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Hydrazido(2−) complexes of niobocene

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The new compounds [Nb(η-C_5H_4R)(η-C_5H_4R')Cl($NNMe_2$)] (R = H or Me; R′ = H or Me), [Nb(η^5-C_5H_4R)$_2$-(η^1-C_5H_4R)($NNMe_2$)] (R_3 = H_x or Me_y, $x + y = 3$), [Nb{CMe_2(η^5-C_5H_4)(η^1-C_5H_4)}(η^5-C_5H_5)($NNMe_2$)] and [Nb(η-C_5H_5)$_2$(thf)($NNMe_2$)][BPh_4] (thf = tetrahydrofuran) have been prepared. The crystal structure of [Nb(η-C_5H_4Me)$_2$Cl($NNMe_2$)] has been determined. A variable-temperature NMR study of [Nb(η^5-C_5H_5)$_2$-(η^1-C_5H_5)($NNMe_2$)] reveals a fluxional interchange of the three cyclopentadienyl rings. This compound has been shown to react with the electrophiles $SiMe_3Cl$, $FeCl_2$·1.5thf, [NMe_3H]Cl and [Nb(η-C_5H_5)Cl_2($NNMe_2$)] to form in each case [Nb(η-C_5H_5)$_2$Cl($NNMe_2$)]. A variable-temperature NMR study of [Nb{CMe_2(η^5-C_5H_4)(η^1-C_5H_4)}-(η^5-C_5H_5)($NNMe_2$)] shows the presence of two interconvertible diastereomers. The bis- and tris-cyclopentadienyl compounds have been shown to undergo exchange of their cyclopentadienyl rings in solution with each other or Li(C_5H_4R). The compound [Nb(η-C_5H_5)(OBu^t)$_2$($NNMe_2$)] has also been shown to undergo a cyclopentadienyl ligand-exchange reaction.

In recent years the synthesis of so-called ‘π-loaded’ systems has attracted much interest.[1] In particular, compounds with a local pseudo-C_{3v} array of σ + 2π ligands have one combination of the ligand-based orbitals for which there is no match on the metal centre, leading to formal 20-electron counts.[2,3] The σ + 2π ligands include oxide, imide and alkyne, provided they are acting as four-electron ligands, and also η^5-cyclopentadienyl. Compounds with these ligands have found applications in homogeneous catalysis.[4] Hydrazido(2−) metallocene complexes known prior to this work are [M(η-C_5H_5)$_2${NN($SiMe_3$)$_2$}] (M = Ti,[5] V,[5,6] Cr[5] or Mn[5]) and [WH(η-C_5H_5)$_2${NNH(*p*-C_6H_4F)}][BF_4],[7] although only the vanadium and tungsten examples were crystallographically characterised. Here we report the synthesis and reactivity of a range of hydrazido(2−) niobocene derivatives.

Results and Discussion

Treatment of [Nb(η-C_5H_5)Cl_2($NNMe_2$)][8] with 1 equivalent, or an excess, of Li(C_5H_5) in tetrahydrofuran resulted in a rapid change from deep red to orange and yellow needles of the compound [Nb(η-C_5H_5)$_2$Cl($NNMe_2$)] **1** were isolated. The substitution of the second chlorine atom to form a tris(cyclopentadienyl) compound proceeds much more slowly than the initial substitution of the first. For this reason, a slight excess of Li(C_5H_5) was used to ensure removal of the toluene-soluble starting material. Similarly, reaction of [Nb(η-C_5H_4Me)-Cl_2($NNMe_2$)][8] with Na(C_5H_5) resulted in formation of the mixed-ring compound [Nb(η-C_5H_5)(η-C_5H_4Me)Cl($NNMe_2$)] **2**.

Treatment of [Nb(η-C_5H_4Me)Cl_2($NNMe_2$)] with a large excess of Li(C_5H_4Me) gave an orange solution. Despite stirring for 42 h, in an attempt to form the trisubstituted compound [Nb(η-C_5H_4Me)$_3$($NNMe_2$)], only [Nb(η-C_5H_4Me)$_2$Cl($NNMe_2$)] **3** was formed. The NMR and mass spectral data showed no evidence for [Nb(η-C_5H_4Me)$_3$($NNMe_2$)]. Also there was only one signal in the NMe_2 region. Crystals of **3** were grown by slow evaporation of a pentane solution, one of which was selected for a structure determination. The molecular structure is shown in Fig. 1, and selected bond lengths and angles in Table 1.

Compound **3** is monomeric in the solid state. The structure may be compared to those of [V(η-C_5H_5)$_2${NN($SiMe_3$)$_2$}][5,6] and [WH(η-C_5H_5)$_2${NNH(*p*-C_6H_4F)}][BF_4].[9] In the former the short V–N bond, the long N–N bond and the V–N–N bond angle of 180° indicate that the hydrazide ligand acts as a four-electron donor. However, the bond angle of 146.6(5)° in the tungsten compound, together with the long W–N bond, suggests that the hydrazide ligand acts as a two-electron donor. The hydrazide ligand in **3** is linear, the Nb–N bond length of 1.794(2) Å compares with 1.789(2) Å for the eighteen-electron compound [Nb(η-C_5H_5)Cl_2($NNMe_2$){P(OMe)$_3$}][8] and with 1.756(3) Å in the analogous imido compound [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)-(NBu^t)].[10] The N–N bond length of 1.340(3) Å in **3** is similar to that found in [Nb(η-C_5H_5)Cl_2($NNMe_2$){P(OMe)$_3$}] [1.338(2) Å] and to 1.369(9) Å in the vanadium compound [V(η-C_5H_5)$_2$-{NN($SiMe_3$)$_2$}].[6] However, the N–N bond length in [{Nb(η-C_5H_5)Cl_2}(μ-$NNMe_2$){Nb(η-C_5H_5)Cl_2($NNMe_2$)}] is 1.39(2) Å.[8] The sum of the bond angles around the NMe_2 group in compound **3** is 342.1° and compares with a sum of 340.2° for [Nb-(η-C_5H_5)Cl_2($NNMe_2$){P(OMe)$_3$}]. This suggests the terminal nitrogen atom is tending towards sp^3 hybridisation. It thus appears that the Nb–N bond order in **3** is slightly less than three and the N–N bond order is slightly greater than one.

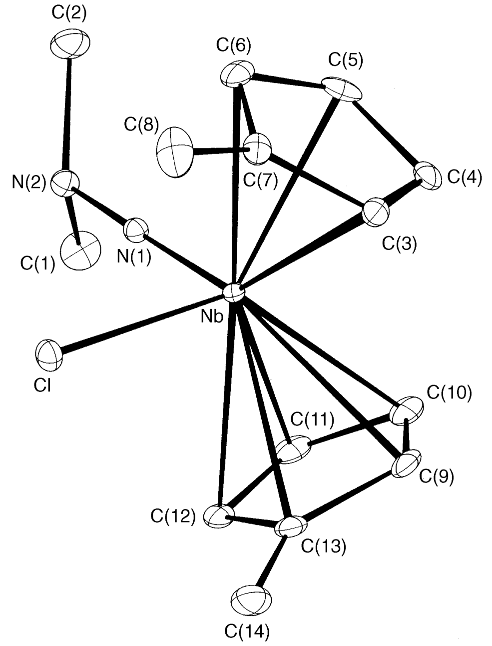


Fig. 1 Perspective view of the structure of compound **3**. Hydrogen atoms are omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) in $[Nb(\eta\text{-}C_5H_4Me)_2Cl(NNMe_2)]$

