°) for complex **8** [a]

Nb(1)–N(1)	1.787(3)	Nb(1)–C(21)	2.486(3)
Nb(1)–Cl(2)	2.457(3)	Nb(1)–C(22)	2.527(4)
Nb(1)–Cent(1)	2.189(1)	Nb(1)–C(23)	2.553(4)
Nb(1)–Cent(2)	2.188(1)	Nb(1)–C(24)	2.480(4)
Nb(1)–C(11)	2.506(3)	Nb(1)–C(25)	2.429(4)
Nb(1)–C(12)	2.539(4)	N (1)–C(1)	1.379(4)
Nb(1)–C(13)	2.544(4)	C(4)–O(1)	1.370(4)
Nb(1)–C(14)	2.429(4)	C(7)–O(1)	1.423(6)
Nb(1)–C(15)	2.458(4)		
Cent(1)–Nb(1)–Cent(2)	125.23(2)	Cent(2)–C(21)–Si(3)	173.1(3)
Cent(1)–Nb(1)–Cl(2)	104.26(4)	Nb(1)–N(1)–C(1)	163.0(2)
Cent(1)–Nb(1)–N(1)	108.67(9)	C(4)–O(1)–C(7)	117.7(3)
Cent(2)–Nb(1)–Cl(2)	105.36(4)	C(5)–C(4)–O(1)	124.8(3)
Cent(2)–Nb(1)–N(1)	109.56(9)	C(3)–C(4)–O(1)	116.0(3)
N(1)–Nb(1)–Cl(2)	100.82(10)	N(1)–C(1)–C(2)	121.7(3)
Cent(1)–C(11)–Si(4)	173.0(3)	N(1)–C(1)–C(6)	120.5(3)

[a] Cent(1) and Cent(2) are the centroids of the Cp rings C(11)–C(15) and C(21)–C(25), respectively.

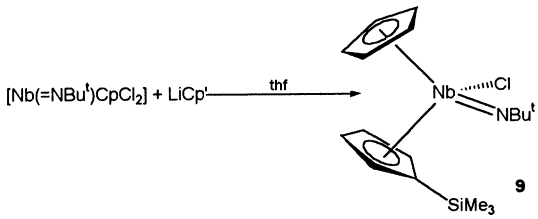
Table 3
Comparison of Nb–Cent distances in selected Cp′-containing niobocene complexes

Compound	Average Nb–Cent [a] (Å)	Ref.
[Nb(=NC$_6$H$_4$OMe-4)Cp$'_2$Cl] (**8**)	2.189	This work
[Nb(=NPh)Cp$'_2$Cl]	2.180	[2]
[{NbCp$'_2$Cl}$_2$(μ-1,3-N$_2$C$_6$H$_4$)]	2.188	[14]
[Nb(=O)Cp$'_2$Me]	2.181	[17]
[NbCp$'_2$Cl(η^2-*N*,*C*-OCNPh)]	2.121	[14]
[{NbCp$'_2$Cl}$_2$]	2.07	[2]
[NbCp$'_2$Cl$_2$]	2.079	[17,18]
[NbCp$'_2$(C$_6$F$_5$)(CO)]	2.04	[17]

[a] Cent, the centroid of the C$_5$ ring.

electrons and this fact may have an effect in the lengthening of the Nb–Cent distances of these formally ‘20-electron’ complexes in comparison to their 18- and 17-electron analogues (see Table 3). Indeed such lengthening has also been observed in metallocene imidos of titanium [10] and molybdenum [11]. The bonding in the ‘19-electron’ vanadium complex [V(=NC$_6$H$_3$Me$_2$-2,6)(η^5-C$_5$Me$_5$)$_2$] has previously been studied by MO 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 [12]. Similar calculations have been carried out for ’20-electron’ osmium complexes [Os(NR)$_3$] [13].

The mixed sandwich complex [Nb(=NBu^t)CpCp′Cl] (**9**) was prepared by the addition of LiCp′ to a THF solution of **3** (Eq. (5)). The reaction always gave, regardless of the excess of LiCp′ used, an essentially inseparable mixture, which by NMR spectroscopy was shown to contain only **3** and the title complex. Complex **9** was characterised by ^{1}H- and ^{13}C-NMR spectroscopy. Four multiplets (5.75, 5.80, 6.18 and 6.23 ppm) and a singlet (0.28 ppm) pertaining to the Cp′ ligand and a singlet (5.88 ppm) corresponding to the Cp ligand were observed in the ^{1}H-NMR spectrum of **9**.



