Synthesis and Reactivity of Ene-Diamido and Ene-Diolato [(Trimethylsilyl)-cyclopentadienyl]niobium(V) Complexes and a Comparative DFT Study of the Bonding Capabilities of Diazabutadiene and Butadiene Ligands

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The reactions of [NbCp′Cl$_2$(Me$_3$SiCCSiMe$_3$)] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) with 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph-DAD) and diketones R–CO–CO–R (R = Me, Ph) gave ene-diamido complexes [NbCp′Cl$_2$(Me,Ph-DAD)] (**1**) and ene-diolato complexes [NbCp′Cl$_2${O(R)CC(R)O}] (R = Me, **2**; Ph, **3**), respectively, with simultaneous elimination of bis(trimethylsilyl)acetylene. The NMR spectroscopic data of these compounds are in agreement with a *supine* conformation, with respect to the Cp′ ring, of the ene-diamido and ene-diolato ligands. In order to gain further information concerning the bonding capabilities of the ene-diamido ligand, a DFT study of the model complex [NbCpCl$_2$(HNCHCHNH)] (**I**) was performed. For comparison, a DFT analysis of the model compound [NbCpCl$_2$(η^4-CH$_2$CHCHCH$_2$)] (**II**) was also carried out. Differences in the bonding description of the diazabutadiene and butadiene ligands bonded to a common [NbCpCl$_2$] moiety are discussed. A detailed analysis of the fragment orbital interactions in **I** provides no evidence for any positive overlap between the Nb centre and the inner carbon atoms of the DAD ligand. Dialkylation of the dichloro complex **1** gave dialkyl derivatives [NbCp′R$_2$(Me,Ph-DAD)] (R = Me, **4**; CH$_2$SiMe$_3$, **5**; CH$_2$C$_6$H$_5$, **6**), for which the NMR spectroscopic data suggests a *prone* conformation of the DAD ligand. Treatment of the dimethyl derivative **4** with carbon monoxide and 2,6-dimethylphenyl isocyanide led to the formation of the oxa- and azaniobacyclopropane complexes [NbCp′{η^2-(E)CMe$_2$}(Me,Ph-DAD)] [E = O, **7**; N(2,6-Me$_2$C$_6$H$_3$), **8**], respectively. Subsequent insertion of isocyanide into the Nb–C bond of **7** proceeds with formation of derivatives [NbCp′{η^2-(O)CMe$_2$-(CNAr)$_x$}(Me,Ph-DAD)], (Ar = 2,6-Me$_2$C$_6$H$_3$; x = 1, **9**; 2, **10**). All the complexes isolated were characterized by IR and NMR (^{1}H, ^{13}C{^{1}H}) spectroscopy.

Introduction

Recent developments in the organometallic chemistry of early transition metals is due to the participation of metallocene systems as catalysts in important inorganic and organic reactions.[1] Modification of the cyclopentadienyl ligand by introduction of specific substituents, including an ansa-type bis(cyclopentadienyl) ligand, was the first strategy[2] in order to respond to each problem created in such processes. Another, more flexible approach, may be a half-metallocene system, in which one Cp ligand of the metallocene is replaced by different ancillary ligands. In any case, mono- and bis(cyclopentadienyl) complexes of early transition metals are now well established as important types of olefin polymerisation catalysts.[3] Although many systems are highly active and widely studied, precise reasons why certain ligands or ligand combinations produce effective catalysts remains obscure. In this context, nitrogen donor ligands have been incorporated into the cyclopentadienyl ring, such as the "constrained geometry" complexes,[4] and also mono- and polydentate amido complexes[5] without cyclopentadienyl ligands have been reported. In addition, dienes have been integrated as ligands, because [M(η^5-C$_5$R$_5$)(1,3-diene)] (M = Nb, Ta) fragments are isoelectronic and isolobal[6] to Group-4 metallocene fragments [M(η^5-C$_5$R$_5$)$_2$]. This relationship is extremely useful, since the metallocene species involved in synthetic and catalytic processes can potentially be replaced by monocyclopentadienyl(diene) complexes. In fact, these metallocene-like fragments stabilize reactive benzyne[7] species and their *cis*-dialkyl derivatives are catalyst precursors for the living polymerization of ethylene[8] and the stereoselective ROMP of norbornene.[9]

Several coordination modes have been reported[10] for transition metal complexes containing substituted 1,4-diaza-1,3-butadiene ligands (R,R′-DAD[11]). Scheme 1 shows a representation of the bonding modes found in mononuclear complexes in which the DAD ligand is bonded to the

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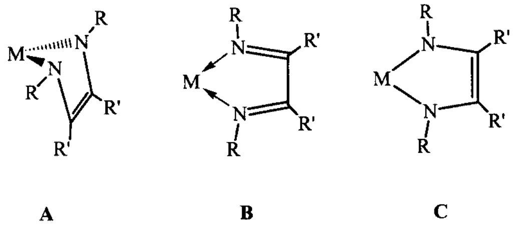


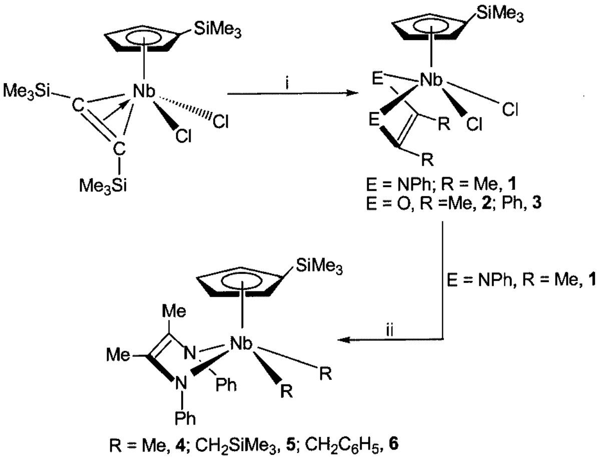
Scheme 1. Coordination bonding modes of 1,4-diaza-1,3-butadiene ligand (R,R′-DAD) found in mononuclear complexes in which the ligand is bonded to the metal centre through the two N atoms

metal centre through both N atoms. In the majority of early transition metals the diazabutadiene ligand acts as a dianionic ene-diamido chelate (mode **A**) and the metal-DAD moiety is characterized by a nonplanar disposition (folded envelope). The coordination mode **B**, α-diimine ligand, is well represented for many late transition metal complexes; meanwhile, bonding type **C**, a planar 2,5-diaza-1-metallacyclopent-3-ene, is less common in early transition metals.[12] In the last few years, the synthesis and characterization of a series of niobium and tantalum complexes containing 1,4-diaza-1,3-diene R,R′-DAD ligands[12a,13] (or closely related *o*-phenylenediamido ligands[14]) have been reported, in which the diazabutadiene behaves as a dianionic ene-diamido ligand (mode **A**) and shows a folded envelope geometry. When the compound has a cyclopentadienyl co-ligand, the DAD can adopt two conformations − *supine* and *prone* − relative to the Cp ring, depending on the coordination environment of the metal centre.[15]

In this paper, we report a synthetic study of half-sandwich niobium complexes containing ene-diamido and ene-diolato ligands and their chemical behaviour in alkylation and insertion reactions. Also, we present a comparative DFT study of the 1,4-diaza-1,3-butadiene and 1,3-butadiene ligands coordinated to the common [$NbCpCl_2$] moiety, in order to look into the bonding capabilities of the diazabutadiene and butadiene ligands on high-valent complexes of early transition metals.

