Half-sandwich hydrazido(2−) complexes of niobium†

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The compounds [Nb(η-C₅H₄R)Cl₂(NNMeR′)] (R = H or Me, R′ = Me or Ph), [Nb(η-C₅H₄R)(OBuᵗ)₂(NNMe₂)] (R = H or Me), [Nb(η-C₅H₄Me)Br(OBuᵗ)(NNMe₂)], [Nb(η-C₅H₅)(NMe₂)₂(NNMe₂)], [Nb(η-C₅H₄R)-(CH₂CMe₂Ph)₂(NNMe₂)] (R = H or Me), [Nb(η-C₅H₅)(CH₂SiMe₃)₂(NNMe₂)], *cis*-[Nb(η-C₅H₅)Cl₂(NNMe₂)], *cis*-[Nb(η-C₅H₄R)Cl₂(NNMe₂)(PMe₃)] (R = H or Me), *trans*-[Nb(η-C₅H₄R)Cl(NNMe₂)(PMe₃)₂]Cl (R = H or Me) and *trans*-[Nb(η-C₅H₅)Cl(NNMe₂)(PMe₃)₂][PF₆] have been prepared and characterised. A structure determination of [Nb(η-C₅H₅)Cl₂(NNMe₂)] showed it to be a dimer with one hydrazide ligand acting as monodentate to one metal centre and a second hydrazide bridging both metal centres in a μ-η² fashion. The structure of [Nb(η-C₅H₅)Cl₂(NNMe₂){P(OMe)₃}] shows a *cis* disposition of the hydrazide and phosphite ligands.

Whilst the chemistry of transition-metal organoimido compounds is comparatively well developed,[1] complexes containing a heteroatom-substituted imido group have been less extensively explored. We have been interested in the chemistry of transition-metal compounds containing the moiety M=N−X in which X is a formal one-electron donor. Examples of terminal imido complexes in which X is B(C₆H₂Me₃-2,4,6)₂,[2] SnMe₃,[3,4] NR₂,[5,6] P(S)Ph₂,[7,8] SR,[9–11] SeR,[12] SCl,[13] SeCl,[14–17] SO₂Ph,[18] SO₂NH₂[19] and halide[20] have been described (R = alkyl or aryl). We have recently reported the first example of the terminal alkoxyimide ligand in which X = OBuᵗ.[21] Examples in which X = N₃[22] or PPh₂[20] have been briefly mentioned. The co-ordination chemistry of the hydrazido(2−) (or isodiazene) ligand NNR₂ is particularly diverse.[5,6] According to the steric and electronic requirements of a metal centre, the ligand may bind in an η¹, μ-η¹ or μ-η² fashion, and additionally the M−N−N linkage may be linear or bent. Most known hydrazido(2−) compounds are derivatives of molybdenum and tungsten and the majority of these also contain strong σ-donor ligands such as phosphines. As far as we are aware there are no reported hydrazido(2−) complexes of niobium. The known half-sandwich hydrazido compounds are [{Mo(η-C₅H₅)(NO)I}₂(μ-η²-NNMe₂)][23,24] and the series [M(η-C₅Me₅)Me₃(NNMeₓHᵧ)] (M = Mo or W; x + y = 2).[23–28] Here we describe the syntheses and characterisation of new hydrazido(2−) complexes of the type [Nb(η-C₅H₄R)Cl₂(NNMeR′)] and their reactivity towards a variety of Lewis bases and anionic reagents.

Results and Discussion

The compound [Nb(η-C₅H₅)Cl₂(NNMe₂)] **1** was synthesized by addition of a dichloromethane solution of *N,N*-dimethylhydrazine and 2 equivalents of triethylamine to a dichloromethane suspension of [Nb(η-C₅H₅)Cl₄] (Scheme 1). On addition of the amine there was an instantaneous evolution of white fumes, presumably of triethylammonium chloride, followed by a gradual change to deep red with the concomitant dissolution of all solids. Removal of volatiles and crystallisation from toluene afforded **1** as a red solid. In a similar fashion, [Nb(η-C₅H₄Me)Cl₂(NNMe₂)] **2** could be synthesized from [Nb(η-C₅H₄Me)Cl₄]. The compound [Nb(η-C₅H₅)Cl₂-(NNMePh)] **3** was obtained in analogous fashion from [Nb-(η-C₅H₅)Cl₄], *N*-methyl-*N*-phenylhydrazine and triethylamine and recrystallised from boiling light petroleum (b.p. 100–120 °C) yielding metallic green plates.

† *Non-SI unit employed*: mmHg ≈ 133 Pa.