(5)

Table 2
Selected structural data of niobocene imido complexes

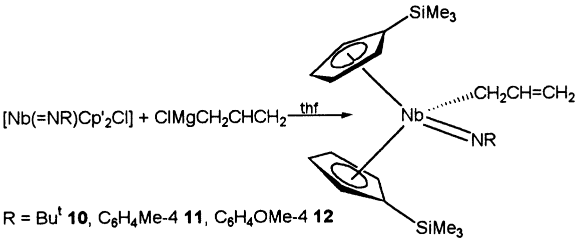
	Cent [c]–Nb–Cent (°)	Nb–N–C (°)	Nb–N (Å)	Ref.
[Nb(=NC$_6$H$_4$OMe-4)Cp$'_2$Cl] (**8**)	125.23	163.0(2)	1.787(3)	This work
[(Nb(=NPh)Cp$'_2$Cl]	124.9	165.1(2)	1.792(2)	[2]
[{NbCp$'_2$Cl}$_2$(μ-1,3-N$_2$C$_6$H$_4$)]	124.5, 125.6	167(2), 168(2)	1.75(2), 1.76(2)	[14]
[Nb(=NBu^t){(η^5-C$_5$H$_4$)$_2$(μ-SiMe$_2$)}Cl]	121.21	178.8(2)	1.756(3)	[15]
[Nb(=NSiMe$_3$){(η^5-C$_5$H$_4$)$_2$(μ-CMe$_2$)}Cl]	114.2	167.71(7)	1.777(1)	[16]
[Nb(=NBu^t){(η^5-C$_5$H$_4$)$_2$(μ-Cme$_2$)}Cl]	113.3	178.4(3)	1.762(3)	[16]
[Nb(=NBu^t){(η^5-C$_5$H$_4$)$_2$(μ-Cme$_2$)}Br]	113.4	178.3(2)	1.765(2)	[16]
[Nb(=NBu^t){(η^5-C$_5$H$_4$)$_2$(μ-Cme$_2$)}I]	114.2	171.8(2)	1.770(2)	[16]
[Nb(=NAr*){(η^5-C$_5$H$_4$)$_2$(μ-CMe$_2$)}Cl] [a]	Not reported	167.5(1)	1.798(2)	[5b]
[Nb(=NAr*){(η^5-C$_5$H$_4$)$_2$(μ-CMe$_2$)}(NMe$_2$){B(C$_6$H$_5$)$_4$}] [a]	Not reported	166.8(1)	1.803(2)	[5b]
[Nb(=NBu^t)Cp$_2$Cl] [b]	122.7, 124.0	173.6(4), 179.4(5)	1.789(4), 1.737(6)	[3a]

[a] Ar, C$_6$H$_3$Pr$^i_2$-2,6.

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

[c] Cent, the centroid of the C$_5$ ring.

Complexes **6**–**8** can be considered as 20-electron complexes and therefore it is not surprising that their reaction with the allyl Grignard reagent $ClMgCH_2CHCH_2$ yielded only the η^1-allyl complexes $[Nb(=NR)Cp'_2(CH_2CH=CH_2)]$ ($R = Bu^t$ (**10**), C_6H_4Me-4 (**11**), C_6H_4OMe-4 (**12**) (Eq. (6)). This phenomenon is clearly illustrated by ^1H-NMR spectroscopy in which the signals and couplings normally associated with an η^1-allyl system (e.g. $[Nb(=NBu^t)\{(\eta^5\text{-}C_5H_4)_2(\mu\text{-}SiMe_2)\}(\eta^1\text{-}CH_2CHCH_2)]$ [15], $[Nb(=O)Cp'_2(\eta^1\text{-}CH_2CHCH_2)]$ [19] and $[Nb(=NBu^t)Cp(\eta^1\text{-}CH_2CHCH_2)Cl]$ [19]) are observed (see Section 3), namely, three signals corresponding to the CH_2 bonded to the metal centre, the central group CH and the olefinic protons for the terminal CH_2. The various coupling constants are given in Table 4.