Nb–Cl	2.4608(7)	C(13)–C(14)	1.504(5)
Nb–N(1)	1.794(2)	N(2)–C(2)	1.462(4)
Nb–C(3)	2.572(3)	C(11)–C(12)	1.398(4)
Nb–C(4)	2.472(3)	C(12)–C(13)	1.430(4)
Nb–C(5)	2.410(3)	C(13)–C(9)	1.386(4)
Nb–C(6)	2.471(3)	C(9)–C(10)	1.414(5)
Nb–C(7)	2.580(2)	C(10)–C(11)	1.410(5)
Nb–C(9)	2.566(3)	C(3)–C(4)	1.395(4)
Nb–C(10)	2.444(3)	C(4)–C(5)	1.418(4)
Nb–C(11)	2.455(3)	C(5)–C(6)	1.403(5)
Nb–C(12)	2.473(3)	C(6)–C(7)	1.402(4)
Nb–C(13)	2.572(2)	C(7)–C(3)	1.412(4)
N(1)–N(2)	1.340(3)	C(7)–C(8)	1.492(4)
N(2)–C(1)	1.458(4)		
Cl–Nb–N(1)	92.74(7)	Nb–N(1)–N(2)	178.8(2)
Cl–Nb–Cp(1)	105.35	N(1)–N(2)–C(1)	113.9(2)
Cl–Nb–Cp(2)	104.39	N(1)–N(2)–C(1)	114.4(2)
N(1)–Nb–Cp(1)	112.07	C(1)–N(2)–C(2)	113.8(3)
N(1)–Nb–Cp(2)	111.84	Bending angle, θ	126.74

Cp(1) and Cp(2) denote the centroids of the C(3)–C(7) and C(9)–C(13) rings respectively; θ is the angle between the normals to these ring planes.

The Nb–C (ring) bond distances of compound **3** vary between 2.410(3) and 2.580(2) Å and occur as two short, two medium and one long bonds to each ring. A similar distribution was observed in other cyclopentadienylmetal hydrazido and alkoxylimido compounds.[8,11] However, the Nb–C bonds are all *ca.* 0.05–0.1 Å longer than in the eighteen-electron compound $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)\{P(OMe)_3\}]$. This lengthening suggests the hydrazide acts as a four-electron ligand in which case two electrons must be accommodated in a ligand-based orbital which has some niobium–ring antibonding character.[3] Similar lengthening of the Nb–C bonds has been noted in the closely related complex $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NBu^t)]$. There is no evidence in **3** for an 'allyl-ene' type distortion of the C_5 rings since all the C–C bonds lie in the range 1.386(4)–1.430(4) Å. The (ring centroid, Cp)–niobium–(ring centroid) angle of 126.74° compares well with those of 124.51, 127.9 and 125.4° found for the analogous imido complexes $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NBu^t)]$, $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ and $[Mo(\eta\text{-}C_5H_4Me)_2(NBu^t)Me]I$.[3] In each case these angles are considerably compressed from values typically found for niobocene compounds, such as 141.6° in $[NbH_3(\eta\text{-}C_5H_5)_2]$,[12] 141.2° in $[K(18\text{-}crown\text{-}6)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane),[13] 132.4° in $[Nb(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Et]$[14,15] and 130.9° in $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$.[16] This compression of the Cp–M–Cp angles suggests that the hydrazide(2−) ligand acts as a good π acceptor and poor σ donor.[17] The Nb–Cl single bond length of 2.4608(7) Å compares with that found in $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)\{P(OMe)_3\}]$, indicating that no d_π–p_π bonding is taking place.[18]

Treatment of either $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$ or compound **1** with an excess of $Li(C_5H_5)$ in tetrahydrofuran for *ca.* 48 h gave the tris(cyclopentadienyl) compound $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ **4** as a yellow powder. Similarly, $[Nb(\eta^5\text{-}C_5H_4Me)_2(\eta^1\text{-}C_5H_4Me)(NNMe_2)]$ **5** could be synthesized from $[Nb(\eta\text{-}C_5H_4Me)Cl_2(NNMe_2)]$ using an excess of $Li(C_5H_4Me)$. However, in this case *ca.* 3 weeks were required to give a complete reaction. Attempts to accelerate the reactions by refluxing resulted in lower yields and increased difficulty of purification. The compounds **4** and **5** are fluxional on the NMR time-scale. The ^1H NMR spectrum of **4** at 223 K shows the presence of three slightly broad bands in the ratio 2:2:1 assignable to a $\sigma\text{-}C_5H_5$ ring undergoing rotation about the Nb–C bond. The slightly broad singlet at δ 5.12 is attributable to the two $\eta\text{-}C_5H_5$ rings. The NMR spectrum of the related compound $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NBu^t)]$ at 223 K shows slow-exchange conditions about the Nb–C bond for the $\sigma\text{-}C_5H_5$ ring.[10] This presumably reflects the greater steric bulk of a *tert*-butylimido group relative to a dimethylhydrazide(2−) ligand.

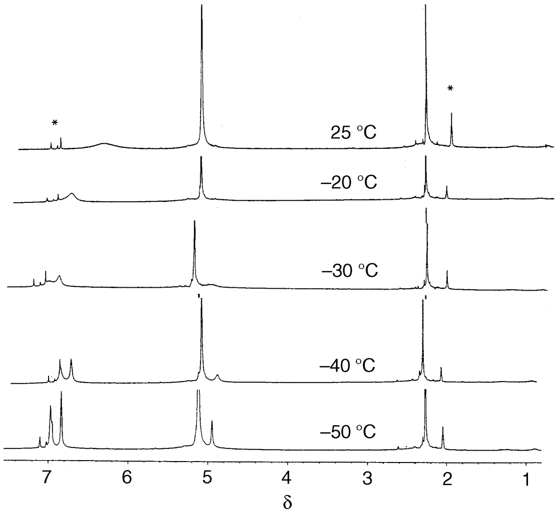


Fig. 2 Variable-temperature ^1H NMR spectra of $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ **4** recorded in $C_6D_5CD_3$ at 500 MHz. * Denotes the residual solvent peaks

On warming the spectrum of compound **4** changes and the peaks attributable to the $\eta^1\text{-}C_5H_5$ ring broaden and disappear, and at 20 °C a new broad peak appears with a chemical shift corresponding to the weighted average of the slow-exchange spectrum. This behaviour is consistent with the onset of a 1,3 ring-shift process of the $\eta^1\text{-}C_5H_5$ ring.[19] The spectra are shown in Fig. 2. The signal at δ 5.12 remains unchanged at 20 °C but further warming causes it to broaden and coalesce with that of the $\eta^1\text{-}C_5H_5$, consistent with the onset of fast exchange between the three rings. These fluxional processes are analogous to those in the isoelectronic species $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NOBu^t)]$,[20] $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NBu^t)]$[10] and $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NO)]$.[21] Green *et al.*[10] have suggested that the mechanism of the scrambling of the η^1- and $\eta^5\text{-}C_5H_5$ rings in the analogous compound $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NBu^t)]$ proceeds *via* an $\eta^3:\eta^3$ intermediate and a similar mechanism seems reasonable in the present case.

By analogy with recent studies on the synthesis of *ansa*-metallocenes of zirconium[22,23] and niobium[24] the reaction between the compound $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$ and $Li_2[CMe_2(C_5H_4)_2]$ has been explored. The ^1H NMR and mass spectra of the pentane-soluble extract from this reaction show the presence of three compounds, namely $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$ **1**, $[Nb\{CMe_2(\eta\text{-}C_5H_4)_2\}Cl(NNMe_2)]$ **6** and $[Nb\{CMe_2(C_5H_4)_2\}(C_5H_5)(NNMe_2)]$ **7**. The solubility of **6** was intermediate between those of **1** and **7** and it could not be crystallised in a pure state. Hence full characterising data for **6** were not obtained.