Results and Discussion

The treatment of [$NbCp'Cl_2(Me_3SiCCSiMe_3)$][16] (Cp′ = η^5-$C_5H_4SiMe_3$) with 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph-DAD) or diketones R−CO−CO−R (R = Me, Ph) in hexane leads to the precipitation of the corresponding half-sandwich complexes [$NbCp'Cl_2$(Me,Ph-DAD)] (**1**) and [$NbCp'Cl_2\{O(R)CC(R)O\}$] (R = Me, **2**; Ph, **3**), respectively, with elimination of bis(trimethylsilyl)acetylene (Scheme 2). The closely related half-sandwich 1,4-diaza-1,3-butadiene complexes with the general formula [$Nb(\eta^5\text{-}C_5R_5)Cl_2$(DAD)][13d,13f,14a,14b] were previously known and they were essentially isolated by treatment of the tetrachloro compounds [$Nb(\eta^5\text{-}C_5R_5)Cl_4$] (R = H, Me) with a dilithium salt of different DAD ligands. However, there is an example in which the experimental procedure is related to the synthesis of **1** and the DAD derivative was formed by a photochemical ligand-exchange reaction between [$NbCpCl_2(PMe_3)_3$] and the *t*Bu,H-DAD ligand.[13a]



Scheme 2. Reagents and conditions: i: 1 equiv. E(R)C-C(R)E (E = NPh, R = Me, **1**; E = O, R = Me, **2**; Ph, **3**), hexane, 12 h, room temp.; ii: 2 equiv. MgClR (R = Me, **4**; CH_2SiMe_3, **5**; $CH_2C_6H_5$, **6**), diethyl ether, 12 h, room temp. (except for R = $CH_2C_6H_5$, −78 °C)

The IR spectra (Table 1) of **1**−**3** (and those of the other complexes of this work) show the characteristic absorptions for the (trimethylsilyl)cyclopentadienyl ring ($\nu_{C-H} \approx 841$ cm^{-1})[17] and the trimethylsilyl substituent [$\nu\delta_{as}(CH_3) \approx 1255$ cm^{-1}].[18] Absorptions due to the C=N, C=C, C−O, Nb−O, Nb−C and Nb−Cl stretching vibrations are observed at $\tilde{\nu} \approx$ 1630,[19] 1594,[20] 1173,[20e,21] 734,[22] 482[20e,21b] and 320[17,22,23] cm^{-1}, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data (Table 2) are consistent with the stoichiometries and expected geometries of these complexes. The inner carbon atoms of the ene-diamido and ene-diolato ligands were observed as a singlet in the olefinic region between δ = 96 and 120. By contrast, the corresponding resonances of the uncoordinated DAD ligands are usually found in the region at δ ≈ 160 and those for 1,4-diazabuta-1,3-dienes coordinated in mode **B** the diene ^{13}C resonance occurs at an even lower field.[10a,24] This NMR spectroscopic data suggest an ene-diamido structure (mode **A**) for **1** and an ene-diolato one for the complexes **2** and **3**. Mashima et al. have recently highlighted[15] the geometric preferences of 1,4-diazadiene ligands on half-sandwich metallocene complexes of early transition metals. The ene-diamido ligand can adopt two conformations, *supine* and *prone*, relative to the η^5-C_5R_5 moiety. The adoption of a particular conformation depends on the coordination environment on the metal centre and the steric properties of the substituents of the DAD ligand. In most of the dichloro compounds this ligand adopts a *supine* conformation, except for a bulky substituted *t*Bu,H-DAD derivative [TaCp*Cl_2(*t*Bu,H-DAD)][13e] and for the bis(trialkylsilyl)-*o*-phenylenediamido complexes, [TaCp*$Cl_2\{(i\text{Pr}_3\text{SiN})_2\text{-}o\text{-}C_6H_4\}$][14a]

Table 1. IR data (Nujol mull, $\tilde{\nu}$, cm^{-1}) of the new complexes

	C=C	$SiMe_3$	C−H (Cp′)	Nb−Cl	Others
1	1588 (m)	1258 (vs)	841 (s)	313 (m)	1172 (w), 1078 (w), 1050 (m), 901 (w), 700 (w), 637 (m), 506 (m, ν_{Nb-N})
2	1653 (w)	1250 (m)	841 (m)	319 (w)	1172 (w), 1134 (m, ν_{C-O}), 1048 (w), 900 (w), 722 (w, ν_{Nb-O}), 651 (w),629 (w)
3	1569 (w)	1259 (s)	851 (s)	328 (w)	1174 (m), 1154 (m, ν_{C-O}), 1046 (m), 901 (w), 724 (w, ν_{Nb-O}), 662 (w), 616 (w)
4	1588 (m)	1249 (s)	839 (s)		1169 (w), 1074 (w), 1049 (m), 909 (w), 697 (m), 635 (w), 488 (w, ν_{Nb-C})
5	1590 (vs)	1253 (vs)	845 (vs)		1175 (m), 1075 (w), 1050 (w), 905 (w), 699 (m), 638 (w), 492 (w, ν_{Nb-C})
6	1592 (m)	1250 (m)	840 (s)		1172 (w), 1080 (w), 1045 (m), 904 (w), 697 (w)
7	1591 (s)	1257 (s)	834 (s)		1205 (m, ν_{C-O}), 1170 (m), 1087 (m), 1049 (w), 906 (m), 745 (s, ν_{Nb-O}), 697 (m), 632 (m), 473 (w, ν_{Nb-C})
8	1592 (m)	1257 (s)	836 (m)		1169 (w), 1072 (m), 1047 (w), 905 (w), 692 (m, ν_{Nb-N}), 499 (w)
9	1591 (m)	1259 (m)	839 (m)		1615 (m, $\nu_{C=N}$), 1197 (m, ν_{C-O}), 1169 (w), 1090 (w), 1047 (w), 904 (w), 740 (m, ν_{Nb-O}), 698 (w), 631 (w), 504 (m, ν_{Nb-C})
10	1590 (s)	1255 (vs)	834 (s)		1645 (m, $\nu_{C=N}$), 1197 (m, ν_{C-O}), 1169 (w), 1091 (w), 1049 (w), 907 (w), 741 (m, ν_{Nb-O}), 698 (m), 638 (w), 456 (m, ν_{Nb-C})

and $[M\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}Cl_2\{(Me_3SiN)_2\text{-}o\text{-}C_6H_4\}]$[14b] (M = Nb, Ta). On the basis of the steric properties of the ligands and the NMR spectroscopic data of complexes **1−3** we conclude that both ene-diamido and ene-diolato ligands adopt the *supine* conformation (see Scheme 2).

Mealli, Ienco and Galindo have recently communicated a re-interpretation of the bonding scheme of the ene-diamido ligand in d^0-metal complexes.[25] Essentially, the folding of the DAD ligand (folded envelope geometry, mode **A**) in such complexes cannot be explained by using the standard description of σ^2,π adopted for the η^4 bonding of butadiene ligands to early transition metals. The experimentally observed folding cannot be attributed to the π donation from the central C=C linkage to the unsaturated metal centre, because this interaction is negligible, according to calculations.