(6)

In conclusion, we have reported the synthesis and characterisation of various sandwich and half-sandwich niobium imido complexes and the reactivity of the former with the allyl Grignard reagent $ClMgCH_2CHCH_2$. The X-ray structure of $[Nb(=NC_6H_4OMe\text{-}4)Cp'_2Cl]$ (**8**) confirms that in this type of formally '20-electron' complexes that there is a lengthening of the Centroid–Nb distance in order to recover the more stable eighteen electron core.

3. Experimental

3.1. General procedures

All operations were performed under an inert atmosphere using standard vacuum-line (Schlenk) techniques or a Vac glovebox. Solvents were purified by distillation from appropriate drying agents and degassed before use. IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. $[Nb(=NBu^t)Cl_3(py)_2]$ was prepared as described earlier [8]. $NbCl_5$, $H_2N(C_6H_4Me\text{-}4)$, $H_2N(C_6H_4OMe\text{-}4)$ and THF solutions of $ClMgCH_2CHCH_2$ were purchased from Aldrich and used directly.

3.2. Synthesis of $[Nb(=NC_6H_4Me\text{-}4)Cl_3(dme)]$ (1)

To a mixture of $NbCl_5$ (3.68 g, 14.00 mmol) and $ZnCl_2$ (3.82 g, 28.00 mmol) in CH_2Cl_2 (150 ml) was added dme (2.5 ml). To this mixture, at −30°C, was then added a solution of $H_2NC_6H_4Me$-4 (1.33 g, 14.00 mmol) and pyridine (2.26 cm^3, 28.00 mmol) in CH_2Cl_2 (50 cm^3). This resultant mixture was allowed to stir at r.t. for 16 h. The suspension was allowed to decant and filtered. Solvent was removed, from the filtrate, under reduced pressure to yield a red solid of the title complex (5.15 g, 96%). Crystals were obtained by cooling (−30°C) a CH_2Cl_2/hexane solution of **1**. IR (Nujol mull): $\nu_{Nb=N}$ 1255 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 1.95 (s, 3H, NC_6H_4Me), 2.88 (2H), 2.93 (2H) (t, $CH_3OCH_2CH_2OCH_3$), 3.13 (3H), 3.42 (3H) (s, $CH_3OCH_2CH_2OCH_3$), 6.71 (2H), 7.34 (2H) (J 8.14 Hz) (d, NC_6H_4Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 300 MHz): δ 21.27 (NC_6H_4Me), 62.73, 68.54 ($CH_3OCH_2CH_2OCH_3$), 70.85, 75.34 ($CH_3OCH_2CH_2OCH_3$), 125.13, 125.82 (C_{ipso}), 128.88, 137.67 (C_{ipso}) (NC_6H_4Me). Anal. Calc. for $C_{11}H_{17}Cl_3NNbO_2$: C, 33.49; H, 4.34; N, 3.55. Found: C, 33.25; H, 4.12; N, 3.76%.

3.3. Synthesis of $[Nb(=NC_6H_4OMe\text{-}4)Cl_3(dme)]$ (2)

The synthesis of **2** was carried out in an identical manner to that of **1**. $NbCl_5$ (2.99 g, 11.07 mmol), $ZnCl_2$ (3.02 g, 22.14 mmol), dme (2.0 cm^3), $H_2NC_6H_4OMe$-4 (1.36 g, 11.07 mmol) and pyridine (1.79 ml, 22.14 mmol). Yield 4.16 g, 92%. IR (Nujol mull): $\nu_{Nb=N}$ 1235 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 3.08 (s, 3H, NC_6H_4OMe), 2.85 (2H), 2.90 (2H) (t, $CH_3OCH_2CH_2OCH_3$), 3.13 (3H), 3.41 (3H) (s, $CH_3OCH_2CH_2OCH_3$), 6.45 (2H), 7.37 (2H) (J 9.0 Hz) (d, NC_6H_4OMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 300 MHz): δ 55.52 (NC_6H_4OMe), 62.70, 68.40 ($CH_3OCH_2CH_2OCH_3$), 70.83, 75.29 ($CH_3OCH_2CH_2$-

Table 4
Coupling constants for the η^1-allyl complexes **10**–**12**

	$^3J(^1H–^1H)$ (Hz)	$^2J_{gem}(^1H–^1H)$ (Hz)	$^3J_{cis}(^1H–^1H)$ (Hz)	$^3J_{trans}(^1H–^1H)$ (Hz)
$[Nb(=NBu^t)Cp'_2(\eta^1\text{-}CH_2CHCH_2)]$ (**10**)	8.5	2.5	9.9	16.9
$[Nb(=NC_6H_4Me\text{-}4)Cp'_2(\eta^1\text{-}CH_2CHCH_2)]$ (**11**)	8.1	2.5	9.9	16.8
$[Nb(=NC_6H_4OMe\text{-}4)Cp'_2(\eta^1\text{-}CH_2CHCH_2)]$ (**12**)	8.3	2.4	10.0	16.8