There are a number of possible isomeric forms of compound **7**, with the added complication that it is also fluxional on the NMR time-scale. Thus the room-temperature ^1H NMR spectrum is broad and shows peaks from *ca.* δ 1 to 7. Cooling to −40 °C causes these signals to sharpen showing there are two different molecules present in the ratio of *ca.* 2:1. Thus, there are two signals attributable to the NMe_2 groups, two pairs of signals attributable to the CMe_2 groups and two large singlets attributable to the C_5H_5 ligands. This ratio changes as the temperature is changed. The singlets for the cyclopentadienyl ligands show both the molecules have the general form $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)(NNMe_2)]$, rather than the alternative formulation $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)_2\}(\eta^1\text{-}C_5H_5)(NNMe_2)]$. Since the molecules possess two chiral centres, one at niobium

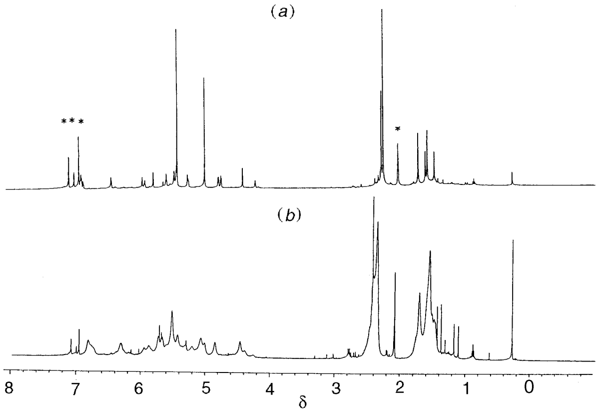


Fig. 3 Proton NMR spectra of $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)(NNMe_2)]$ **7** recorded at 500 MHz in $C_6D_5CD_3$. * Denotes the residual solvent peaks. (*a*) At −40 °C, (*b*) at 25 °C

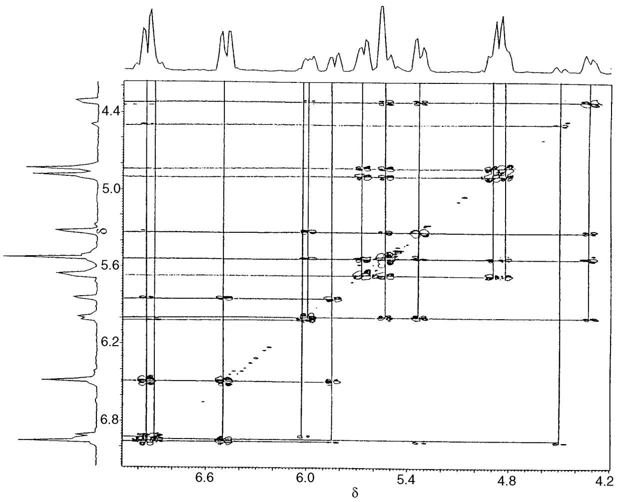
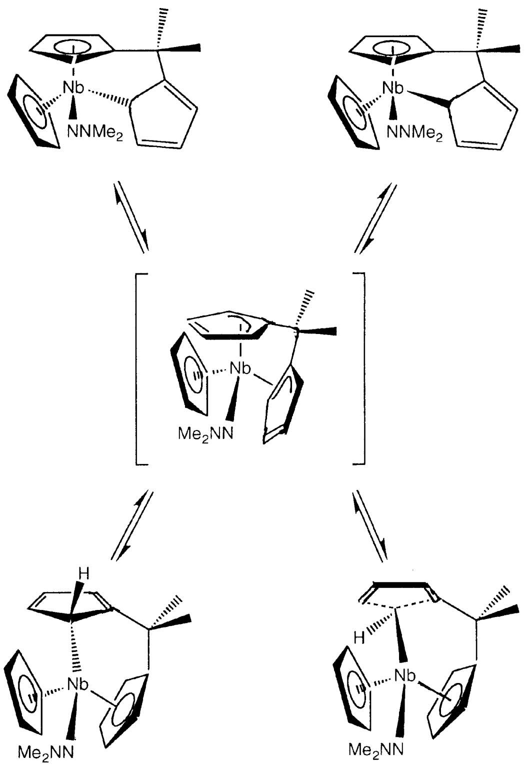


Fig. 4 The ^1H–^1H COSY NMR spectrum recorded at −40 °C of the ring-proton region of $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)(NNMe_2)]$ **7**



Scheme 1 Proposed mechanism for the interconversion of the diastereomers of compound **7**. Note that molecules on the same horizontal row are diastereomers, distinguishable by NMR spectroscopy, whereas those in vertical columns are enantiomers and are indistinguishable by NMR spectroscopy

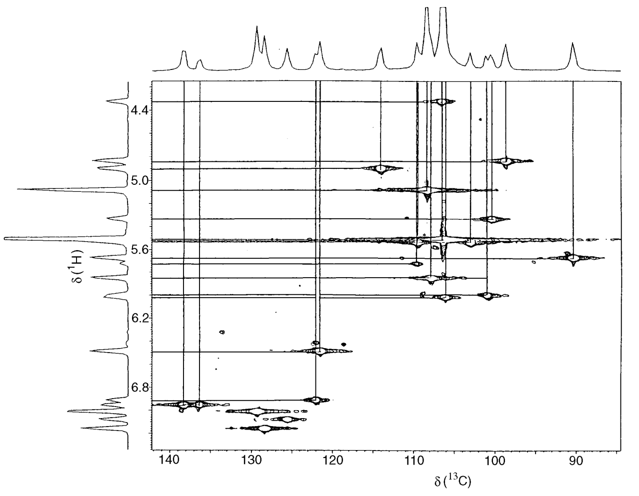


Fig. 5 The ^{13}C–^1H COSY NMR spectrum recorded at −40 °C of the ring region of $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)(NNMe_2)]$ **7**

and the other at the σ-bound carbon atom, the spectra may be assigned to the presence of two diastereomers.

Comparison of the spectrum at −40 [Fig. 3(*a*)] with that at 20 °C [Fig. 3(*b*)] reveals that all the peaks become broad as the temperature increases, including those attributable to the NMe_2 groups. This suggests that a fluxional process occurs which involves a change of environment for every ligand in the molecule. This is in contrast to the unbridged analogue $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ **4** in which the NMe_2 group maintains a constant environment and gives rise to a sharp ^1H NMR signal at all temperatures. The spectra are consistent with the interconversion of the two pairs of diastereomers in which the bridging ligand varies from η^5:η^1 to an η^3:η^3 intermediate. This intermediate has a plane of symmetry and can relax to each of either of the pairs of enantiomers in solution. This mechanism is shown in Scheme 1.

A detailed assignment of the spectra of compound **7** has been made assisted by ^1H–^1H and ^{13}C–^1H NMR correlation (COSY) spectra. The one-dimensional proton spectra recorded at 25 and −40 °C are shown in Fig. 3 and the ^1H–^1H and ^{13}C–^1H correlation spectra in Figs. 4 and 5 respectively. Whilst the ^{13}C NMR spectrum recorded at −40 °C is fully resolved, showing all 30 separate resonances arising from the two diastereomers, the ^1H NMR spectrum, which is spread over a smaller chemical shift range, displays some overlapping of resonances, complicating the assignment. In each diastereomer the C–H correlations for the NMe_2 group, the backbone CMe_2 group and the cyclopentadienyl ring are clear. These can be assigned to the major and minor isomers of the molecule by virtue of the proton integrals, which show that the two isomers exist in a roughly 2 : 1 ratio at −40 °C. There remains the problem of assigning the eight protons and associated carbon atoms of each *ansa* ligand. These can be divided into four groups of four protons each, with associated carbons, which will be termed the A, B, C and D rings. In the ^{13}C-{^1H} NMR spectrum the signals attributable to the sp^3-hybridised carbon atoms which form the bridge and the NMe_2 group are found in the high-field region, below δ 50, whilst the signals from the carbon atoms in the cyclopentadienyl rings are at low field, above δ 90. The two remaining signals at δ 54.7 and 58.6 are then assigned to the *ipso* Nb–C carbon atoms for the two diastereomers.