In order to confirm this analysis we have performed DFT studies on the model complex $[NbCpCl_2(HNCHCHNH)]$ (**I**) analogous to derivative **1**. Also for comparison we have extended our calculations to the model complex $[NbCpCl_2(\eta^4\text{-}CH_2CHCHCH_2)]$ (**II**). Therefore, in this paper, we compare the ligands 1,4-diaza-1,3-butadiene (in its ene-diamido form) and 1,3-butadiene (in its 2-butene-1,4-diyl form) coordinated to the common moiety $[NbCpCl_2]$ (with a formal d^0 configuration). Full geometry optimisations were performed for the model compounds **I** and **II**. According to the remarks of Mashima et al.,[15] in dichloro(cyclopentadienyl) Group-5 compounds the DAD ligand adopts a *supine* conformation, except for bulky substituted DAD derivatives. No steric crowding can be expected in model **I**, because it contains the simplest DAD ligand and, subsequently, only the *supine* orientation of the DAD ligand was calculated.[26] Analogously, for **II**, just the *supine* orientation of butadiene ligand was considered.[27] The use of BP86 or B3LYP functionals did not produce significant changes in the structural parameters and only data calculated at the B3LYP level of theory are discussed, while those at the BP86 level of theory are given as Supporting Information. The resulting final optimised geometries at the B3LYP level of theory are shown in Figure 1 and their coordinates are included as Supporting Information. Selected calculated parameters of complexes **I** and **II** and, for comparison, selected experimental data from X-ray crystallography have been collected in Tables 3 and 4, respectively.

In Table 3 we contrasted selected experimental data for several complexes containing the 1,4-diaza-1,3-butadiene fragment coordinated to the NbCp moiety with calculated parameters. Similarly, in Table 4 we made an analogous comparison for complexes containing the butadiene ligand coordinated to the same NbCp moiety. A general satisfactory agreement between the calculated and experimental values of geometrical parameters was found. In both cases (see Figure 1) the ligand was folded towards the metal centre and computed torsion angles of 120.7 (Nb−N1−N2−C2) and 92.8° (Nb−C1−C4−C3) for **I** and **II**, respectively, gave Nb−C contacts within the range of bonding distances (2.532 Å for **I** and 2.431 Å for **II**). The C1−C2 and C2−C3 bond lengths (1.407 Å in **I** and 1.395 Å in **II**, respectively) were shorter than that expected for a single C−C bond. In addition, the N1−C1 and N2−C2 bond lengths in **I** (1.366 Å) were longer than expected for a double N=C bond. The principal difference found in the common $[NbCpCl_2]$ fragment was the Cl−Nb−Cl bond angle, which opened up from 82.1° in **I** to 96.1° in **II**.

A qualitative FMO analysis helped to elucidate the major bonding components between 1,4-diaza-1,3-butadiene and 1,3-butadiene ligands and the common $[NbCpCl_2]$ fragment. When considering the substitution of 1,3-butadiene by the 1,4-diaza-1,3-butadiene ligand, we are replacing a ligand, capable of donating two pairs of electrons (two π pairs in the neutral form) by a ligand which is able to donate up to a maximum of four electron pairs (the equivalent two π pairs plus two in-plane σ pairs in the neutral form). A representation of the FMOs corresponding to the 1,4-diaza-1,3-butadiene ligand is shown in Scheme 3, in conjunction with the energy disposition of such orbitals and those well known for butadiene. Taking into account the

Table 2. ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data ([D$_6$]benzene) of the new complexes; chemical shifts in δ