OCH_3), 113.43, 119.48 (C_{ipso}), 126.97, 138.05 (C_{ipso}) (NC_6H_4OMe). Anal. Calc. for $C_{11}H_{17}Cl_3NNbO_3$: C, 32.18; H, 4.17; N, 3.41. Found: C, 32.04; H, 4.11; N, 3.58%

3.4. Synthesis of [Nb(=NBu^t)CpCl$_2$] (**3**)

To a solid mixture of NaCp (0.92 g, 10.50 mmol) and [Nb(=NBu^t)Cl$_3$(py)$_2$] (4.50 g, 10.50 mmol) was added THF (150 ml). The mixture was allowed to stir, at r.t. for 16 h. Solvent was removed under reduced pressure and the resulting residue extracted in hexane (3 × 150 ml). The removal of hexane, in vacuo, yielded a yellow crystalline solid of **3** (2.66 g, 84%).

3.5. Synthesis of [Nb(=NC$_6$H$_4$Me-4)CpCl$_2$] (**4**)

The synthesis of **4** was carried out in an identical manner to that of **3**. NaCp (0.67 g, 7.60 mmol) and **1** (3.00 g, 7.60 mmol). Yield 1.82 g, 72%. IR (Nujol mull): $\nu_{Nb=N}$ 1254 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 2.12 (s, 3H, NC_6H_4Me), 5.75 (s, 5H, C_5H_5), 6.46 (2H), 6.88 (2H) (J 8.1 Hz) (d, NC_6H_4Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 300 MHz): δ 25.36 (NC_6H_4Me), 115.47 (C_5H_5), 126.05, 129.38 (C_{ipso}), 130.95, 140.93 (C_{ipso}) (NC_6H_4Me). Anal. Calc. for $C_{12}H_{12}Cl_2NNb$: C, 43.15; H, 3.62; N, 4.19. Found: C, 42.90; H, 3.52; N, 4.07%

3.6. Synthesis of [Nb(=NBu^t)Cp′Cl$_2$] (**5**)

3.6.1. Method A

To a solid mixture of LiCp′ (0.84 g, 5.83 mmol) and [Nb(=NBu^t)Cl$_3$(py)$_2$] (2.50 g, 5.83 mmol) was added THF (150 ml). The yellow solution was allowed to stir at r.t. for 16 h. Solvent was removed under reduced pressure and hexane (150 ml) added and the mixture was filtered. Solvent was removed, from the filtrate, to give a yellow oil. ^1H-NMR spectroscopy showed this oil to be uniquely a mixture (ca. 1:1) of the title complex **5** and **6**.

3.6.2. Method B

To a solid mixture of [Nb(=NBu^t)Cl$_3$(py)$_2$] (1.30 g, 3.03 mmol) and **6** (1.44 g, 3.03 mmol) was added THF (150 ml). The yellow solution was allowed to stir at r.t. for 16 h. Solvent was removed under reduced pressure and hexane (150 ml) added and the mixture was filtered. Solvent was removed, from the filtrate, to give a yellow oil. ^1H-NMR spectroscopy showed this oil to be uniquely a mixture (ca. 1:1) of the title complex **5** and **6**. ^1H-NMR (C_6D_6, 200 MHz): δ 0.20 (s, 9H, $SiMe_3$), 1.02 (s, 9H, CMe_3), 6.11 (2H), 6.35 (2H) (m, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$-NMR (C_6D_6, 300 MHz): δ 0.51 ($SiMe_3$), 30.4 (CMe_3), 70.1 (CMe_3), 110.4, 112.4, 116.0 (C^1) ($C_5H_4SiMe_3$).

3.7. Synthesis of [Nb(=NBu^t)Cp′$_2$Cl] (**6**)

3.7.1. Method A

To a solid mixture of LiCp′ (1.92 g, 13.30 mmol) and [Nb(=NBu^t)Cl$_3$(py)$_2$] (2.85 g, 6.65 mmol) was added THF (150 ml). The yellow solution was allowed to stir at r.t. for 16 h. Solvent was removed under reduced pressure and hexane (150 ml) added and the mixture was filtered. Solvent was removed, from the filtrate, to give a yellow oil. Cooling (−30°C) a hexane (30 ml) solution of this oil yielded yellow crystals of **6** (2.31 g, 73%).