The proton signals can be divided into four groups of four, corresponding to the four ring systems, as follows: ring A, δ 4.50, 6.90, 6.02, either 5.50 or 5.72; ring B, δ 4.32, 5.32, 5.53, 5.95; ring C, δ 4.84, 4.90, 5.32, 5.66; ring D, δ 5.85, 6.48, 6.96, either 5.72 or 5.50. The signals at δ 4.50 and 5.32 correlate with the *ipso*-carbon atoms. Thus it can be seen that ring A is an η^1-C$_5$H$_4$ ring. Unfortunately, since two proton peaks overlap at δ 5.32, it cannot be definitely determined which of rings B and C is the other η^1-C$_5$H$_4$ ring. Ring D is assigned to an η^5-C$_5$H$_4$ ring. The assignments of rings A–D to major and minor diastereomers were made by consideration of the integrals of the carbon signals and are shown in Table 2. The rings A and B belong to the minor isomer, and C and D to the major isomer. Secondly, since A is an η^1-C$_5$H$_4$ ring, then B must be η^5-C$_5$H$_4$ and so C must be the second η^1-C$_5$H$_4$ ring. The signal at δ 5.50 may be assigned to ring D and that at δ 5.72 to A. The full correlation is set out in Table 3.

Whether the *ipso*-carbon in the η^1-C$_5$H$_4$ rings is α or β to the bridgehead quaternary carbon cannot be answered definitively from the NMR data. However, the crystallographically characterised complex [Nb{CMe$_2$(η^5-C$_5$H$_4$)(η^1-C$_5$H$_4$)}(η^5-C$_5$H$_5$)(NBu^t)] showed that the *ipso*-carbon was α to the bridgehead,[25] and so it seems likely that a similar situation holds here. The data do not allow identification of the relative stereochemistries of the two stereocentres. The large chemical shift difference between the signals due to the two chemically similar *ipso*-protons (δ 4.50 and 5.32) would seem to suggest they are in magnetically very distinct environments, possibly due to the fact that the *ipso*-proton lies on the same side of the molecule as the hydrazide ligand in one diastereomer but on the opposite side in the other.

It was noticed that a ligand-exchange reaction took place during the synthesis of compound **7** in which a cyclopentadienyl ligand was transferred from one niobium centre to another. A similar reaction has been reported for related twenty-electron molybdenum compounds in the reaction between [Mo(η-C$_5$H$_5$)$_2$(NBu^t)] and Na(C$_5$H$_4$Me) which led to all three possible compounds [Mo(η-C$_5$H$_5$)$_2$(NBu^t)], [Mo(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)(NBu^t)] and [Mo(η-C$_5$H$_4$Me)$_2$(NBu^t)].[26,27] Accordingly, the conditions under which the ligand-exchange reaction occurs have been examined. The reaction between compound **1** and a slight excess of Li(C$_5$H$_4$Me) was monitored by ^{1}H NMR and mass spectrometry. The NMR spectrum showed the presence of three major components corresponding to the bis(cyclopentadienyl) compounds [Nb(η-C$_5$H$_5$)$_2$Cl(NNMe$_2$)] **1** and [Nb(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)Cl(NNMe$_2$)] **2** and an unidentified tris(cyclopentadienyl) compound. The mass spectrum allowed five products to be identified, namely, **1**, **2**, **4**, [Nb(C$_5$H$_5$)$_2$(C$_5$H$_4$Me)(NNMe$_2$)] **8** and [Nb(C$_5$H$_5$)(C$_5$H$_4$Me)$_2$(NNMe$_2$)] **9**. In each case, the parent ion and the $[M - 58]^+$ peak (*i.e.* $[M - \mathrm{NNMe_2}]^+$, which was generally the first strong peak in mass spectra of the pure compounds) could be identified. The two remaining possible equilibrium products are [Nb(η-C$_5$H$_4$Me)$_2$Cl(NNMe$_2$)] **3** and [Nb(η^5-C$_5$H$_4$Me)$_2$(η^1-C$_5$H$_4$Me)(NNMe$_2$)] **5** and these were not detected. This is consistent with the long reaction times required for their synthesis.

Table 2 Partial C–H correlation for the ring protons in compound **7**

δ(^{13}C)	δ(^{1}H)	Ring
121.6	6.48	D
98.8	4.85	C
107.9	5.84	D
138.8	6.96	D
90.5	5.66	C
109.6	5.50	D or A
114.1	4.90	C
122.2	6.90	A
106.2	6.02	A
109.8	5.72	A or D
101.2	5.95	B
100.5	5.32	B
103.1	5.53	B
106.6	4.32	B

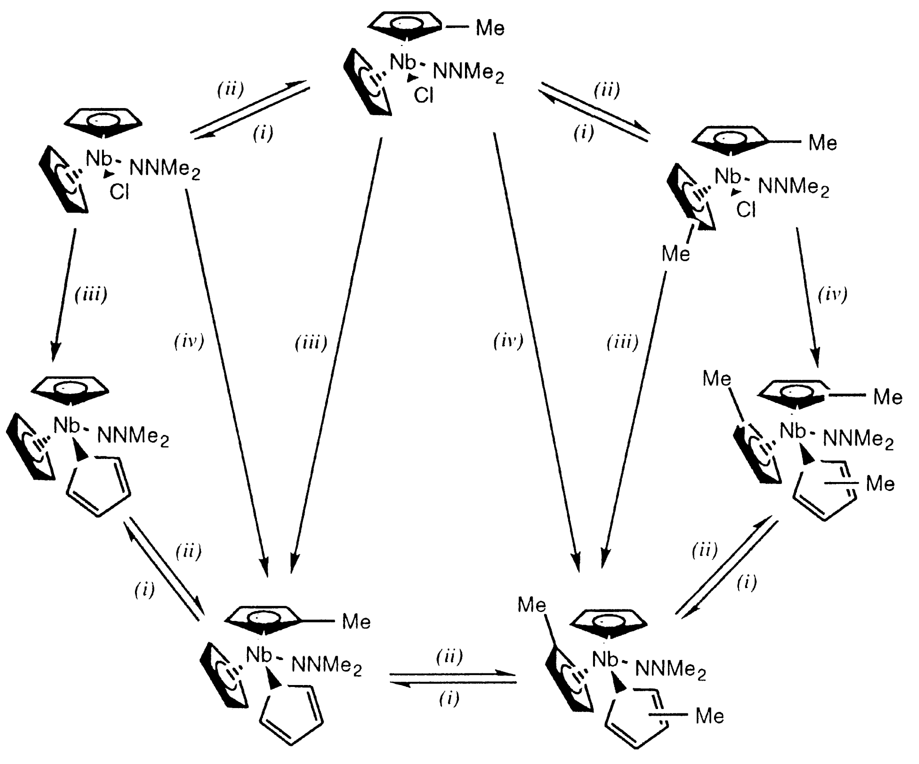
An exchange study was attempted using a mixture of the tris(cyclopentadienyl) compound **4** and Li(C$_5$H$_4$Me). The mixture was allowed to stir in tetrahydrofuran for 19 d. The ^{1}H NMR spectrum, recorded in C$_6$D$_6$, showed four peaks in the NMe$_2$ region at chemical shifts of δ 2.39, 2.43, 2.46 and 2.49. All other peaks were broad, as is to be expected from a mixture of fluxional compounds. The mass spectrum showed that each of the four possible tris(cyclopentadienyl) compounds {*i.e.* [Nb(C$_5$H$_5$)$_x$(C$_5$H$_4$Me)$_{3-x}$(NNMe$_2$)], $x = 0$–3, compounds **4**, **5**, **8** and **9**} had been formed. It is thus clear that the cyclopentadienyl ligand substitution may occur in the presence of either chloride or η^1-cyclopentadienyl ligands.