Table 1 Interatomic distances (Å) and angles (°) in complex **1**

Nb(1)–C(11)	2.47(2)	Nb(2)–Cl(2)	2.510(3)
Nb(1)–C(12)	2.42(1)	C(2)–N(22)	1.36(2)
Nb(1)–C(13)	2.37(1)	C(11)–C(12)	1.41(2)
Nb(1)–N(11)	1.88(1)	C(12)–C(13)	1.42(2)
Nb(1)–N(12)	2.15(2)	C(13)–C(13ᴵ)	1.37(2)
Nb(1)–Cl(1)	2.352(3)	C(21)–C(22)	1.40(2)
Nb(2)–C(21)	2.64(2)	C(22)–C(23)	1.44(3)
Nb(2)–C(22)	2.50(2)	C(23)–C(23ᴵ)	1.37(3)
Nb(2)–C(23)	2.41(1)	N(11)–N(12)	1.39(2)
Nb(2)–N(11)	2.28(1)	N(21)–N(22)	1.38(2)
Nb(2)–N(21)	1.67(2)		
N(11)–Nb(1)–N(12)	39.7(5)	Nb(1)–C(13)–C(12)	74.8(6)
N(11)–Nb(1)–Cl(1)	110.8(2)	Nb(2)–C(22)–C(21)	79.5(11)
N(12)–Nb(1)–Cl(1)	88.5(2)	Nb(1)–N(11)–Nb(2)	151.4(7)
Cl(1)–Nb(1)–Cl(1ᴵ)	108.2(2)	Nb(1)–N(11)–N(12)	80.8(9)
N(11)–Nb(2)–N(21)	105.0(6)	Nb(2)–N(11)–N(12)	127.9(10)
N(11)–Nb(2)–Cl(2)	76.52(7)	Nb(1)–N(12)–C(1)	125.1(7)
N(21)–Nb(2)–Cl(2)	89.8(1)	C(1)–N(12)–C(1ᴵ)	107.2(14)
Cl(2)–Nb(2)–Cl(2ᴵ)	152.0(1)	Nb(1)–N(12)–N(11)	59.5(7)
Nb(1)–C(11)–C(12)	71.2(8)	C(1)–N(12)–N(11)	114.7(8)
C(12)–C(11)–C(12ᴵ)	107.7(15)	Nb(2)–N(21)–N(22)	168.7(17)
Nb(1)–C(12)–C(11)	75.3(9)	C(2)–N(22)–C(2ᴵ)	121.0(22)
Nb(1)–C(12)–C(13)	70.8(6)	C(2)–N(22)–N(21)	118.7(12)

Symmetry code: I *x*, ½ − *y*, *z*.

The hydrazide compounds **1** and **2** were characterised by ¹H and ¹³C-{¹H} NMR spectroscopy, electron-impact (EI) mass spectrometry and microanalysis. The analytical and spectroscopic data characterising these and all other new compounds presented in this work are given in the Experimental section. These data will not be further discussed unless the interpretation is not straightforward. Both **1** and **2** were very air sensitive, decomposing to a yellow powder in air within *ca.* 15 s. The mass spectra showed very clean fragmentation patterns. No evidence of dimer formation could be seen, the highest mass ion in each case being the parent ion, showing the correct 9:6:1 isotope pattern due to the presence of two chlorine atoms. The identity of each compound was further confirmed by its subsequent reaction chemistry.