3.7.2. Method B

The synthesis was carried out in an identical manner to Method A except the reaction was carried out at 0°C and only stirred for 2 h. LiCp′ (0.96 g, 6.65 mmol) and [Nb(=NBu^t)Cl$_3$(py)$_2$] (2.85 g, 6.65 mmol). Yield (with reference to LiCp′) 1.09 g, 69%.

3.8. Synthesis of [Nb(=NC$_6$H$_4$Me-4)Cp′$_2$Cl] (**7**)

The synthesis of **7** was carried out in an identical manner to that of **6** (Method A). LiCp′ (1.54 g, 10.64 mmol) and **1** (2.10 g, 5.32 mmol). Yield 1.82 g, 67%. IR (Nujol mull): $\nu_{Nb=N}$ 1258 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 0.23 (s, 18H, $SiMe_3$), 2.10 (s, 3H, NC_6H_4Me), 5.51 (2H), 5.96 (2H) 6.25 (2H) 6.33 (2H) (m, $C_5H_4SiMe_3$), 6.45 (2H), 6.89 (2H) (J 9.10 Hz) (d, NC_6H_4Me). $^{13}C\{^1H\}$-NMR (acetone-d_6, 300 MHz): δ −0.25 ($SiMe_3$), 20.8 (NC_6H_4Me), 116.0, 116.9, 117.8, 118.0, 122.0 (C^1) ($C_5H_4SiMe_3$), 126.8, 126.1 (C_{ipso}), 130.2, 130.3 (C_{ipso}) (NC_6H_4Me). Anal. Calc. for $C_{23}H_{33}ClNNbSi_2$: C, 54.37; H, 6.55; N, 2.76. Found: C, 54.11; H, 6.39; N, 2.81%

3.9. Synthesis of [Nb(=NC$_6$H$_4$OMe-4)Cp′$_2$Cl] (**8**)

The synthesis of **8** was carried out in an identical manner to that of **6** (Method A). LiCp′ (1.58 g, 10.96 mmol) and **2** (2.25 g, 5.48 mmol). Yield 2.13 g, 74%. IR (Nujol mull): $\nu_{Nb=N}$ 1296 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 0.23 (s, 18H, $SiMe_3$), 3.21 (s, 3H, NC_6H_4OMe), 5.56 (2H), 5.99 (2H) 6.26 (2H) 6.33 (2H) (m, $C_5H_4SiMe_3$), 6.47 (2H), 6.67 (2H) (J 8.9 Hz) (d, NC_6H_4OMe). $^{13}C\{^1H\}$-NMR (acetone-d_6, 300 MHz): δ 0.2 ($SiMe_3$), 55.8 (NC_6H_4OMe), 112.0, 113.2, 114.0, 114.1 (C^1), 115.2 ($C_5H_4SiMe_3$), 120.2, 118.8 (C_{ipso}), 120.4, 127.5 (C_{ipso}) (NC_6H_4OMe). Anal. Calc. for $C_{23}H_{33}ClNNbOSi_2$: C, 52.71; H, 6.35; N, 2.67. Found: C, 52.43; H, 6.25; N, 2.71%

3.10. Synthesis of [Nb(=NBu^t)CpCp′Cl] (**9**)

To a solid mixture of LiCp′ (0.56 g, 3.85 mmol) and **3** (1.05 g, 3.50 mmol) was added THF (150 ml). The yellow solution was heated, under reflux, for 8 h. The solvent was removed under reduced pressure and hexane (150 ml) added and the mixture was filtered. The solvent was removed from the filtrate to give a yellow oil. ^{1}H-NMR spectroscopy showed this oil to be uniquely a mixture (ca. 1:1) of the title complex **9** and **3**. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.28 (s, 9H, Si*Me*$_3$), 0.94 (s, 9H, C*Me*$_3$), 5.88 (s, 5H, C_5H_5), 5.75 (1H), 5.80 (1H), 6.18 (1H), 6.23 (1H) (m, $C_5H_4SiMe_3$): $^{13}C\{^1H\}$-NMR (C_6D_6, 300 MHz,) δ 0.53 (Si*Me*$_3$), 30.0 (C*Me*$_3$), 69.8 (*C*Me$_3$), 105.28, 114.89, 117.20 (C^1), 122.34, 125.65 ($C_5H_4SiMe_3$).