It was of interest to see whether the presence of 'free cyclopentadienide' was needed to effect the ligand-exchange reaction, or whether a niobium-co-ordinated cyclopentadienyl ligand would be sufficient. Accordingly, a mixture of [Nb(η^5-C$_5$H$_5$)$_2$(η^1-C$_5$H$_5$)(NNMe$_2$)] and [Nb(η^5-C$_5$H$_4$Me)$_2$(η^1-C$_5$H$_4$Me)(NNMe$_2$)] was allowed to stir for 20 d in tetrahydrofuran (thf). The ^{1}H NMR spectrum of the pentane extract at the end of that time showed four peaks, attributable to the four possible mixed-ring compounds **4**, **5**, **8** and **9**. As a control experiment the mass spectrum of a mixture of solid **4** and **5** was determined. Only peaks attributable to **4** and **5** were observed, indicating that no ligand exchange had occurred. This shows that the ligand-exchange reaction is a genuine solution phenomenon and does not arise by scrambling within the mass spectrometer.

Compound **4** and an excess of LiCl were dissolved in thf and allowed to stir for 3 weeks. After that time no substitution of the η^1-cyclopentadienyl ligand had taken place, as evidenced by the mass and ^{1}H NMR spectra of the product. It is thus appar-

Table 3 Complete NMR data for compound **7** recorded at −40 °C in C$_6$D$_5$CD$_3$

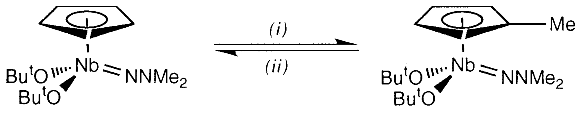
	Major isomer			Minor isomer		
Assignment	δ(^{1}H)	δ(^{13}C)	Ring	δ(^{1}H)	δ(^{13}C)	Ring
η^5-C$_5$H$_4$, q	—	132.0 or 158.8	D	—	162.0 or 139.1	B
η^5-C$_5$H$_4$	6.96	138.8	D	5.95	101.2	B
η^5-C$_5$H$_4$	6.48	121.6	D	5.53	103.1	B
η^5-C$_5$H$_4$	5.84	107.9	D	5.32	100.5	B
η^5-C$_5$H$_4$	5.50	109.6	D	4.32	106.6	B
η^1-C$_5$H$_4$, q	—	158.8 or 132.0	C	—	139.1 or 162.0	A
η^1-C$_5$H$_4$	5.66	90.5	C	6.90	122.2	A
η^1-C$_5$H$_4$	4.90	114.1	C	6.02	106.2	A
η^1-C$_5$H$_4$	4.85	98.8	C	5.72	109.8	A
η^1-C$_5$H$_4$, *ipso*	5.32	54.7	C	4.50	58.5	A
η^5-C$_5$H$_5$	5.51	106.5		5.01	108.4	
N(CH$_3$)$_2$	2.34	44.0		2.38	45.4	
C(CH$_3$)$_2$, q	—	35.8		—	35.7	
C(*C*H$_3$)$_2$	1.65	31.2		1.55	32.9	
C(*C*H$_3$)$_2$	1.80	26.2		1.69	25.7	



Scheme 2 The cyclopentadienyl exchange reactions amongst compounds **1**–**5**, **8** and **9**. (*i*) $+\mathrm{Li(C_5H_5)}$, $-\mathrm{Li(C_5H_4Me)}$; (*ii*) $+\mathrm{Li(C_5H_4Me)}$, $-\mathrm{Li(C_5H_5)}$; (*iii*) $+\mathrm{Li(C_5H_5)}$, $-\mathrm{LiCl}$; (*iv*) $+\mathrm{Li(C_5H_4Me)}$, $-\mathrm{LiCl}$

ent that substitution of a cyclopentadienyl ligand by lithium cyclopentadienide is a reversible reaction, but substitution of chloride is irreversible. The available pathways for the cyclopentadienyl exchange reactions are shown in Scheme 2.

It was of interest to see if similar ring-exchange reactions would occur with the related compound $[\mathrm{Nb(\eta\text{-}C_5H_5)(OBu^t)_2(NNMe_2)}]$,[8] which by virtue of the lone pairs on the alkoxide ligands may also be considered to be π loaded. A mixture of $[\mathrm{Nb(\eta\text{-}C_5H_5)(OBu^t)_2(NNMe_2)}]$ and $\mathrm{Li(C_5H_4Me)}$ was allowed to react in tetrahydrofuran for 19 d and the products then analysed by ^{1}H NMR spectroscopy. This showed that a ligand exchange had occurred such that the major component of the mixture was the starting material with a small amount of the methylcyclopentadienyl analogue $[\mathrm{Nb(\eta\text{-}C_5H_4Me)(OBu^t)_2(NNMe_2)}]$. These products were identified by comparison of their ^{1}H NMR spectra with those of authentic samples. No other species were present, *i.e.* no signals attributable to a compound such as $[\mathrm{Nb(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)(OBu^t)(NNMe_2)}]$ derived from substitution of an alkoxide ligand. This reaction is outlined in Scheme 3.



Scheme 3 The cyclopentadienyl exchange reaction at $[\mathrm{Nb(C_5H_4R)(OBu^t)_2(NNMe_2)}]$. (*i*) $\mathrm{Li(C_5H_4Me)}$; (*ii*) $\mathrm{Li(C_5H_5)}$

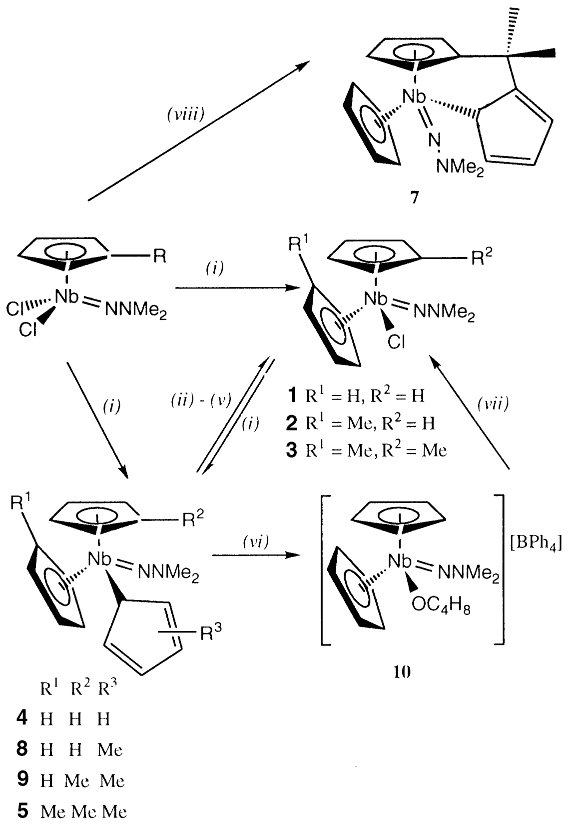
In a further study of the lability of the σ-cyclopentadienyl ring the tris(cyclopentadienyl) compound **4** in tetrahydrofuran was treated with an excess of trimethylsilyl chloride. The ^{1}H NMR spectrum of the product showed a *ca.* 4:3 ratio of the starting material **4** and the bis(cyclopentadienyl) compound $[\mathrm{Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)}]$ **1**. Similarly, a mixture of **4** and an excess of iron(II) chloride was stirred in tetrahydrofuran. After removal of solvent, volatiles sublimation under reduced pressure gave ferrocene. The involatile residue was shown by ^{1}H NMR spectroscopy to be compound **1**. Despite the excess of iron(II) chloride, there was no evidence for the substitution of a second cyclopentadienyl ligand to form the monocyclopentadienyl compound $[\mathrm{Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)}]$. Also the compound **4** in tetrahydrofuran reacted with $[\mathrm{NMe_3H}]\mathrm{Cl}$ to give **1**. Finally, reaction between **4** and $[\mathrm{Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)}]$ resulted in the formation of the comproportionation product **1**.