Prismatic crystals of compound **1** suitable for X-ray diffraction were grown by the slow cooling of a hot toluene solution. The crystal structure has been determined and the molecular structure is given in Fig. 1 and bond lengths and angles in Table 1. Compound **1** is a dimer in which the two hydrazide ligands display different co-ordination modes. At Nb(2) this ligand is linear, whereas at Nb(1) it bonds in an η² fashion and additionally bridges the two niobium centres. There are many crystallographically characterised examples of linear hydrazide species
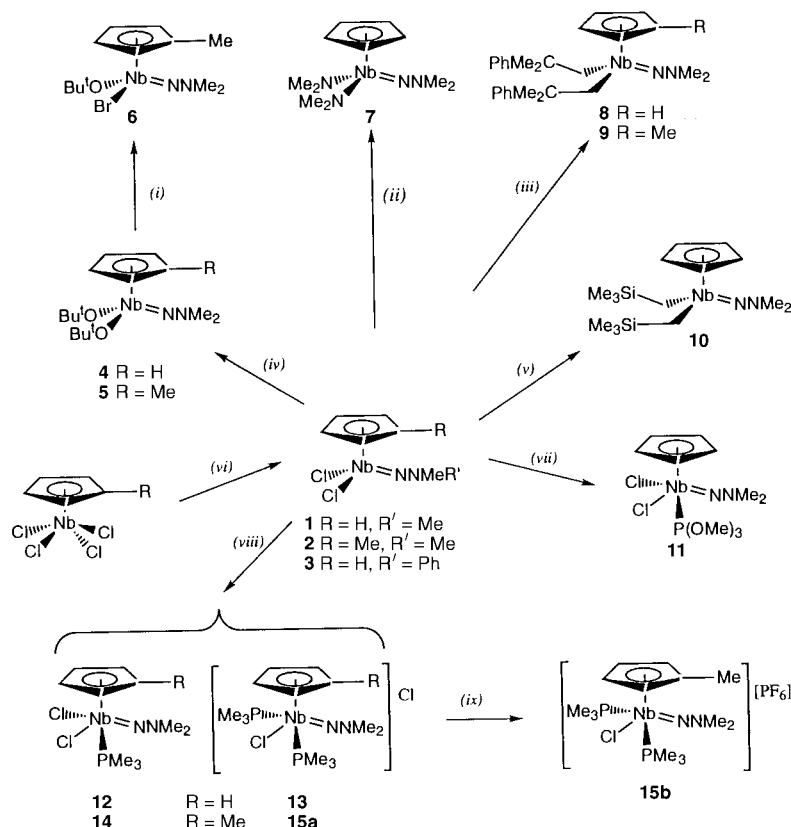
Scheme 1 (*i*) SiMe$_3$Br, thf, 1 h; (*ii*) LiNMe$_2$, thf, 2.5 h; (*iii*) Mg(CH$_2$CMe$_2$Ph)Cl, thf, 72 h; (*iv*) LiOBu^t, thf, 30 min; (*v*) Li(CH$_2$SiMe$_3$), thf, 1 h; (*vi*) H$_2$NNMeR, 2NEt$_3$, CH$_2$Cl$_2$, 3.5 h; (*vii*) P(OMe)$_3$, toluene, 24 h; (*viii*) PMe$_3$, toluene, 24 h; (*ix*) PMe$_3$, thf, [NH$_4$][PF$_6$]
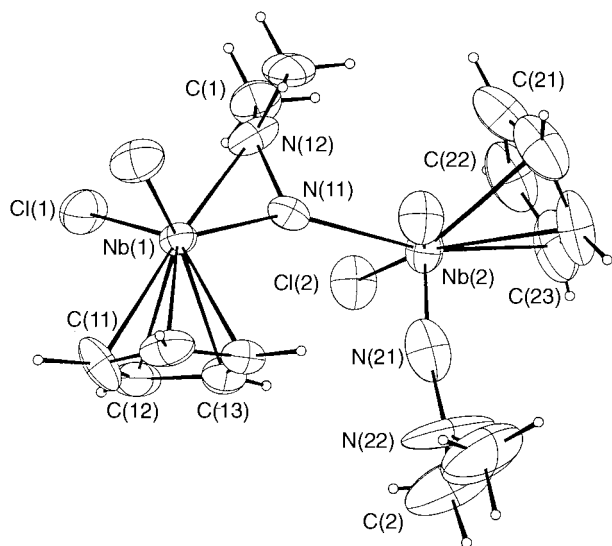
Fig. 1 Molecular structure of compound **1**, viewed perpendicular to the mirror plane

and three previous examples of the μ-η^2 mode are in the compounds [{Mo(η-C$_5$H$_5$)(NO)I}$_2$(μ-η^2-NNMe$_2$)], [{Ti(η-C$_5$H$_5$)Cl(NNPh$_2$)}$_2$] and [{Zr(η-C$_5$H$_5$)$_2$(NNPh$_2$)}$_2$].[24]

The hydrazide ligand at Nb(2) is essentially linear [Nb(2)–N(21)–N(22) 168.1(17)°], indicating sp hybridisation at N(21). The Nb(2)–N(21) bond length of 1.67(2) Å is exceptionally short, shorter even than that found in the imido compound [Nb(η-C$_5$H$_5$)Cl$_2$(NBu^t)],[29] where a value of 1.752(2) Å was reported. Thus it appears that the hydrazide ligand acts as a four-electron donor to Nb(2). If N(11) is then considered to act as a dative two-electron ligand to Nb(2), this atom then achieves a formal eighteen-electron count. In agreement with this, the Nb(2)–Cl(2) bond length of 2.510(3) Å is similar to that found in [Nb(η-C$_5$H$_5$)Cl$_2$(NBu^t)(PMe$_3$)] but longer than

that in [Nb(η-C$_5$H$_5$)Cl$_2$(NBu^t)], in which the short Nb–Cl bond was thought to be due to Nb–Cl d$_\pi$–p$_\pi$ bonding.[29] The sum of the bond angles around N(22) is 358.7°, indicating sp^2 hydridisation. The N(21)–N(22) bond length of 1.38(2) Å is slightly shorter than that in hydrazine, but nonetheless still consistent with a single bond, indicating little through conjugation to the niobium atom.

The second hydrazide ligand acts in an η^2 fashion to Nb(1) and unsymmetrically bridges the two niobium atoms. Atoms Nb(1), Nb(2), N(11) and N(12) lie on the crystallographic mirror plane, restraining the sum of the bond angles at N(11) to be 360°. The N(11)–N(12) bond length of 1.39(2) Å is the same as that between N(21) and N(22). The short N(11)–Nb(1) bond length indicates that there is some double-bond character to this bond. The hydrazide ligand thus acts as a formal four-electron donor to Nb(1) and a two-electron donor to Nb(2). The formal electron count at Nb(1) is thus sixteen, and in accord with the result found for the analogous imido compound the Nb(1)–Cl(1) bond length is shortened, indicating significant Nb–Cl d$_\pi$–p$_\pi$ bonding with concomitant increase of the electron count to eighteen. The dimeric structure of **1** implies the existence of two different cyclopentadienyl and two amido environments within the molecule, whereas in the NMR spectra only one set of resonances was observed. This may reflect a rapid equilibration process between the terminal and bridging hydrazide ligands, or that the dimer is dissociated in solution. An attempt was made to measure the molecular mass in solution by the Signer method.[30,31] Unfortunately, the poor solubility of compound **1** in either benzene or CH$_2$Cl$_2$, coupled with its tendency to decompose in solution within a few days, prevented an accurate measurement being made. However, the results indicated that there was some degree of aggregation giving a molecular mass in CH$_2$Cl$_2$ of *ca.* 550 g mol^{-1}.