3.11. Synthesis of [Nb(=NBu^t)Cp′$_2$(η^1-$CH_2CH{=}CH_2$) (**10**)

A 2 M solution of $ClMgCH_2CH{=}CH_2$ in THF (0.66 ml, 1.32 mmol) was added to a stirring solution of **6** (0.52 g, 1.10 mmol) in THF (50 ml) at −30°C and allowed to stir for 3 h at this temperature. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane (50 ml). Solvent was removed in vacuo and the remaining yellow oil extracted in hexane. A yellow crystalline solid was obtained by concentrating (15 ml) and cooling (−30°C) the solution (0.29 g, 55%). IR (Nujol mull): $\nu_{Nb=N}$ 1240 cm^{-1}. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.22 (s, 18H, Si*Me*$_3$), 0.96 (s, 9H, C*Me*$_3$), 2.75 (d, 2H, $CH_2CH{=}CH_2$) $^3J(^1H-^1H)$ 8.5 Hz, 4.83 (*cis*), 5.02 (*trans*) (dd, 2H, $CH_2CH{=}CH_2$) $^2J_{gem}(^1H-^1H)$ 2.5, $^3J_{cis}(^1H-^1H)$ 9.9, $^3J_{trans}(^1H-^1H)$ 16.9 Hz, 5.76 (2H), 5.77 (2H), 5.95 (2H), 6.06 (2H) (m, $C_5H_4SiMe_3$), 6.55 (m, 1H, $CH_2CH{=}CH_2$). $^{13}C\{^1H\}$-NMR (C_6D_6, 300 MHz): δ 0.57 (Si*Me*$_3$), 30.92 (C*Me*$_3$), 37.45 ($CH_2CH{=}CH_2$), 70.72 (*C*Me$_3$), 106.81, 111.64, 118.88, 124.73, 109.91 (C^1) ($C_5H_4SiMe_3$), 104.18 ($CH_2CH{=}CH_2$), 151.29 ($CH_2CH{=}CH_2$). Anal. Calc. for $C_{23}H_{40}NNbSi_2$: C, 57.59; H, 8.41; N, 2.92. Found: C, 57.61; H, 8.52; N, 2.81%

3.12. Synthesis of [Nb(=NC_6H_4Me-4)Cp′$_2$(η^1-$CH_2CH{=}CH_2$)] (**11**)

The synthesis of **11** was carried out in an identical manner to that of **10**. A 2 M solution of $ClMgCH_2CH{=}CH_2$ in THF (0.77 ml, 1.54 mmol) and **7** (0.65 g, 1.28 mmol). Yield 0.38 g, 58%. IR (Nujol mull): $\nu_{Nb=N}$ 1260 cm^{-1}. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.14 (s, 18H, Si*Me*$_3$), 2.09 (s, 3H, NC_6H_4Me), 2.82 (d, 2H, $CH_2CH{=}CH_2$) $^3J(^1H-^1H)$ 8.1 Hz, 4.83 (*cis*), 5.00 (*trans*) (dd, 2H, $CH_2CH{=}CH_2$) $^2J_{gem}(^1H-^1H)$ 2.5, $^3J_{cis}(^1H-^1H)$ 9.9, $^3J_{trans}(^1H-^1H)$ 16.8 Hz, 5.52 (2H), 5.65 (2H), 5.91 (2H), 5.98 (2H) (m, $C_5H_4SiMe_3$), 6.52 (m, 1H, $CH_2CH{=}CH_2$), 6.49 (2H), 6.89 (2H) (*J* 8.0 Hz) (d, NC_6H_4Me). $^{13}C\{^1H\}$-NMR (C_6D_6, 300 MHz): δ 0.26 (Si*Me*$_3$), 20.92 (NC_6H_4Me), 37.23 ($CH_2CH{=}CH_2$), 110.82, 113.71, 113.98 (C^1), 116.18, 119.28 ($C_5H_4SiMe_3$), 105.21 ($CH_2CH{=}CH_2$), 149.96 ($CH_2CH{=}CH_2$), 126.35, 129.10, 129.96 (C_{ipso}), 139.03 (C_{ipso}) (NC_6H_4Me). Anal. Calc. for $C_{26}H_{38}NNbSi_2$: C, 60.79; H, 7.46; N, 2.73. Found: C, 60.48; H, 7.35; N, 2.84%