	^{1}H	^{13}C{^{1}H}
1	7.30 (m), 7.20 (m), 7.01 [m, 10 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$], 6.71 (m, 2 H), 5.71 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.84 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 0.28 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	150.22 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 129.11, 126.13, 125.13 [C_o, C_p, C_m, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 126.87 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 119.34 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 115.81, 115.43 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 14.34 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.52 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
2	6.68 (m, 2 H), 6.37 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.94 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2O_2}$), 0.22 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	138.21 (C_i, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 123.20, 123.09 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 96.26 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{O_2}$), 13.67 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2O_2}$), −0.90 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
3	7.68 (m), 6.90 [m, 10 H, $\mathrm{2,3\text{-}(}\mathit{H}_5\mathrm{C_6)_2C_2O_2}$], 6.71 (m, 2 H), 6.47 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 0.28 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	136.23 [C_i, $\mathrm{2,3\text{-}(}\mathit{C}_6\mathrm{H_5)_2C_2O_2}$], 131.95, 131.02, 130.39 [C_o, C_p, C_m, $\mathrm{2,3\text{-}(}\mathit{C}_6\mathrm{H_5)_2C_2O_2}$], 125.64 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 123.89, 123.24 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 101.51 ($\mathrm{2,3\text{-}Ph_2}\mathit{C}_2\mathrm{O_2}$), −0.79 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
4	7.16 (m), 6.99 [m, 10 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$], 6.40 (m, 2 H), 6.25 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.71 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 0.15 (s, 6 H, $\mathrm{Nb\text{-}}\mathit{Me}_2$), −0.41 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	151.26 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 128.91, 123.90, 123.25 [C_o, C_p, C_m, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 116.47 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 114.94, 114.71 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 108.29 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 24.51 ($\mathrm{Nb\text{-}}\mathit{Me}_2$), 14.62 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.58 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
5	7.18 (m), 7.00 (m), 6.92 [m, 10 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$], 6.77 (m, 2 H), 5.55 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.77 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 0.31 [s, 18 H, $\mathrm{Nb\text{-}(CH_2Si}\mathit{Me}_3\mathrm{)_2}$], 0.12, −0.07 [AB, 4 H, $^2J_{\mathrm{H-H}} = 11.7$ Hz, $\mathrm{Nb\text{-}(C}\mathit{H}_2\mathrm{SiMe_3)_2}$], −0.54 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	150.93 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 128.70, 124.49, 123.84 [C_o, C_p, C_m, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 118.52 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 116.80, 113.14 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 108.89 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 31.95 [$\mathrm{Nb\text{-}(}\mathit{C}\mathrm{H_2SiMe_3)_2}$], 15.49 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 4.18 [$\mathrm{Nb\text{-}(CH_2Si}\mathit{Me}_3\mathrm{)_2}$], −0.70 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
6	7.61, 6.95, 6.87, 6.66 [$\mathrm{Nb\text{-}(CH_2C_6}\mathit{H}_5\mathrm{)_2}$; $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$], 6.38 (m, 2 H), 6.27 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 2.31, 2.05 [AB, 4 H, $^2J_{\mathrm{H-H}} = 10$ Hz, $\mathrm{Nb\text{-}(C}\mathit{H}_2\mathrm{C_6H_5)_2}$], 1.77 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.62 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	154.66, 150.43 [C_i, $\mathrm{Nb\text{-}(CH_2}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 128.71, 127.53, 124.20, 123.55 [C_i, $\mathrm{Nb\text{-}(CH_2}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 121.81, 120.13 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 116.39 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 110.06 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 52.82 [$\mathrm{Nb\text{-}(}\mathit{C}\mathrm{H_2C_6H_5)_2}$], 14.99 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.59 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
7	7.20 (m), 6.90 [m, 10 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$], 5.65 (m, 2 H), 5.29 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.65 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 1.58 (s, 6 H, $\mathrm{Nb{-}C}\mathit{Me}_2\mathrm{{-}O}$), 0.28 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	148.55 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 122.80, 122.48 [$\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$], 119.13 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 113.57, 110.96 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 108.24 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 92.57 ($\mathrm{Nb{-}CMe_2{-}O{-}}$), 30.15 ($\mathrm{Nb{-}C}\mathit{Me}_2\mathrm{{-}O{-}}$), 15.21 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 0.20 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
8	7.02 (m), 6.77 [m, 13 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$; $\mathrm{Nb{-}N(2,6\text{-}Me_2C_6}\mathit{H}_3\mathrm{)}$], 6.11 (m, 2 H), 5.42 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 1.85 [s, 6 H, $\mathrm{Nb{-}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 1.64 (s, 6 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 1.46 (s, 6 H, $\mathrm{Nb{-}C}\mathit{Me}_2\mathrm{{-}}$), 0.14 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	153.83, 148.02 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$], 134.13, 127.80, 123.08 [$\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$], 123.81, 109.45 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), 110.18 ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 109.00 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 65.70 ($\mathrm{Nb{-}CMe_2{-}}$), 30.70 ($\mathrm{Nb{-}C}\mathit{Me}_2\mathrm{{-}}$), 20.39 [$\mathrm{Nb{-}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 16.07 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 0.64 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
9	7.30 (m), 6.90 [m, 13 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2C_6}\mathit{H}_3\mathrm{)}$], 6.74 (m, 1 H), 6.56 (m, 1 H), 6.45 (m, 1 H), 5.89 (m, 1 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 2.54 (s, 3 H), 2.00 (s, 3 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 1.92 (s, 3 H), 1.88 [s, 3 H, $\mathrm{Nb{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 1.47 (s, 3 H), 1.03 (s, 3 H, $\mathrm{Nb{-}OC}\mathit{Me}_2\mathrm{{-}}$), −0.51 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	216.56 [$\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2C_6H_3)}$], 153.20, 151.13, 150.15 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$], 129.26, 127.65, 126.18, 125.24 [$\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$], 124.45, 121.55, 113.82, 110.05 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), not observed ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 108.22 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 98.80 ($\mathrm{Nb{-}O{-}CMe_2{-}}$), 27.44, 26.86 ($\mathrm{Nb{-}O{-}C}\mathit{Me}_2\mathrm{{-}}$), 19.59, 19.30 [$\mathrm{Nb{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 16.98, 14.77 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.97 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)
10	7.20 (m), 6.80 [m, 16 H, $\mathrm{2,3\text{-}Me_2C_2N_2(C_6}\mathit{H}_5\mathrm{)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2C_6}\mathit{H}_3\mathrm{){-}}$; $\mathrm{Nb{-}C{=}NAr{-}C{=}N(2,6\text{-}Me_2C_6}\mathit{H}_3\mathrm{)}$], 6.59 (m, 2 H), 6.50 (m, 2 H, $\mathit{H}_4\mathrm{C_5SiMe_3}$), 2.58 (s, 3 H), 2.04 (s, 3 H, $\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), 2.02 (s, 3 H), 1.89 [s, 3 H, $\mathrm{Nb{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3){-}}$], 1.88 (s, 3 H), 1.74 [s, 3 H, $\mathrm{Nb{-}C{=}NAr{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 1.06 (s, 3 H), 0.76 (s, 3 H, $\mathrm{Nb{-}O{-}C}\mathit{Me}_2\mathrm{{-}}$), −0.41 (s, 9 H, $\mathit{Me}_3\mathrm{SiC_5H_4}$)	not observed ($\mathrm{Nb{-}}\mathit{C}\mathrm{{=}NAr}$), 176.73 ($\mathrm{Nb{-}C{=}NAr{-}}\mathit{C}\mathrm{{=}NAr}$), 155.11, 151.39, 151.08, 148.17 [C_i, $\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$; $\mathrm{Nb{-}C{=}NAr{-}C{=}N(2,6\text{-}Me_2C_6H_3)}$], 128.80, 127.67, 127.62, 127.59, 125.98, 125.81 [$\mathrm{2,3\text{-}Me_2C_2N_2(}\mathit{C}_6\mathrm{H_5)_2}$; $\mathrm{Nb{-}C{=}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$; $\mathrm{Nb{-}C{=}NAr{-}C{=}N(2,6\text{-}Me_2}\mathit{C}_6\mathrm{H_3)}$], 118.41, 115.04, 112.52, 111.96 ($\mathit{C}_5\mathrm{H_4SiMe_3}$), not observed ($\mathrm{C}_i$, $\mathit{C}_5\mathrm{H_4SiMe_3}$), 109.87 ($\mathrm{2,3\text{-}Me_2}\mathit{C}_2\mathrm{N_2Ph_2}$), 81.90 ($\mathrm{Nb{-}O{-}CMe_2{-}}$), 29.24, 28.33 ($\mathrm{Nb{-}O{-}C}\mathit{Me}_2\mathrm{{-}}$), 20.55, 20.10, 19.12, 18.73 [$\mathrm{Nb{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$; $\mathrm{Nb{-}C{=}NAr{-}C{=}N(2,6\text{-}}\mathit{Me}_2\mathrm{C_6H_3)}$], 16.64, 14.83 ($\mathrm{2,3\text{-}}\mathit{Me}_2\mathrm{C_2N_2Ph_2}$), −0.87 ($\mathit{Me}_3\mathrm{SiC_5H_4}$)

known structural parameters of related complexes and the computed data, the best description would be to consider a formal d^0 configuration at the metal centre and dianionic ene-diamido (**I**) or 2-butene-1,4-diyl (**II**) ligands. The MCpX$_2$ metal fragment orbitals have been discussed[28] and they are a subset of three low-lying frontier orbitals, two

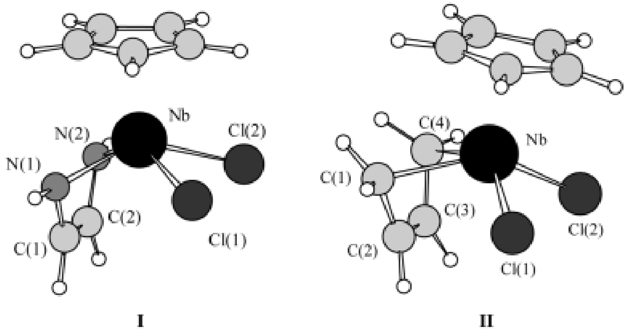


Figure 1. Optimised structures of the $[NbCpCl_2(HNCHCHNH)]$ (**I**) and $[NbCpCl_2(CH_2CHCHCH_2)]$ (**II**) model complexes

Table 3. Selected bond lengths [Å], angles and torsion angles [°] for calculated $[NbCpCl_2(HNCHCHNH)]$ model complex **I** and, for comparison, selected experimental data for compounds $[NbCp^*Cl_2(p\text{-}MeO{-}C_6H_4,H\text{-}DAD)]$, CSD refcode = LIWVES,[13f] and $[NbCpCl_2(tBu,H\text{-}DAD)]$, CSD refcode = WASHON[13a]