Recently, electron-poor metallocene compounds have received much attention as Ziegler–Natta catalysts[28] and C–H activation agents.[29,30] Compound **4** appeared to be a suitable starting material to attempt to synthesize such a compound since it was clear that the η^1 ring could be readily substituted. A tetrahydrofuran solution of $[\mathrm{C_6H_5NMe_2H}][\mathrm{BPh_4}]$ was added to a tetrahydrofuran solution of **4** to give the salt $[\mathrm{Nb(\eta\text{-}C_5H_5)_2(thf)(NNMe_2)}][\mathrm{BPh_4}]$ **10** as an orange powder. The ^{1}H NMR spectrum shows peaks attributable to two equivalent cyclopentadienyl rings, the $\mathrm{NMe_2}$ group, the ligated tetrahydrofuran molecule and the phenyl groups in the counter ion. The signal attributable to the $\mathrm{NMe_2}$ group is shifted strongly upfield (δ 3.24 in $[^2\mathrm{H_2}]$dichloromethane) in comparison with a shift of δ 2.92 for compound **1** in the same solvent); this upfield shift reflects the decreased electron density at the niobium centre in the cationic species. Attempts to measure the ^{13}C-{^{1}H} NMR spectrum of **10** were foiled by the decomposition of the $[^2\mathrm{H_2}]$dichloromethane solution of the compound, even in a sealed NMR tube. Over the course of a few hours the peaks attributable to **10** disappeared, to be replaced by peaks attributable to the bis(cyclopentadienyl) compound $[\mathrm{Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)}]$ **1**. A large singlet appeared in the aromatic region, which was assigned as $\mathrm{C_6H_5D}$. An ^{11}B NMR spectrum showed the disappearance of the quaternary peak at δ −6.5, attributable to the $\mathrm{BPh_4}^-$ ion, and the formation of a new tertiary boron peak at δ 67, which was assigned to $\mathrm{BPh_3}$. It thus appeared that the dichloromethane solvent was causing decomposition of the cation.

Scheme 4 sets out the syntheses and reactivity of the new compounds discussed in this paper.

Experimental

All preparations and manipulations of air- and/or moisture-



Scheme 4 Summary of the new syntheses: (*i*) Li(C_5H_4R), thf; (*ii*) [NMe_3H]Cl, thf; (*iii*) $FeCl_2$·1.5thf, thf; (*iv*) $SiMe_3Cl$, thf; (*v*) [Nb(η-C_5H_5)Cl_2($NNMe_2$)], thf; (*vi*) [$C_6H_5NMe_2H$][BPh_4], thf; (*vii*) CD_2Cl_2; (*viii*) Li[$CMe_2(C_5H_4)_2$], thf

sensitive materials were carried out under an inert atmosphere of dinitrogen using standard Schlenk-line techniques or in an inert-atmosphere dry-box containing dinitrogen using previously described procedures. Solvents were distilled from appropriate reagents.[31] The compound Li(C_5H_5) was obtained from Aldrich and used as received; $SiMe_3Cl$ (Aldrich, 98%) was purified before use by three freeze–pump–thaw cycles. The compounds [Nb(η-C_5H_4R)X_2($NNMe_2$)] (X = Cl or OBu^t, R = H or Me),[8] Li(C_5H_4Me)[32] and $CMe_2(C_5H_5)_2$[33] were prepared according to the literature procedures, $Li_2[CMe_2(C_5H_4)_2]$ from $CMe_2(C_5H_5)_2$ and 2 equivalents of LiBu in diethyl ether[34] and $FeCl_2$·1.5thf by Soxhlet extraction of crude $FeCl_2$ with thf followed by crystallisation from the same solvent.[35] The salt [$C_6H_5NMe_2H$][BPh_4] was precipitated from a concentrated aqueous solution of Na[BPh_4] and dimethylaniline in concentrated hydrochloric acid.

Preparations

Chloro bis(η-cyclopentadienyl)(2,2-dimethylhydrazido)niobium 1. Lithium cyclopentadienide (125 mg, 1.73 mmol) in thf (20 cm^3) was added dropwise with stirring at room temperature to [Nb(η-C_5H_5)Cl_2($NNMe_2$)] (250 mg, 0.87 mmol) in thf (50 cm^3). There was an instant change to pale orange. The solution was stirred for 30 min and the volatiles were removed under reduced pressure to afford a yellow solid. The solid was washed in pentane to ensure complete precipitation of lithium salts; the pentane was then removed under reduced pressure. The solid was extracted in toluene (3 × 15 cm^3); the volume was reduced to 20 cm^3 to give an orange solution, which yielded yellow needles upon cooling to −80 °C. Yield 170 mg (56%), based on [Nb(η-C_5H_5)Cl_2($NNMe_2$)] (Found: C, 45.45; H, 5.0; Cl, 11.45; N, 8.7. $C_{12}H_{16}ClN_2Nb$ requires C, 45.5; H, 5.1; Cl, 11.2; N, 8.85%). NMR (C_6D_6): ^1H (300 MHz), δ 5.77 (s, 10 H, C_5H_5) and 2.44 [s, 6 H, $NN(CH_3)_2$]; $^{13}C-\{^1H\}$ (75.5 MHz), δ 109.8 (C_5H_5) and 44.5 [$NN(CH_3)_2$]. Mass spectrum: *m/z* 316 (M^+, 29), 258 (100, $M^+ - NNMe_2$) and 193 (15%, $M^+ - NNMe_2 - C_5H_5$).

Chloro(η-cyclopentadienyl)(2,2-dimethylhydrazido)(η-methylcyclopentadienyl)niobium 2. Sodium cyclopentadienide (134 mg, 1.51 mmol) in thf (10 cm^3) was added with stirring over 1 h to [Nb(η-C_5H_4Me)Cl_2($NNMe_2$)] (447 mg, 1.49 mmol) in thf (20 cm^3). The solution was stirred for 2 h during which time it turned yellow. Volatiles were removed under reduced pressure to yield a yellow solid which was extracted in pentane (4 × 60 cm^3) to give a bright yellow solution. Slow evaporation yielded yellow needles of [Nb(η-C_5H_5)(η-C_5H_4Me)Cl($NNMe_2$)]. Yield 160 mg (33%) (Found: C, 47.05; H, 5.45; Cl, 13.2; N, 8.15. $C_{13}H_{18}ClN_2Nb$ requires C, 47.2; H, 5.5, Cl, 10.7; N, 8.5%). NMR: ^1H (C_6D_6, 300 MHz), δ 5.83 (m, 1 H, $C_5H_4CH_3$), 5.77 (s, 5 H, C_5H_5), 5.54 (m, 1 H, $C_5H_4CH_3$), 5.47 (m, 1 H, $C_5H_4CH_3$), 5.16 (m, 1 H, $C_5H_4CH_3$), 2.45 [s, 6 H, $NN(CH_3)_2$] and 2.19 (s, 3 H, $C_5H_4CH_3$); $^{13}C-\{^1H\}$ (CD_2Cl_2, 75.5 MHz), δ 125.2 ($C_5H_4CH_3$ quaternary), 113.2 (C_5H_5), 109.9 ($C_5H_4CH_3$), 109.4 ($C_5H_4CH_3$), 106.4 ($C_5H_4CH_3$), 105.6 ($C_5H_4CH_3$), 45.3 [$NN(CH_3)_2$] and 15.3 ($C_5H_4CH_3$). Mass spectrum: *m/z* 330 (M^+, 27), 272 (100, $M^+ - NNMe_2$), 236 (72, $M^+ - NNMe_2 - Cl$), 207 [13, $Nb(C_6H_7)Cl^+$], 193 [32, $Nb(C_5H_5)Cl^+$], 172 [8, $Nb(C_6H_7)^+$] and 158 [36, $Nb(C_5H_5)^+$].