The substitution reactions of the two chloride ligands of compound **1** by a variety of lithium, sodium and magnesium reagents have been explored. Treatment of **1** in tetrahydrofuran (thf) with 2 equivalents of LiOBu^t gave a pale orange solution

Table 2 Interatomic distances (Å) and angles (°) in complex **11**

Nb–P	2.6030(6)	O(1)–C(8)	1.399(4)
Nb–N(1)	1.789(2)	O(2)–C(9)	1.455(4)
Nb–C(1)	2.494(3)	O(3)–C(10)	1.454(3)
Nb–C(2)	2.393(3)	N(1)–N(2)	1.338(2)
Nb–C(3)	2.408(3)	N(2)–C(6)	1.460(3)
Nb–C(4)	2.458(3)	N(2)–C(7)	1.467(4)
Nb–C(5)	2.443(3)	C(1)–C(4)	1.367(5)
Nb–Cl(1)	2.4896(6)	C(1)–C(5)	1.395(6)
Nb–Cl(2)	2.4947(5)	C(2)–C(3)	1.399(6)
P–O(1)	1.597(2)	C(2)–C(5)	1.405(6)
P–O(2)	1.571(2)	C(3)–C(4)	1.379(5)
P–O(3)	1.581(2)	Nb–Cp$_{cent}$	2.1342
P–Nb–N(1)	82.98(6)	Nb–N(1)–N(2)	170.4(2)
P–Nb–C(1)	103.6(1)	N(1)–N(2)–C(6)	113.8(2)
N(1)–Nb–C(1)	147.2(1)	N(1)–N(2)–C(7)	112.3(2)
P–Nb–Cl(1)	74.42(2)	C(6)–N(2)–C(7)	114.1(2)
N(1)–Nb–Cl(1)	116.53(6)	N(1)–Nb–Cp$_{cent}$	118.85
C(1)–Nb–Cl(1)	96.07(8)	Cl(1)–Nb–Cp$_{cent}$	123.82
P–Nb–Cl(2)	149.81(2)	Cl(2)–Nb–Cp$_{cent}$	104.91
N(1)–Nb–Cl(2)	92.35(6)	P–Nb–Cp$_{cent}$	103.41
Cl(1)–Nb–Cl(2)	81.27(2)		

Cp$_{cent}$ refers to the computed ring centroid.

Fig. 2 Perspective view of the molecular structure of compound **11**

from which the compound [Nb(η-C$_5$H$_5$)(OBu^t)$_2$(NNMe$_2$)] **4** was obtained as a red oil in 87% yield. The ^{1}H and ^{13}C-{^{1}H} NMR spectra indicated the oil was essentially pure, but was further purified by distillation using a Pardy apparatus (55 °C, 10^{-2} mmHg) to give a mobile yellow liquid. Similarly, reaction of compound **2** with LiOBu^t in tetrahydrofuran afforded [Nb(η-C$_5$H$_4$Me)(OBu^t)$_2$(NNMe$_2$)] **5** as a red oil in 85% yield. Treatment of this compound with 2 equivalents of trimethylsilyl bromide gave the monobromo compound [Nb(η-C$_5$H$_4$Me)-Br(OBu^t)(NNMe$_2$)] **6**. An oily residue left after extraction of **6** with pentane was shown by EI mass spectrometry to contain the dibromo-compound [Nb(η-C$_5$H$_4$Me)Br$_2$(NNMe$_2$)] but no tractable pure product could be isolated.

In an analogous fashion to the reaction with LiOBu^t, compound **1** reacted rapidly with LiNMe$_2$ in tetrahydrofuran to afford [Nb(η-C$_5$H$_5$)(NMe$_2$)$_2$(NNMe$_2$)] **7** as an air-sensitive dark red oil. Attempts to purify this oil by sublimation failed and the compound decomposed on heating. However, the ^{1}H and ^{13}C NMR spectra revealed it to be a single compound, and the electron-impact mass spectrum showed it to be free of the monosubstitution product [Nb(η-C$_5$H$_5$)(NMe$_2$)Cl(NNMe$_2$)].