Complex or CSD refcode:[a]	I	LIWVES	WASHON
Nb−Cl(1)	2.487	2.483(1)	2.505(1)
Nb−Cl(2)	2.487	2.494(1)	2.527(1)
Nb−N1	2.051	2.049(3)	2.015(4)
Nb−C1	2.532	2.480(4)	2.409
Nb−C2	2.532	2.474(4)	2.402
Nb−N2	2.051	2.038(3)	2.021(4)
C1−C2	1.407	1.379(5)	1.402
N1−C1	1.366	1.367(5)	1.354
C2−N2	1.366	1.371(5)	1.364
Cl1−Nb−Cl2	82.1	79.39(4)	78.78(5)
Cl1−Nb−N1	85.3	83.76(9)	85.5(1)
Cl1−Nb−N2	139.7	138.4	140.4(1)
Cl2−Nb−N1	139.7	138.6	138.2(1)
Cl2−Nb−N2	85.3	85.25(9)	83.5(1)
N1−Nb−N2	80.0	82.8(1)	84.7(2)
Nb−N1−C1	93.5	90.9(2)	89.1
Nb−N2−C2	93.5	90.9(2)	88.2
N1−C1−C2	116.8	118.7(4)	118.7
C1−C2−N2	116.8	119.0(4)	119.2
Nb−N1−N2−C2	120.7	120.62(3)	118

[a] Cambridge Structural Database System, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

of *a'* (1*a'*, $d_{x^2-y^2}$, and 2*a'*, d_{z^2}) and one of *a''* (1*a''*, d_{xy}) symmetries, and a second subset, higher in energy, of two frontier orbitals (3*a'*, d_{xz} and 2*a''*, d_{yz}).

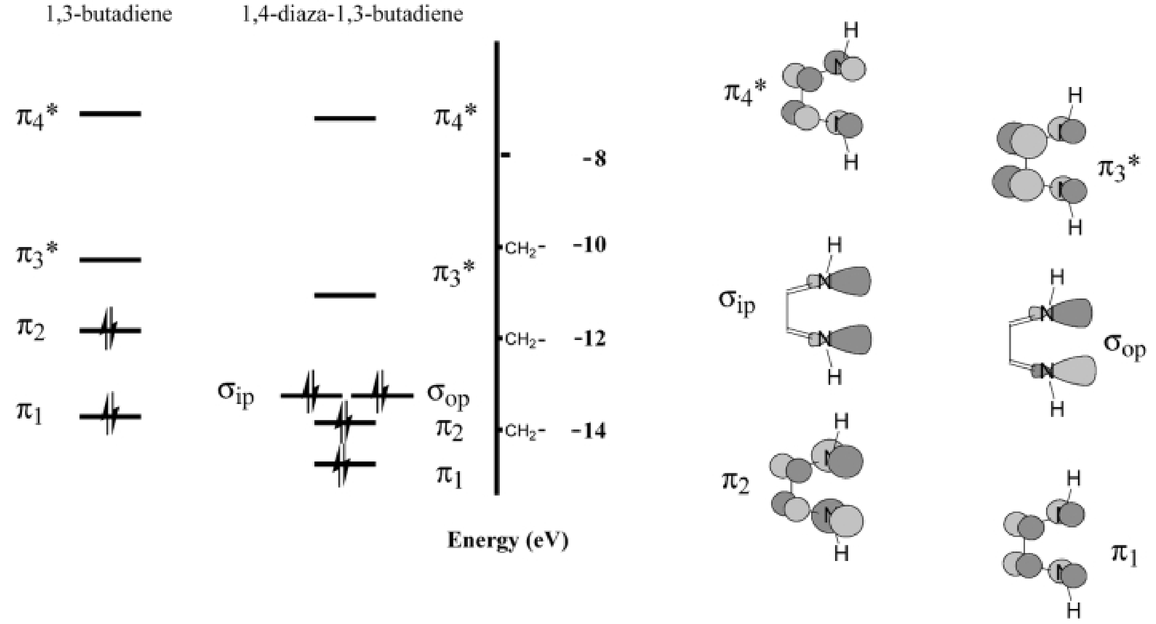
The interpretation of the bonding scheme of the η^4-butadiene ligand bound to early transition metals is well established.[29] In particular, a detailed early EHMO analysis was reported[30] for (cyclopentadienyl)tantalum complexes containing the bent 1-metallacyclopent-3-ene structure. The bonding description in **II** is similar and can be briefly summarized as follows: The strongest interactions are the donation of the π_2 orbital to 1*a''* and the donation of π_3* to 1*a'*, and also in minor proportion to the 2*a'* FMOs. Other minor details require no further discussion. The computed bond lengths in the butadiene fragment show the expected long-short-long bond alternation, indicating the involvement of the σ^2,π bonding contribution, and compare well with other bond lengths reported in recent related DFT studies.[31]

Table 4. Selected bond lengths [Å], angles and torsion angles [°] for calculated $[NbCpCl_2(CH_2CHCHCH_2)]$ model complex **II** and, for comparison, selected experimental data for compounds $[NbCp^*\{o\text{-}(CH_2)_2C_6H_4\}Cl_2]$, CSD refcode = JABTIP,[44] $[NbCp^*(butadiene)(\eta^3\text{-}cot)]$, CSD refcode = JABYEQ[44] and $[NbCp^*(butadiene)\{CH_2CH(C_{10}H_6)CH\}]$, CSD refcode = ROMSIV01[9c]

Complex or CSD refcode:	II	JABTIP	JABYEQ	ROMSIV01
Nb−Cl(1)	2.445	2.409(1)	−	−
Nb−Cl(2)	2.445	2.419(1)	−	−
Nb−C1	2.302	2.240(5)	2.307(4)	2.18(3)
Nb−C2	2.431	2.544(4)	2.424(4)	2.34(2)
Nb−C3	2.430	2.556(4)	2.393(4)	2.33(2)
Nb−C4	2.302	2.236(5)	2.270(4)	2.28(2)
C2−C3	1.395	1.415(6)	1.382(6)	1.38(3)
C1−C2	1.449	1.457(7)	1.415(6)	1.38(3)
C3−C4	1.449	1.455(7)	1.423(6)	1.40(3)
Cl1−Nb−Cl2	96.1	92.58(5)		
Cl1−Nb−C1	83.4	83.8(2)		
Cl1−Nb−C4	138.8	138.9(2)		
Cl2−Nb−C1	138.8	137.9(1)		
Cl2−Nb−C4	83.4	84.2(2)		
C1−Nb−C4	71.3	72.2(2)	72.2(2)	71(1)
Nb−C1−C2	77.1	84.1(3)	84.1(3)	78(2)
Nb−C4−C3	77.1	84.9(3)	84.9(3)	74(1)
C1−C2−C3	116.4	115.4(5)	115.4(5)	116(3)
C2−C3−C4	116.4	114.2(5)	114.2(5)	115(2)
Nb−C1−C4−C3	92.8	101.8	101.8	93.6

With reference to **I**, the FMO analysis shows that the strongest interaction is also the donation of the π_2 orbital (that is now substantially lower in energy in comparison with the similar π_2 orbital in the butadiene ligand, see Scheme 3) to 1*a''*. This donation is now completed by the participation of the *out-of-phase* σ_{op} contribution. The donation of the π_3* orbital is also active but is now directed preferentially to the 2*a'* FMO and only in a small percentage to 1*a'*. The latter metal orbital is substantially saturated by the donation of *in-phase* σ_{ip} FMO. These subtle dissimilarities in the bonding analysis in **I** with respect to **II** are responsible for the important differences found in the HOMO of the two model complexes (see Figure 2).