Chloro (2,2-dimethylhydrazido)bis(η-methylcyclopentadienyl)niobium 3. The compound Li(C_5H_4Me) (300 mg, 3.49 mmol) and [Nb(η-C_5H_4Me)Cl_2($NNMe_2$)] (307 mg, 1.01 mmol) were mixed and then dissolved in thf (50 cm^3). The solution was stirred for 42 h during which time it became yellow. Volatiles were removed under reduced pressure to yield a yellow oily solid. This was washed in pentane to ensure precipitation of LiCl; the pentane was then removed under reduced pressure. The residue was extracted into pentane (4 × 25 cm^3) to yield a bright yellow solution. This was concentrated to 20 cm^3 under reduced pressure and cooled to −25 °C to yield yellow needles. Yield 87 mg (26%) (Found: C, 48.5; H, 5.1; Cl, 10.1; N, 7.8. $C_{14}H_{20}ClN_2Nb$ requires C, 48.8; H, 5.85; Cl, 10.3; N, 8.15%). NMR (C_6D_6): ^1H (300 MHz), δ 5.87 (m, 1 H, $C_5H_4CH_3$), 5.55 (m, 1 H, $C_5H_4CH_3$), 5.52 (m, 1 H, $C_5H_4CH_3$), 5.12 (m, 1 H, $C_5H_4CH_3$), 2.47 [s, 6 H, $NN(CH_3)_2$] and 2.18 (s, 6 H, $C_5H_4CH_3$); $^{13}C-\{^1H\}$ (C_6D_6, 75.5 MHz), δ 125.4 ($C_5H_4CH_3$ quaternary), 113.2 ($C_5H_4CH_3$), 108.7 ($C_5H_4CH_3$), 106.0 ($C_5H_4CH_3$), 105.5 ($C_5H_4CH_3$), 45.1 [$NN(CH_3)_2$] and 15.4 ($C_5H_4CH_3$). Mass spectrum: *m/z* 344 (54, M^+), 286 (100, $M^+ - NNMe_2$), 250 (36, $M^+ - NNMe_2 - Cl$), 207 (34, $M^+ - NNMe_2 - C_6H_7$) and 171 [9%, $(C_6H_7)Nb^+$].

Bis(η⁵-cyclopentadienyl)(η¹-cyclopentadienyl)(2,2-dimethylhydrazido)niobium 4. *Method* 1 *from* [Nb(η-C_5H_5)Cl_2($NNMe_2$)]. The compound Li(C_5H_5) (2.45 g, 34 mmol) in thf (200 cm^3) was added with stirring to a solution of [Nb(η-C_5H_5)Cl_2($NNMe_2$)] (1.08 g, 3.77 mmol) in thf (50 cm^3) at room temperature over the course of 10 min. The solution rapidly became pale orange. It was stirred for 48 h and slowly darkened to deep red. Volatiles were removed under reduced pressure and the resulting red solid was extracted in pentane (3 × 50 cm^3). The volume was decreased under reduced pressure to 100 cm^3 and cooled to −25 °C to afford yellow crystals. These were filtered off, washed in cold pentane and dried *in vacuo*.

Method 2 *from* [Nb(η-C_5H_5)$_2$Cl($NNMe_2$)]. The compounds Li(C_5H_5) (350 mg, 4.9 mmol) and [Nb(η-C_5H_5)$_2$Cl($NNMe_2$)] (120 mg, 0.42 mmol) were mixed and dissolved in thf (30 cm^3). The solution was stirred for 48 h and slowly darkened to deep red. Volatiles were removed under reduced pressure and the resulting red solid was washed in pentane to ensure complete precipitation of LiCl. The pentane was removed under reduced pressure and the solid was extracted into pentane (3 × 10 cm^3). The volume was decreased under reduced pressure to 10 cm^3

resulting in the precipitation of a yellow solid. This was filtered off and washed in ice cold pentane; the combined washings were reduced in volume to 5 cm^3 and cooled to −20 °C to afford a second crop of crystals. Combined yield 93 mg (64%) based on $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$ (Found: C, 59.1; H, 6.5; N, 8.0. $C_{17}H_{21}N_2Nb$ requires C, 58.95; H, 6.1; N, 8.1%). NMR ($C_6D_5CD_3$): ^1H (500 MHz, 223 K), δ 6.97 (m, 2 H, $\eta^1\text{-}C_5H_5$), 6.83 (m, 2 H, $\eta^1\text{-}C_5H_5$), 5.12 (s, 10 H, $\eta^5\text{-}C_5H_5$), 4.95 (s, 1 H, $\eta^1\text{-}C_5H_5$, *ipso*) and 2.27 [s, 6 H, $NN(CH_3)_2$]; $^{13}C\text{-}\{^1H\}$ (75.5 MHz, high-temperature limit, 298 K), δ 107.6 (C_5H_5) and 44.6 [$NN(CH_3)_2$]. Mass spectrum: *m/z* 346 (M^+, 20), 304 [1, $Nb(C_5H_5)_3NH^+$], 288 [2, $M^+ - NNMe_2$], 281 (27, $M^+ - C_5H_5$), 267 (5, $M^+ - C_5H_5 - Me$), 251 (6, $M^+ - C_5H_5 - 2\,Me$), 238 [13, $Nb(C_5H_5)_2NH^+$], 223 [100, $Nb(C_5H_5)_2{}^+$], 197 [9, $Nb(C_5H_5)(C_3H_3)^+$], 171 [10, $Nb(C_3H_3)_2{}^+$] and 158 [5%, $Nb(C_5H_5)^+$]. IR (CCl_4 solution): $\tilde{\nu}_{max}/cm^{-1}$ 2979, 2917, 2834, 1442, 1216, 1090 and 1056.

(2,2-Dimethylhydrazido)bis(η⁵-methylcyclopentadienyl)(η¹-methylcyclopentadienyl)niobium 5. The compound $Li(C_5H_4Me)$ (0.8 g, 9.3 mmol) and $[Nb(\eta\text{-}C_5H_4Me)Cl_2(NNMe_2)]$ (1.06 g, 3.52 mmol) were mixed and dissolved in thf (50 cm^3). The solution was then stirred at room temperature for 3 weeks and slowly became dark red. Small aliquots were taken at regular intervals and examined by ^1H NMR and mass spectrometry to monitor the reaction. Volatiles were removed under reduced pressure and the residue was extracted into pentane (3 × 20 cm^3). The extract was reduced to 10 cm^3 and cooled to −20 °C to afford the product as an oily red solid. Yield 408 mg (30%) based on $[Nb(\eta\text{-}C_5H_4Me)_2Cl(NNMe_2)]$ (Found: C, 62.3; H, 7.45. $C_{20}H_{27}N_2Nb$ requires C, 61.85; H, 7.0%). ^1H NMR (C_6D_6, 300 MHz, 293 K): δ 6.6–4.9 (br unresolved signals, $C_5H_4CH_3$), 2.49 [s, 6 H, $NN(CH_3)_2$] and 1.90 (br s, 9 H, $C_5H_4CH_3$). Mass spectrum: *m/z* 389 (19, M^+), 345 (32, $M^+ - NMe_2$), 310 (56, $M^+ - C_6H_7$), 287 (91, $M^+ - NNMe_2 - HCCMe$) and 250 (100%, $M^+ - C_6H_7 - NNMe_2$).

(η-Cyclopentadienyl)(2,2-dimethylhydrazido)[η⁵,κ$C^{2'}$-propane-2,2-diylbis(cyclopentadienyl)]niobium 7. The compound $Li_2[CMe_2(C_5H_4)_2]$ (161 mg, 0.87 mmol) in thf (20 cm^3) was added rapidly with stirring at room temperature to $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$ (246 mg, 0.86 mmol) in thf (50 cm^3). The solution rapidly turned pale orange and was stirred for 2.5 h. Volatiles were removed under reduced pressure and the resulting solid was washed in pentane. Volatiles were removed under reduced pressure and the solid was extracted in pentane. On standing some more LiCl precipitated, so the solution was refiltered and the volume was then decreased to 10 cm^3 under reduced pressure to afford a yellow solid. This was shown to be $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$. The filtrate was cooled to −80 °C to afford $[Nb\{CMe_2(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)(NNMe_2)]$ as a yellow powder, which was filtered off and washed in cold pentane. Yield 100 mg (60%) (Found: C, 63.35; H, 7.0; N, 7.7. $C_{20}H_{25}N_2Nb$ requires C, 62.2; H, 6.5; N, 7.25%). Mass spectrum: *m/z* 386 (73, M^+), 343 {42, $Nb(C_5H_5)[CMe_2(C_5H_4)_2]NH^+$}, 328 (100, $M^+ - NNMe_2$), 278 {57, $Nb[CMe_2(C_5H_4)_2]NH^+$} and 263 {80%, $Nb[CMe_2(C_5H_4)_2]^+$}.