Treatment of compound **1** or **2** in tetrahydrofuran with 2 equivalents of Mg(CH$_2$CMe$_2$Ph)Cl in tetrahydrofuran gave the dialkyl compounds [Nb(η-C$_5$H$_4$R)(CH$_2$CMe$_2$Ph)$_2$(NNMe$_2$)] (R = H **8** or Me **9**) respectively. The ^{1}H NMR spectra of both compounds show a very wide separation of the two resonances attributable to the CH$_2$ group. For example, for the methylcyclopentadienyl compound these resonances are seen at δ 2.31 and −0.15 in [^{2}H$_2$]dichloromethane. The reason for this wide separation appears to be that one of these protons is shielded by the ring currents in the phenyl group, whereas the other lies closer to one of the methyl groups and accordingly experiences no such shielding. Treatment of compound **1** in tetrahydrofuran with 2 equivalents of Li(CH$_2$SiMe$_3$) resulted in a rapid change to pale orange. After removal of volatiles under reduced pressure the compound [Nb(η-C$_5$H$_5$)(CH$_2$SiMe$_3$)$_2$(NNMe$_2$)] **10** could be extracted as an air-sensitive red oil in high yield. Attempts at sublimation led to decomposition. The extreme air sensitivity of these compounds precluded accurate microanalytical data being obtained.

Compounds **1** and **2** have a formal sixteen-electron count. Therefore, addition reactions with donor phosphite and phosphine ligands have been explored. A toluene solution of **1** was exposed to trimethyl phosphite vapour for 24 h, after which time large ruby red crystals separated from the reaction mix-

ture. The spectroscopic data showed the product to be the 1:1 adduct [Nb(η-C$_5$H$_5$)Cl$_2$(NNMe$_2$){P(OMe)$_3$}] **11**. The crystal structure of **11** has been determined and the molecular structure is shown in Fig. 2 and Table 2 gives selected bond lengths and angles. The structure can be described as a four-legged piano-stool, with the two chlorine atoms mutually *cis* and the hydrazide and donor ligand also *cis*. In this respect it resembles that of [Nb(η-C$_5$H$_5$)Cl$_2$(NBu^t)(PMe$_3$)][29] and compound **14**, but differs from **1** in which, at the Nb(2) atom, the hydrazide and donor ligand are mutually *trans*. This *cis* disposition of the hydrazide and phosphite ligands appears to be the less-favoured conformation on steric grounds. The cyclopentadienyl ligand shows some deviations from symmetrical η^5 coordination. Thus the Nb–C(1) bond, which is *trans* to the hydrazide ligand, is considerably lengthened with respect to Nb–C(4) and Nb–C(5) and Nb–C(2) and Nb–C(3), which are *cis* to the hydrazide ligand, are shortened. This deviation from ideal geometry in cyclopentadienyl ligands *trans* to an imido group has been noticed before[21,29,32,33] and reflects the competition for the same d$_\pi$ orbital between the imido group and the cyclopentadienyl ligand.
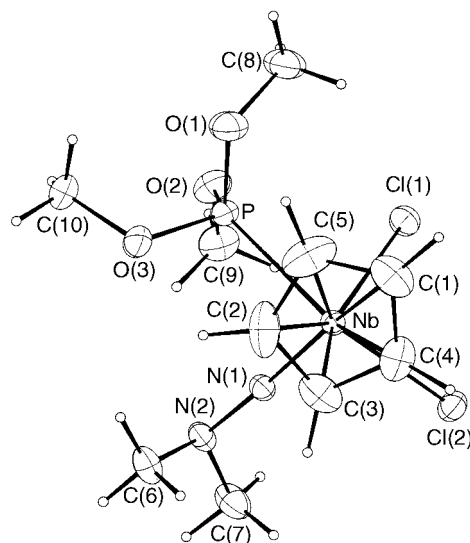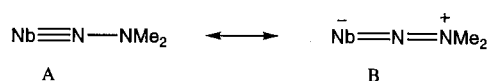
The Nb–N(1) bond length in complex **11** [1.789(2) Å] is slightly longer than in the analogous imido complex [Nb-(η-C$_5$H$_5$)Cl$_2$(NBu^t)(PMe$_3$)] [1.772(4) and 1.782(4) Å for the two independent molecules[29]] but is considerably longer than in **1**, where Nb(2)–N(21) is 1.67(2) Å. Conversely, the N–N bond length [1.338(2) Å] is considerably shorter than in **1** [1.39(3) Å]. This suggests that through conjugation of the type implied by the resonance form **B** is more significant in the current case. This can be rationalised by the assumption that trimethyl phosphite is a strong π acid, and will stabilise high electron density on the metal by back bonding using the phosphorus–oxygen σ* orbitals. In the case of compound **1** the bridging hydrazide ligand acts solely as a σ donor, and not as a π acid and hence the terminal hydrazide ligand is better described by resonance form **A**.

The Nb–Cl bond lengths are similar to those found at the eighteen-electron centre in both compound **1** and [Nb(η-C$_5$H$_4$Me)Cl$_2$(NNMe$_2$)(PMe$_3$)], but *ca.* 6% longer than those found in the sixteen-electron centre in **1**. This reflects the fact that the phosphorus atom is using the vacant metal orbital, preventing Cl–Nb p$_\pi$–d$_\pi$ overlap. Similar lengthening of Nb–Cl bonds upon complexation of a donor ligand was noticed

between the crystal structures of $[Nb(\eta-C_5H_5)Cl_2(NBu^t)]$ and $[Nb(\eta-C_5H_5)Cl_2(NBu^t)(PMe_3)]$.[29]