In the HOMO of **I** the nitrogen π lobes overlap significantly with the lobes of the 2*a'* ($d_{x^2-y^2}$) orbital while the carbon π orbitals (part of the ligand's HOMO π_3*) do not overlap with the metal lobes and are only involved in the C−C bonding interaction. Moreover, a detailed analysis of the fragment orbital interactions provides no evidence for carbon π electron donation toward the metal centre. Contrarily, the HOMO of **II** shows the overlap of all carbon π lobes of π_3* with both the 1*a'* and 2*a'* FMOs. In conclusion, the bonding of the ene-diamido (or diazabutadiene) ligand is different with respect to the conventional σ^2,π-description of the butadiene ligand. The donation through the π component is contributed by the nitrogen atoms, con-



Scheme 3. Representation of the FMOs corrresponding to the 1,4-diaza-1,3-butadiene ligand and energy distribution of such orbitals in comparison with those of 1,3-butadiene ligand

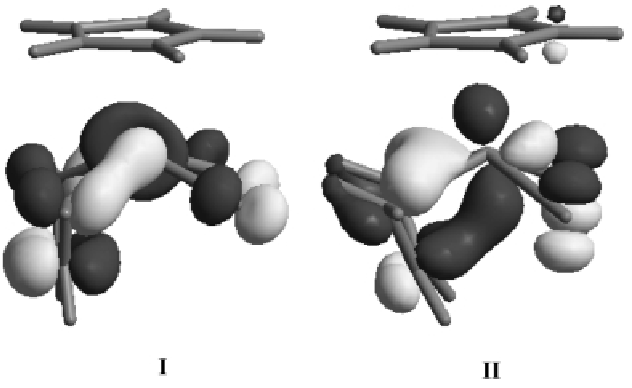
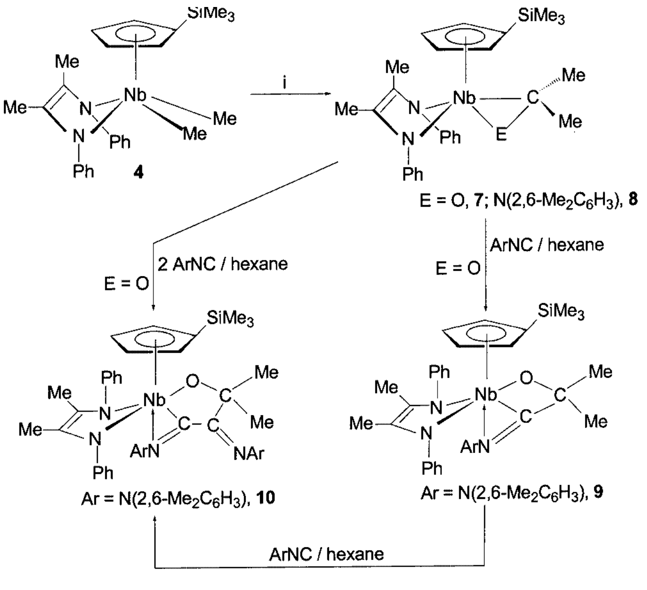


Figure 2. 3D isosurfaces corresponding to the HOMO of the [$NbCpCl_2(HNCHCHNH)$] (**I**) and [$NbCpCl_2(CH_2CHCHCH_2)$] (**II**) model complexes

sequently, the interaction between the Nb and carbon atoms is not significant.

Alkylation of **1** with Grignard reagents, in a 1:2 molar ratio, yields the dialkyl complexes [$NbCp'R_2$(Me,Ph-DAD)] (R = Me, **4**; CH_2SiMe_3, **5**; $CH_2C_6H_5$, **6**) as red-brown microcrystalline solids (Scheme 2). The ^1H NMR spectrum of **4** displays a singlet at $\delta = 0.15$ due to Nb−Me and show an AB spin system for diastereotopic α-CH_2 protons of alkyl groups in the complexes **5** and **6**. A singlet due to the methyl substituents of the ene-diamido ligand emerges at $\delta \approx 1.75$, this being at higher field compared with that ($\delta = 1.84$) of the starting dichloro complex **1**. Additionally, the ^{13}C resonances of the inner carbon atoms show a high field displacement. The data, along with the preferential orientation discussed by Mashima et al.[15] in related complexes, suggest that the alkylation reactions of the dichloro complex involves an orientation change in the ene-diamido ligand from the *supine* conformation in **1** to the *prone* form in the dialkyl derivatives **4**−**6**.[32]

Dimethyl complex **4** reacts with carbon monoxide (1 atm) at room temperature in toluene to give the oxaniobacyclopropane complex [NbCp'{η^2-(O)CMe_2}(Me,Ph-DAD)] (**7**), in good yield (Scheme 4), as a result of a double migration of two methyl groups, first to the electrophilic carbon atom of the coordinated CO and then to the related η^2-acyl intermediate, which cannot be detected. The oxaniobacyclopropane moiety which is not further transformed, is analogous to that reported for (acetone)tantalum complexes [TaCp*



Scheme 4. Reagents and conditions: i: E = O, CO (1 atm), toluene, 5 d, room temp.; E = N(2,6-$Me_2C_6H_3$), 1 equiv. 2,6-$Me_2C_6H_3NC$, hexane, 12 h, room temp.

$X_2\{\eta^2\text{-(O)CMe}_2\}]$ (X = Cl,[20e] Me[33]). When 1 equiv. of isocyanide 2,6-$Me_2C_6H_3NC$ is added to a hexane solution of **4** under rigorously anhydrous conditions, an orange solution is obtained, which after evaporation of the solvent produces the azaniobacyclopropane complex $[NbCp'\{\eta^2\text{-(ArN)CMe}_2\}(\text{Me,Ph-DAD})]$ (Ar = 2,6-$Me_2C_6H_3$, **8**). Formation of this compound can be explained as the result of two consecutive steps. The first step involves migration of one methyl group to the electrophilic isocyanide carbon atom, giving an η^2-iminoacyl intermediate,[19,34] which cannot be detected during monitoring of the entire reaction by ^{1}H NMR spectroscopy. Subsequent migration of the second methyl group to the iminoacyl carbon centre yields an azaniobacyclopropane system.[20a,20b,35] Dialkyl complexes **5**, **6** do not react with isocyanide at room temperature and 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.

On the other hand, azaniobacyclopropane complex **8** is obtained upon reaction of 2 equiv. of isocyanide with the dimethyl derivative **4**, in contrast to that observed in the case of the azatantalacyclopropane species $[TaCp^*\{\eta^2\text{-(ArN)CMe}_2\}]$[35b] (Ar = 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$), which in the presence of isocyanides gives the corresponding dichloro(imido) complexes $[TaCp^*Cl_2(NAr)]$ with elimination of the arylimine ketene Ar−N=C=CMe_2. However, the oxaniobacyclopropane complex **7** reacts with 1 or 2 equiv. of 2,6-$Me_2C_6H_3NC$ leading to the expected insertion products $[NbCp'\{\eta^2\text{-(O)CMe}_2\text{-(CNAr)}_x\}(\text{Me,Ph-DAD})]$ (Ar = 2,6-$Me_2C_6H_3$; x = 1, **9**; 2, **10**). Compound **9** can be transformed into **10** by a simple isocyanide insertion reaction.