Bis(η-cyclopentadienyl)(2,2-dimethylhydrazido)(tetrahydrofuran)niobium tetraphenylborate 10. The salt $[C_6H_5NMe_2H][BPh_4]$ (99 mg, 0.22 mmol) in thf (10 cm^3) was added to $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (75 mg, 0.21 mmol) in thf (10 cm^3). The resulting solution was stirred for 2 h during which it turned slightly darker orange. The volume was decreased under reduced pressure to 5 cm^3, whereupon a microcrystalline precipitate began to form. The solution was then cooled overnight to −20 °C to yield an orange microcrystalline solid. Yield 20 mg (14%) (Found: C, 71.4; H, 6.4; N, 3.8. $C_{40}H_{44}BN_2NbO$ requires C, 71.45; H, 6.6; N, 4.15%). ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.36 (br unresolved multiplet, 8 H, C_6H_5), 7.05 (t, 8 H, C_6H_5), 6.90 (t, 4 H, C_6H_5), 6.05 (s, 10 H, C_5H_5), 3.65 (m, 4 H, C_4H_8O), 3.24 [s, 6 H, $NN(CH_3)_2$] and 1.94 (m, 4 H, C_4H_8O).

Reactions of $Li(C_5H_4Me)$

With $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$. The compound $Li(C_5H_4Me)$ (*ca.* 10 mg, 0.12 mmol) was dissolved in thf (5 cm^3) and added to $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$ (35 mg, 0.11 mmol) in thf (10 cm^3). The solution was stirred for 15 h and volatiles were then removed under reduced pressure. The residue was extracted in pentane to free it from LiCl and $Li(C_5H_4Me)$ and the pentane was then removed under reduced pressure to afford a yellow solid.

With $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$. The compounds $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (22 mg, 0.06 mmol) and $Li(C_5H_4Me)$ (*ca.* 20 mg) were mixed in a Youngs' ampoule and thf (20 cm^3) was added. The solution was stirred at room temperature for 19 d and then the volatiles were removed under reduced pressure. The mixture was extracted in pentane (2 × 5 cm^3) which was removed under reduced pressure to afford a yellow powder.

With $[Nb(\eta\text{-}C_5H_5)(OBu^t)_2(NNMe_2)]$. The compound $Li(C_5H_4Me)$ (10 mg) in thf (10 cm^3) was added to $[Nb(\eta\text{-}C_5H_5)(OBu^t)_2(NNMe_2)]$ (10 mg) in thf (5 cm^3). The solution was stirred for 19 d and the volatiles were then removed under reduced pressure to give an orange sticky solid. This solid was extracted in pentane which was removed under reduced pressure to yield a straw coloured oil.

Reactions of $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$

With $SiMe_3Cl$: synthesis of $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$. The compound $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (20 mg, 0.07 mmol) in thf (10 cm^3) was treated with $SiMe_3Cl$ (*ca.* 0.1 cm^3) and the resulting solution stirred for 2 h. Volatiles were removed under reduced pressure and the residue was extracted in C_6D_6; this was shown by ^1H NMR spectroscopy to be a *ca.* 3:4 mixture of $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$ and $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$.

With $FeCl_2\cdot 1.5thf$: synthesis of ferrocene and $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$. The compound $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (45 mg, 0.16 mmol) and $FeCl_2\cdot 1.5thf$ (37 mg, 0.16 mmol) were mixed and dissolved in thf (20 cm^3). The resulting solution was stirred for 18 h and the volatiles removed under reduced pressure to afford a sticky residue. An orange solid sublimed out at room temperature (5×10^{-2} mmHg), *ca.* 6.7 Pa which was shown by ^1H NMR and mass spectroscopy to be ferrocene. The involatile residue was extracted in C_6D_6 and shown by ^1H NMR spectroscopy to be $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$.

With $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$: synthesis of $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$. The compounds $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (45 mg, 0.16 mmol) and $[Nb(\eta\text{-}C_5H_5)Cl_2(NNMe_2)]$ (37 mg, 0.13 mmol) were mixed and dissolved in thf (20 cm^3). The resulting solution was stirred for 42 h and the volatiles were removed under reduced pressure to afford a sticky residue. The residue was extracted in C_6D_6 and shown by ^1H NMR spectroscopy to be a mixture of $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$ and residual $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$.

With $[NMe_3H]Cl$. The compounds $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NNMe_2)]$ (40 mg, 0.14 mmol) and $[NMe_3H]Cl$ (14 mg, 0.14 mmol) were mixed and dissolved in thf (20 cm^3). The resulting solution was stirred for 24 h and the volatiles removed under reduced pressure to afford a pale yellow solid. The residue was extracted in C_6D_6 and shown by ^1H NMR spectroscopy to be $[Nb(\eta\text{-}C_5H_5)_2Cl(NNMe_2)]$.

With LiCl. The compounds [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)(NNMe$_2$)] (10 mg, 0.04 mmol) and LiCl (*ca.* 10 mg, 0.25 mmol) were dissolved in thf (10 cm^3) and stirred for 20 d. Volatiles were then removed under reduced pressure and the residual pale yellow solid extracted into C_6D_6.

With [Nb(η^5-C_5H_4Me)$_2$(η^1-C_5H_4Me)(NNMe$_2$)]. The compounds [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)(NNMe$_2$)] (10 mg, 0.04 mmol) and [Nb(η^5-C_5H_4Me)$_2$(η^1-C_5H_4Me)(NNMe$_2$)] (*ca.* 10 mg, 0.03 mmol) were dissolved in thf (10 cm^3) and stirred for 20 d. Volatiles were then removed under reduced pressure and the residual pale yellow solid extracted into C_6D_6.

Crystallography

Yellow prisms of compound **3** were grown by slow evaporation of a pentane solution and a crystal of dimensions 0.21 × 0.25 × 0.34 mm was mounted in a Lindemann tube. Data were collected at 150 K on an Enraf-Nonius DIP2020 image-plate diffractometer and indexed as orthorhombic with systematic absences consistent with the space group *Pbca*. The structure was solved using direct methods, with a full-matrix least-squares refinement based on *F* with all non-hydrogen atoms refined anisotropically. All hydrogen atoms were located in the Fourier-difference maps and refined isotropically. A Chebychev weighting scheme[36] was applied and corrections made for Lorentz- and polarisation effects, but not for absorption, yielding a final *R* value of 0.038 and $R' = 0.038$. All crystallographic calculations were carried out using the CRYSTALS[37] program package on a PC/AT 486. Neutral atom scattering factors were taken from ref. 38. Crystal data are given in Table 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/433.

Table 4 X-Ray data for [Nb(η-C_5H_4Me)$_2$Cl(NNMe$_2$)]

Formula	$C_{14}H_{20}ClN_2Nb$
M	344.68
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	6.7570(6)
b/Å	16.219(3)
c/Å	27.355(4)
U/Å^3	2997.88
Z	8
D_c/g cm^{-3}	1.53
μ/cm^{-1}	9.34
Radiation (λ/Å)	Mo-Kα (0.710 69)
θ_{max}/°	26° ($-h$ to h, $-k$ to k, $-l$ to l)
Total data collected	12 295
Unique data	3404
Observed data [$I > 4\sigma(I)$]	2630
Merging *R*	0.036
Weighting scheme	Chebychev, parameters 1.60, 0.68, 1.30
Number parameters refined	243
Maximum, minimum residual electron density/e Å^{-3}	0.50, −0.69
R	0.038
R′	0.038

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