Both compounds **1** and **2** reacted rapidly with trimethylphosphine under similar conditions to form bright yellow powders which were soluble in dichloromethane and sparingly soluble in toluene. In both cases two products are formed. On the basis of the ^1H NMR spectrum of the compounds formed from the methylcyclopentadienyl compound **2** these were identified as *cis*-$[Nb(\eta-C_5H_4Me)Cl_2(NNMe_2)(PMe_3)]$ **14** (the major component of the mixture) and *trans*-$[Nb(\eta-C_5H_4Me)Cl(NNMe_2)(PMe_3)_2]Cl$ **15**. The equilibrium mixture could be shifted towards the cation by dissolving the mixture of $[Nb(\eta-C_5H_4Me)Cl(NNMe_2)(PMe_3)_2]Cl$ and $[Nb(\eta-C_5H_4Me)-Cl_2(NNMe_2)(PMe_3)]$ in thf, adding an excess of PMe_3 and then a saturated thf solution of $[NH_4][PF_6]$. A yellow precipitate formed which was shown to be *trans*-$[Nb(\eta-C_5H_4Me)-Cl(NNMe_2)(PMe_3)_2][PF_6]$ **15b**. The products formed between compound **1** and PMe_3 show qualitatively similar NMR spectra; in particular the PMe_3 region shows a doublet and a virtual triplet, and the NMe_2 region a doublet and a triplet. The cyclopentadienyl region also shows a doublet and a triplet. It thus appears that the two compounds formed are *trans*-$[Nb(\eta-C_5H_5)Cl(NNMe_2)(PMe_3)_2]Cl$ **13** and $[Nb(\eta-C_5H_5)Cl_2(NNMe_2)(PMe_3)]$ **12**. By analogy with **14**, this latter compound is presumably the *cis* isomer. The ^1H NMR spectrum shows that the ratio of compounds **12:13** is about 2:3. This leads to a composition of $[Nb(\eta-C_5H_5)Cl_2(NNMe_2)]_5(PMe_3)_8$ or $Nb(\eta-C_5H_5)Cl_2(NNMe_2)(PMe_3)_{1.6}$ and the analytical data are in good agreement with this. In the case of the mixture of compounds **14** and **15** the analytical data are in good agreement with the values required for $Nb(\eta-C_5H_4Me)Cl_2(NNMe_2)(PMe_3)_x$ with x lying in the range 1–1.2. A number of analogous half-sandwich imido niobium phosphine analogues are known. The compounds $[Nb(\eta-C_5H_5)Cl_2(NMe)(PMe_3)]$[29] and $[Nb\{C_5H_4(CH_2)_3N\}Cl_2-(PMe_3)]$[34] have been crystallographically characterised; in each case only a single product formed which was shown crystallographically to have the phosphine *cis* to the imide ligand. This geometry is the sterically more constrained since it places the phosphine adjacent to the bulky imido group, rather than between the two small chlorine atoms. This apparently unfavourable geometry was suggested to arise by interaction of the phosphine ligand with the lowest unoccupied molecular orbital (LUMO) of the $Nb(\eta-C_5H_5)Cl_2(NMe)$ fragment, which is oriented in the $\{NbCl_2\}$ plane. The geometries of the other synthesized phosphine adducts were similarly assumed to be *cis*, and no evidence of geometrical isomerism or addition of a second phosphine ligand was reported.

In conclusion we have synthesized a range of new half-sandwich hydrazido(2−) compounds of niobium. According to the steric and electronic demands of the metal, the hydrazido(2−) ligand adopts either the η^1 or the unusual μ-η^2 bonding mode.

Experimental

All preparations and manipulations of air- and/or moisture-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.[35] Dinitrogen was purified by passage through columns filled with molecular sieves (4 Å) and either manganese(II) oxide suspended on vermiculite for the vacuum line or BASF catalyst for the dry-box. Solvents and solutions were transferred through stainless-steel cannulæ, using a positive pressure of inert gas. Filtrations were similarly performed using modified stainless-steel cannulæ which could be fitted with glass-fibre filter discs. All glassware and cannulæ were thoroughly dried at 150 °C before use. Celite (Fluka) was dried overnight at 150 °C before use. All solvents were thoroughly deoxygenated before use either by repeated evacuation followed by admission of dinitrogen, or by bubbling

dinitrogen through the solvent for approximately 15 min. Solvents were predried over activated 4 Å molecular sieves and then distilled over {sodium [toluene, light petroleum (b.p. 100–120 °C)], sodium–potassium alloy [diethyl ether, pentane, light petroleum (b.p. 40–60 °C)], potassium (thf, benzene) or calcium hydride (dichloromethane)} under a slow continuous stream of dinitrogen. Deuteriated solvents for NMR spectroscopy were deoxygenated and dried over calcium hydride (dichloromethane) or potassium (benzene, thf and toluene) and then distilled before use.