The ^{1}H NMR spectra of complexes **7** and **8** show an AA′BB′ spin system for the proton atoms of the $C_5H_4SiMe_3$ ring, whereas the $^{13}C\{^1H\}$ NMR spectra show three carbon resonances for the same group, in agreement with the existence of a symmetry plane perpendicular to such a ring. At room temperature, the equivalence of both methyl groups of the oxa- and azaniobacyclopropane moiety (**7** and **8**), as evidenced by the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, argue a metallacyclic structure whose plane defined by the niobium, oxygen (**7**) or nitrogen (**8**) and carbon atoms is perpendicular to the cyclopentadienyl ring plane. Unfortunately, we were not able to obtain crystals adequate for X-ray diffraction, but the structure must be reasonably similar to that presented for related azametallacyclopropane complexes $[MCp^*X_2\{\eta^2\text{-(ArN)CMe}_2\}]$ (Ar = 2,6-$Me_2C_6H_3$; X = Cl, Me; M = Nb,[35c] Ta[35b]). The chemical shifts of their DAD resonances are similar to that of **4**, indicating a *prone* conformation of the DAD ligand. Thus, the resonance at δ = 109.0 is assigned to the equivalent olefinic carbon atoms of the DAD ligand, while the signals corresponding to the C^α atom of the oxa- and azaniobacyclopropane systems appear at δ = 92.57 (**7**) and 75.7 (**8**); these signals shift to higher fields as compared with the acyl and iminoacyl carbon atom.[36]

In complexes **9** and **10**, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra show four protons (ABCD spin system, although for **10** only two multiplets are observable as a result of the proton overlapped signals) and five carbon resonances for the $C_5H_4SiMe_3$ ring. The data are consistent with a metal centre chiral character and therefore there is not a symmetry plane perpendicular to the (trimethylsilyl)cyclopentadienyl ring. The ^{1}H NMR spectrum of both complexes **9** and **10** show six singlets corresponding to three protons each between δ = 2.54−1.03 and 2.58−0.76, respectively. The lower field resonances in both the interval δ = 2.54, 2.00 (**9**) and 2.58, 2.04 (**10**) can be assigned to the methyl substituents of the DAD ligand. These data suggest a 2,5-diazaniobacyclopent-3-ene mode for the DAD ligand. A similar behaviour has been found by Mashima et al.[13f] in the synthesis of mixed DAD-butadiene complexes of general formulation $[M(\eta^5\text{-}C_5R_5)(\eta^2\text{-Ar,H-DAD})(\eta^4\text{-butadiene})]$ (M = Nb, R = Me, H Ar = 4-$MeOC_6H_4$; M = Ta, R = Me, H Ar = 4-$MeOC_6H_4$, 2-MeC_6H_4, Cy). The signals corresponding to the nonequivalent *o*-methylphenyl groups of the inserted isocyanide are observed as singlets at δ = 1.92 and 1.88 (**9**) and 2.02, 1.89, 1.88 and 1.74 (**10**), the two lower field resonances being assigned to the isocyanide directly bonded to the niobium atom. In addition, the rest of the signals, observed in its NMR spectra, are those expected for the proposed structures.

Conclusion

In this work, we synthesized several [(trimethylsilyl)cyclopentadienyl]niobium complexes with ene-diamido and ene-diolato ligands, through the reaction of $[NbCp'Cl_2(Me_3SiCCSiMe_3)]$ with 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph-DAD) and diketones. The spectroscopic data showed that the coordination mode of the chelating ligand depends, sensitively, on the ligand environment at the metal centre. Dichloro complexes **1**−**3** adopt a *supine* ene-diamido (**1**) or ene-diolato (**2**, **3**) structure. DFT studies have shown that the experimentally observed folding in DAD complexes (mode **A**) cannot be attributed to the π donation from the central C=C linkage because this interaction is negligible. The bonding of the ene-diamido ligand is different with respect to the conventional σ^2,π description of butadiene. The nitrogen atoms contribute to the donation through the π component and, consequently, the interaction between the niobium and carbon atoms is not significant. Reactions of dichloro complex **1** with alkylating reagents gave dialkyl complexes **4**−**6** and during the reaction course, the *supine* orientation of the ene-diamido ligand, bound to the metal centre, was flipped to the *prone* one. Dimethyl complex **4** reacts with carbon monoxide and isocyanide to give oxa- and azaniobacyclopropane derivatives **7** and **8** as a result of the migration of both methyl groups and via η^2-acyl and η^2-iminoacyl intermediates, respectively, which could not be observed. Successive isocyanide insertion reactions into the Nb−C bond take place in the oxaniobacyclopropane complex **7** leading to the expected insertion products **9**, **10**.

Experimental Section

General: All reactions and manipulations were carried out under argon using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glove-box. Solvents were refluxed in the presence of an appropriate drying agent and distilled and degassed prior to use: [D$_6$]benzene and hexane (Na/K alloy), diethyl ether (Na/benzophenone) and toluene (Na). Literature methods were employed for the synthesis of starting materials [Nb(η^5-C$_5$H$_4$SiMe$_3$)Cl$_2$(Me$_3$SiCCSiMe$_3$)][16] and 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph-DAD).[37] Reagent grades were purchased from commercial sources and used without further purification as follows: R−CO−CO−R (R = Me, Aldrich; R = Ph, Avocado), MgClR (Aldrich; R = Me 3 M in diethyl ether; R = CH$_2$SiMe$_3$, 1 M in diethyl ether; R = CH$_2$C$_6$H$_5$, 2 M in tetrahydrofuran), CO (Air Liquide) and 2,6-Me$_2$C$_6$H$_3$NC (Fluka). Infrared spectra were recorded with Perkin−Elmer 883 and Spectrum 2000 spectrophotometers (4000−200 cm^{-1}) with samples as Nujol mulls between CsI plates or polyethylene pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with Varian Unity 300 and Varian Unity 500 Plus spectrometers; chemical shifts were referenced to the ^{13}C (δ = 128) and ^{1}H (δ = 7.15) residual resonances of the [D$_6$]benzene solvent. C, H and N analyses were carried out with a Perkin−Elmer 2400 microanalyser.

[NbCp′Cl$_2$(Me,Ph-DAD)] [Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Me,Ph-DAD = PhNC(Me)C(Me)NPh] (1): A sample of [NbCp′Cl$_2$(Me$_3$SiCCSiMe$_3$)] (0.70 g, 1.49 mmol) was dissolved in hexane (20 mL) in a Schlenk tube. After addition of a hexane (15 mL) solution of 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (0.35 g, 1.49 mmol), the colour of the mixture changed to brown. The reaction mixture was stirred for 12 h at room temperature and then the resulting suspension was decanted and filtered. The residual solid was washed with cold hexane (2 × 5 mL), dried in vacuum and identified as complex **1**. Yield 0.71 g (89%). C$_{24}$H$_{29}$Cl$_2$N$_2$NbSi (537.407): calcd. C 53.64, H 5.44, N 5.21; found C 53.52, H 5.53, N 5.11.