3.13. Synthesis of [Nb(=NC_6H_4OMe-4)Cp′$_2$(η^1-$CH_2CH{=}CH_2$)] (**12**)

The synthesis of **12** was carried out in an identical manner to that of **10**. A 2 M solution of $ClMgCH_2$-$CH{=}CH_2$ in THF (0.62 ml, 1.24 mmol) and **8** (0.54 g, 1.03 mmol). Yield 0.34 g, 61%. IR (Nujol mull): $\nu_{Nb=N}$ 1285 cm^{-1}. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.14 (s, 18H, Si*Me*$_3$), 3.32 (s, 3H, NC_6H_4OMe), 2.82 (d, 2H, $CH_2CH{=}CH_2$) $^3J(^1H-^1H)$ 8.3 Hz, 4.84 (*cis*), 5.01 (*trans*) (dd, 2H, $CH_2CH{=}CH_2$) $^2J_{gem}(^1H-^1H)$ 2.4, $^3J_{cis}(^1H-^1H)$ 10.0, $^3J_{trans}(^1H-^1H)$ 16.8 Hz, 5.53 (2H), 5.70 (2H), 5.91 (2H), 5.99 (2H) (m, $C_5H_4SiMe_3$), 6.53 (m, 1H, $CH_2CH{=}CH_2$), 6.48 (2H), 6.68 (2H) (*J* 9.0 Hz) (d, NC_6H_4OMe). $^{13}C\{^1H\}$-NMR (C_6D_6, 300 MHz): δ 0.48 (Si*Me*$_3$), 57.42 (NC_6H_4OMe), 38.12 ($CH_2CH{=}CH_2$), 105.99, 110.42, 112.17 (C^1), 119.70, 120.61 ($C_5H_4SiMe_3$), 103.85 ($CH_2CH{=}CH_2$), 148.63 ($CH_2CH{=}CH_2$), 124.32, 125.67 (C_{ipso}), 130.17, 131.42 (C_{ipso}) (NC_6H_4OMe). Anal. Calc. for $C_{26}H_{38}NNbOSi_2$: C, 58.96; H, 7.23; N, 2.64. Found: C, 58.63; H, 7.31; N, 2.62%

3.14. Crystallography

Diffraction data for **8** were obtained at 298 K on a Nonius-Mach3 diffractometer with graphite monochromatized Mo–K_α radiation using a $\omega/2\theta$ scan technique. Cell parameters were determined by a least-squares fit on 25 reflections. Data were corrected for Lorentz and polarization effects and absorption correction was not required because the variation in integrated ψ-scan intensities was $<10\%$. The structure was solved by a combination of direct methods [20] and Fourier synthesis and then refined by full-matrix least-squares on F^2 [21]. Anisotropic thermal parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated position but not refined. Final disagreement indices are $R_1 = 0.0325$, $wR_2 = 0.0814$, largest difference peak and hole 0.319 and -0.333 e Å^{-3}. Details are given in Table 5.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CSD-115349 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

Table 5
Crystal data and structure refinement for complex **8**

Empirical formula	$C_{23}H_{33}ClNNbOSi_2$
Formula weight	524.04
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	7.335(9)
b (Å)	17.219(3)
c (Å)	20.682(9)
β (°)	99.42(7)
Volume (Å^3)	2577(3)
Z	4
D_{calc} (g cm^{-3})	1.351
Absorption coefficient (cm^{-1})	6.78
$F(000)$	1088
Crystal size (mm)	0.4 × 0.2 × 0.2
Index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 22$, $-27 \leq l \leq 26$
Data/restraints/parameters	6200/0/262
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0814$