The NMR spectra were recorded on either a Varian Unity-Plus 500 (^1H, ^{13}C and ^{31}P recorded at 499.868, 125.704 and 202.35 MHz respectively) or Bruker AM300 spectrometer (^1H, ^{11}B, ^{13}C and ^{31}P at 300.13, 96.2, 75.5 and 121.6 MHz respectively). Indirect detection (ID) experiments were carried out on a Varian UnityPlus 500 fitted with a pulsed-field-gradient ID probe. The spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances and measured relative to tetramethylsilane (^1H and ^{13}C, δ 0), or externally to 85% H_3PO_4 (^{31}P, δ 0). Electron-impact mass spectra were recorded on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectrometry Services Ltd. All data are quoted for ^{35}Cl unless otherwise stated. Correct isotope patterns were observed. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer in the range 400–4000 cm^{-1}. Samples were prepared as dilute CCl_4 solutions in a solution cell with KBr windows. Solution spectra were referenced to a blank cell containing only the solvent. Elemental analyses were obtained by the microanalysis department of the Inorganic Chemistry Laboratory or by Analytische Laboratorien, D-5270 Gummersbach, Germany.

The compound $NbCl_5$ (99%), $Li(CH_2SiMe_3)$ (1.0 mol dm^{-3} solution in pentane), $LiOBu^t$ (97%) and $LiNMe_2$ (95%) were obtained from Aldrich and used as received, H_2NNMe_2 (98%), $H_2NNMePh$ (97%), $SiMe_3Br$ (97%) and $P(OMe)_3$ (99%) from Aldrich and further purified before use by three freeze–pump–thaw cycles and NEt_3 (Aldrich, 99%) was distilled from CaH_2. Trimethyl phosphine,[36] $SnBu_3(\sigma-C_5H_5)$,[37] $[Nb(\eta-C_5H_5)Cl_4]$,[38] $[Nb(\eta-C_5H_4Me)Cl_4]$[38] and $Mg(CH_2CMe_2Ph)Cl$ were prepared according to the literature procedures; $SnBu_3(\sigma-C_5H_4Me)$ was prepared in an analogous fashion to $SnBu_3(\sigma-C_5H_5)$ but using $Na(C_5H_4Me)$ in place of $Na(C_5H_5)$.

Preparations

Dichloro(η-cyclopentadienyl)(2,2-dimethylhydrazido)niobium 1. The compound $[Nb(\eta-C_5H_5)Cl_4]$ (13.6 g, 45.3 mmol) was slurried in CH_2Cl_2 (300 cm^3). *N,N*-Dimethylhydrazine (3.45 cm^3, 45.3 mmol) and NEt_3 (12.63 cm^3, 91 mmol) in CH_2Cl_2 (10 cm^3) were added with stirring at room temperature over the course of 1 h. White fumes of $NHEt_3Cl$ formed immediately. The solution was stirred for 3.5 h during which time it changed to a deep red. Volatiles were removed under reduced pressure to yield a brown solid which was extracted in toluene (6×100 cm^3). The volume of this solution was reduced to *ca.* 500 cm^3 until a solid precipitated; the solution was then filtered and cooled to −80 °C overnight to yield a brick red microcrystalline powder. Yield 7.35 g (56%) (Found: C, 29.0; H, 5.4; N, 9.75. $C_7H_{11}Cl_2N_2Nb$ requires C, 29.3; H, 3.85; N, 9.75%). NMR (CD_2Cl_2): ^1H (300 MHz), δ 6.29 (s, 5 H, C_5H_5) and 2.92 [s, 6 H, $NN(CH_3)_2$]; ^{13}C-$\{^1H\}$ (125.7 MHz), δ 112.2 (C_5H_5) and 46.2 [$NN(CH_3)_2$]. Mass spectrum: m/z 286 (M^+, 11), 228 ($M -$ $NNMe_2$, 30) and 193 ($M - NNMe_2 - Cl$, 5%).

Dichloro(2,2-dimethylhydrazido)(η-methylcyclopentadienyl)-niobium 2. The compound $[Nb(\eta-C_5H_4Me)Cl_4]$ (10 g, 31.8 mmol) was slurried in CH_2Cl_2 (300 cm^3). *N,N*-Dimethyl-hydrazine (2.42 cm^3, 31.8 mmol) and NEt_3 (8.88 cm^3, 64 mmol) in CH_2Cl_2 (5 cm^3) were added with stirring at room temperature