[NbCp′Cl$_2${O(R)CC(R)O}] (R = Me, 2; Ph, 3): A solution of R−CO−CO−R (2.98 mmol; R = Me, 0.28 ml; Ph, 0.62 g) in hexane (20 mL) was added to a solution of [NbCp′Cl$_2$(Me$_3$SiCCSiMe$_3$)] (1.40 g, 2.98 mmol) in hexane (25 mL) at room temperature. The mixture was stirred for 12 h. The resulting garnet suspension was filtered, the microcrystalline solid washed with cold hexane (2 × 5 mL), dried in vacuum and identified as **2** and **3**. **2:** Yield: 1.14 g (80%). C$_{12}$H$_{19}$Cl$_2$NbO$_2$Si (387.179): calcd. C 37.23, H 4.95; found C 37.27, H 5.01. **3:** Yield: 1.26 g (85%). C$_{22}$H$_{23}$Cl$_2$NbO$_2$Si (511.321): calcd. C 51.68, H 4.53; found C 51.58, H 4.66.

[NbCp′R$_2$(Me,Ph-DAD)] (R = Me, 4; CH$_2$SiMe$_3$, 5; CH$_2$C$_6$H$_5$, 6): A solution of MgClR (2.60 mmol; R = Me, 0.87 mL of a 3 M solution in diethyl ether; CH$_2$SiMe$_3$, 2.60 mL of a 1 M solution in diethyl ether; CH$_2$C$_6$H$_5$, 1.30 mL of a 2 M solution in THF) was added to a solution of **1** (0.70 g, 1.30 mmol) in diethyl ether (30 mL) at room temperature − except for R = CH$_2$C$_6$H$_5$ at −78 °C − and the mixture was stirred for 12 h. The MgCl$_2$ formed was removed by filtration and the resulting filtrate was concentrated to a volume of ca. 10 mL. On cooling to −40 °C, red-brown microcrystalline solids (**4**−**6**) were deposited. **4:** Yield: 0.41 g (64%). C$_{26}$H$_{35}$N$_2$NbSi (496.571): calcd. C 62.89, H 7.10, N 5.74: found C 62.85, H 7.14, N 5.64. **5:** Yield: 0.50 g (60%). C$_{32}$H$_{51}$N$_2$NbSi (584.765): calcd. C 65.73, H 8.79, N 4.79: found C 65.67, H 8.69, N 4.75. **6:** Yield: 0.51 g (60%). Repeated attempts to obtain a satisfactory microanalysis on this material were unsuccessful.

[NbCp′{η^2-(O)CMe$_2$}(Me,Ph-DAD)] (7): A toluene (20 mL) solution of **4** (0.70 g, 1.40 mmol) was placed into an ampoule under CO (1 atm) and then sealed. The reaction mixture was stirred at room temperature for 5 d. Then the ampoule was opened, the solution filtered, concentrated to ca. 5 mL and cooled to −40 °C to give **7** as red microcrystalline solid. Yield 0.55 g (75%). C$_{27}$H$_{35}$N$_2$NbOSi (524.581): calcd. C 61.82, H 6.72, N 5.34; found C 61.72, H 6.68, N 5.27.

[NbCp′{η^2-(ArN)CMe$_2$}(Me,Ph-DAD)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (8): A solution of isocyanide 2,6-Me$_2$C$_6$H$_3$NC (0.18 g, 1.40 mmol) in hexane (10 mL) was added at room temperature to a reddish solution of **4** (0.70 g, 1.40 mmol) in hexane (30 mL) and stirred for 12 h. The resulting orange solution was filtered, concentrated to ca. 10 mL and cooled to −40 °C to give **8** as orange microcrystalline solid. Yield 0.62 g (70%). C$_{35}$H$_{44}$N$_3$NbSi (627.749): calcd. C 66.97, H 7.06, N 6.69; found C 67.02, H 7.16, N 6.58.

[NbCp′{η^2-(O)CMe$_2$−(CNAr)$_x$}(Me,Ph-DAD)] [Ar = 2,6-Me$_2$-C$_6$H$_3$; *x* = 1 (9); 2 (10)]. 9: A stirred solution of **7** (0.70 g, 1.33 mmol) in hexane (25 mL) was treated with 2,6-Me$_2$C$_6$H$_3$NC (0.17 g, 1.33 mmol) in a 1:1 molar ratio and under rigorously anhydrous conditions for 48 h. The resulting solution was concentrated to ca. 10 mL and cooled to −40 °C to give **9** as dark brown microcrystalline solid. Yield 0.52 g (60%). C$_{36}$H$_{44}$N$_3$NbOSi (655.759): calcd. C 65.94, H 6.76, N 6.41; found C 65.90, H 6.67, N 6.39. **10. Method A:** A dark-brown solution of **9** (0.70 g, 1.06 mmol) in hexane (30 mL) under rigorously anhydrous conditions in a Schlenk tube. After addition of a hexane (10 mL) solution of isocyanide 2,6-Me$_2$C$_6$H$_3$NC (0.14 g, 1.06 mmol) the colour of the mixture changed to pale-brown. The reaction mixture was stirred for 48 h at room temperature and then the resulting suspension was decanted and filtered. The residual pale-brown solid was washed with cold hexane (2 × 5 mL), dried in vacuum and identified as **10**. **Method B:** The oxaniobacyclopropane complex **7** (0.70 g, 1.33 mmol) was dissolved in 30 mL of hexane and isocyanide 2,6-Me$_2$C$_6$H$_3$NC (0.34 g, 2.66 mmol) in a 1:2 molar ratio. The solution was stirred and the brown solid formed after 4 d, it was collected by decanting the solvent, washed with 5 mL of cold hexane and identified as **10**. Yield 0.54 g (65%). Repeated attempts to obtain a satisfactory microanalysis on this material were unsuccessful.

Computational Details: The electronic structures and geometries of the model complexes were computed within the density functional theory at the BP86[38] and B3LYP[39] levels using the LANL2DZ[40] basis set. A set of *d* polarisation functions was added to Cl, C and N atoms. Only the results at the B3LYP level of theory have been discussed in the paper. BP86 results are completely equivalent and they have not been discussed but included as Supporting Information. All the optimised geometries were characterized as local energy minima by diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). All the DFT calculations were performed using the Gaussian 98 suite of programs.[41] Molecular orbitals were visualised using the Chem3D Pro program.[42] The FMO analyses were performed with CACAO[43] using the coordinates, at the B3LYP level, of the optimised model complexes.

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proximately planar. This state is characterized by one imaginary frequency: D. del Río, A. Galindo, unpublished results.

[27] The *prone* configuration of butadiene ligand in **II** is 13.6 kcal mol^{-1} less stable than the *supine* isomer: D. del Río, A. Galindo, unpublished results.

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[32] Following the suggestion of one referee, we performed calculations on complex NbCpMe$_2$(HNCHCHNH), as the simplest model of complexes **4**−**6**. The *prone* configuration of the DAD ligand in this model is a local minimum. However, the optimisation of the *supine* conformation was unsuccessful. Efforts to optimise this isomer yielded a planar five-membered ring where the metal−DAD moiety has a 2,5-diaza-1-metallacyclopent-3-ene structure, that is characterized by two imaginary frequencies. A complete report of this analysis will be published separately: D. del Río, A. Galindo, unpublished results.

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