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References

[1] See for example: (a) D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, J. Chem. Soc. Dalton Trans. (1992) 739. (b) V.C. Gibson, D.N. Williams, W. Clegg, D.C.R. Hockless, Polyhedron 8 (1989) 1819. (c) U. Siemeling, V.C. Gibson, J. Organomet. Chem. 426 (1992) C25. (d) V.C. Gibson, A.D. Poole, U. Siemeling, D.N. Williams, W. Clegg, D.C.R. Hockless, J. Organomet. Chem. 462 (1993) C12. (e) T.C. Baldwin, S.R. Huber, M.A. Bruck, D.E. Wigley, Inorg. Chem. 32 (1993) 5682. (f) A.D. Poole, V.C. Gibson, W. Clegg, J. Chem. Soc. Chem. Commun. (1992) 237. (g) J.K. Cockcroft, V.C. Gibson, J.A.K. Howard, A.D. Poole, U. Siemeling, C. Wilson, J. Chem. Soc. Chem. Commun. (1992) 1668. (h) M.C.W. Chan, J.M. Cole, V.C. Gibson, J.A.K. Howard, C. Lehmann, A.D. Poole, U. Siemeling, J. Chem. Soc. Dalton Trans. (1998) 103. (i) M.L.H. Green, J.T. James, J.F. Saunders, J. Souter, J. Chem. Soc. Dalton Trans. (1997) 1281.

[2] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martin-Alonso, A. Otero, J. Chem. Soc. Dalton Trans. (1995) 1007.

[3] (a) A.N. Chernega, M.L.H. Green, A.G. Suarez, J. Chem. Soc. Dalton Trans. (1993) 3031. (b) S. Schmidt, J. Sundermeyer, J. Organomet. Chem. 472 (1994) 127.

[4] M.L.H. Green, J.T. James, A.N. Chernega, J. Chem. Soc. Dalton Trans. (1997) 1719.

[5] (a) W.A. Hermann, W. Baratta, E. Herdtweck, Angew. Chem. Int. Ed. Engl. 35 (1996) 1951. (b) W.A. Hermann, W. Baratta, E. Herdtweck, J. Organomet. Chem. 541 (1997) 445. (c) A.N. Chernega, M.L.H. Green, A.G. Suarez, Can. J. Chem. 73 (1995) 1157.

[6] A.V. Korolev, A.L. Rheingold, D.S. Williams, Inorg. Chem. 36 (1997) 2647.

[7] K.S. Heinseiman, V.M. Miskowski, S.J. Geib, L.C. Wang, M.D. Hopkins, Inorg. Chem. 36 (1997) 5530.

[8] J. Sundermeyer, J. Putterlik, M. Foth, J.S. Field, N. Ramesar, Chem. Ber. 127 (1994) 1201.

[9] (a) G. Parkin, A. van Asselt, D.J. Leahy, L.R. Whinnery, N.G. Hua, R.W. Quan, L.M. Henling, W.P. Schaefer, B.D. Santarsiero, J.E. Bercaw, Inorg. Chem. 31 (1992) 82. (b) K.A. Jørgensen, Inorg. Chem. 32 (1993) 1521.

[10] S.C Dunn, P. Mountford, D.A. Robson, J. Chem. Soc. Dalton Trans. (1997) 293.

[11] J.C. Green, M.L.H. Green, J.T. James, P.C. Konidaris, G.H. Maunder, P. Mountford, J. Chem. Soc. Chem. Commun. (1992) 1361.

[12] J.H. Osborne, A.L. Rheingold, W.C. Trogler, J. Am. Chem. Soc. 107 (1985) 7945.

[13] M.H. Schofield, T.P. Kee, J.T. Anhaus, R.R. Schrock, K.H. Johnson, W.M. Davis, Inorg. Chem. 30 (1991) 3595.

[14] A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, M. Fajardo, A. Garcés, P. Gómez-Sal, C. López-Mardomingo, A. Martín, C. Miranda, J. Chem. Soc. Dalton Trans. (1998) 59.

[15] A. Antiñolo, A. Otero, S. Prashar, A.M. Rodriguez, Organometallics 17 (1998) 5454.

[16] N.J. Bailey, J.A. Cooper, H. Gailus, M.L.H. Green, J.T. James, M.A. Leech, J. Chem. Soc. Dalton Trans. (1997) 3579.

[17] A. Antiñolo, J.M. de Ilarduya, A. Otero, P. Royo, A.M.M. Lanfredi, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1988) 2685.

[18] A.M.M. Lanfredi, A. Tiripicchio, M. Kapon, G.M. Reisner, J. Chem. Soc. Dalton Trans. (1990) 375.

[19] A. Antiñolo, C. Huertas, I. del Hierro, M.F. Lappert, A. Otero, S. Prashar, A.M. Rodriguez, E. Villaseñor, Organometallics 17 (1998) 5874.

[20] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. (1994) 435.

[21] G.M. Sheldrick, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.