over the course of 30 min. White fumes of $NHEt_3Cl$ formed immediately. The solution was stirred for 4.5 h during which time it changed to a deep red. Volatiles were removed under reduced pressure to yield a brown solid which was extracted in toluene $(3 \times 100$ cm^3). The volume of this solution was reduced to *ca.* 100 cm^3 until a solid precipitated; the solution was then filtered and cooled to -80 °C overnight to yield a brick red microcrystalline powder. An analytically pure orange-red crystalline solid was obtained by recrystallisation from boiling light petroleum (b.p. 100–120 °C). Yield 3.52 g (37%) (Found: C, 31.8; H, 4.35; Cl, 22.95; N, 9.1. $C_8H_{13}Cl_2N_2Nb$ requires C, 31.9; H, 4.35; Cl, 23.55; N, 9.3%). NMR: ^1H (C_6D_6, 300 MHz), δ 5.84 (vt, $J_{HH} = 2.7$, 2 H, $C_5H_4CH_3$), 5.59 (vt, $J_{HH} = 2.7$, 2 H, $C_5H_4CH_3$), 2.43 [s, 6 H, $NN(CH_3)_2$], 1.69 (s, 3 H, $C_5H_4CH_3$); (CD_2Cl_2) δ 6.44 (vt, $J_{HH} = 2.7$, 2 H, $C_5H_4CH_3$), 6.18 (vt, $J_{HH} = 2.7$ Hz, 2 H, $C_5H_4CH_3$), 2.90 [s, 6 H, $NN(CH_3)_2$] and 2.26 (s, 3 H, $C_5H_4CH_3$); ^{13}C-$\{^1H\}$ (CD_2Cl_2, 75.4 MHz), δ 131.3 ($C_5H_4CH_3$, quaternary), 112.4 ($C_5H_4CH_3$), 109.4 ($C_5H_4CH_3$), 46.2 [$NN(CH_3)_2$] and 15.0 ($C_5H_4CH_3$). Mass spectrum: *m/z* 300 (M^+, 57), 265 ($M -$ Cl, 3), 242 ($M - NNMe_2$, 100) and 206 [$Nb(C_5H_4Me)Cl$, 44%]. IR: $\tilde{v}_{max}$/cm^{-1} 1464 and 806.

Dichloro(η-cyclopentadienyl)(2-methyl-2-phenylhydrazido)-niobium 3. The compound [$Nb(\eta$-$C_5H_5)Cl_4$] (1.02 g, 3.4 mmol) was slurried in CH_2Cl_2 (20 cm^3). *N*-Methyl-*N*-phenylhydrazine (0.40 cm^3, 3.4 mmol) and NEt_3 (0.95 cm^3, 6.8 mmol) in CH_2Cl_2 (2 cm^3) was added with stirring at room temperature over the course of 1 min. White fumes of $NHEt_3Cl$ formed immediately. The solution was stirred for 17 h during which time it changed to a deep red. Volatiles were removed under reduced pressure to yield a brown solid which was washed in pentane. The residue was extracted in toluene $(3 \times 20$ cm^3); volatiles were then removed under reduced pressure to afford a purple microcrystalline solid. Analytically pure metallic green plates were obtained by slow cooling of a boiling light petroleum (b.p. 100–120 °C) solution of this solid. Yield 250 mg (21%) (Found: C, 41.5; H, 3.75; Cl, 19.7; N, 8.1. $C_{12}H_{13}Cl_2N_2Nb$ requires C, 41.3; H, 3.75; Cl, 20.3; N, 8.05%). NMR: ^1H (C_6D_6, 300 MHz), δ 7.0–6.5 (unresolved m, 5 H, C_6H_5), 5.76 (s, 5 H, C_5H_5) and 2.88 (s, 3 H, CH_3); ^{13}C-$\{^1H\}$ (CD_2Cl_2, 75.5 MHz), δ 129.1 (C_6H_5), 128.3 (C_6H_5, quaternary), 121.5 (C_6H_5), 113.0 or 112.7 (C_6H_5), 112.7 or 113.0 (C_5H_5) and 46.2 [$NN(CH_3)Ph$].

Di-*tert*-butoxo(η-cyclopentadienyl)(2,2-dimethylhydrazido)-niobium 4. The compound LiOBu^t (281 mg, 3.5 mmol) was dissolved in thf (30 cm^3) and added over the course of 10 min at room temperature with stirring to a solution of [$Nb(\eta$-$C_5H_5)Cl_2(NNMe_2)$] (501 mg, 1.75 mmol) in thf (30 cm^3). The solution instantly changed from deep red to pale yellow. The mixture was stirred for 10 min and volatiles were then removed under reduced pressure. Pentane (5 cm^3) was added and then removed under reduced pressure to ensure complete precipitation of LiCl. The mixture was then extracted in pentane $(3 \times 10$ cm^3). Over the course of 30 min more LiCl precipitated so the volatiles were once again removed and the resulting oil re-extracted in pentane. Volatiles were removed under reduced pressure to yield a red oil which was pure according to NMR spectroscopy. An analytically pure straw-coloured oil was obtained by sublimation (55 °C, 10^{-2} mmHg). Yield, 0.56 g (87%) (Found: C, 49.55; H, 7.95; N, 7.65. $C_{15}H_{29}N_2NbO_2$ requires C, 49.75; H, 8.05; N, 7.75%). NMR (C_6D_6): ^1H (300 MHz), δ 6.16 (s, 5 H, C_5H_5), 2.51 [s, 6 H, $NN(CH_3)_2$] and 1.34 [s, 18 H, $C(CH_3)_3$]; ^{13}C-$\{^1H\}$ (75.5 MHz), δ 108.7 (C_5H_5), 76.3 [$C(CH_3)_3$], 47.7 [$NN(CH_3)_2$] and 32.25 [$C(CH_3)_3$]. Mass spectrum: *m/z* 362 (M^+, 65), 306 ($M -$ CH$_2$CMe$_2$, 11), 250 ($M -$ 2CH$_2$CMe$_2$, 100) and 232 ($M -$ OBu$^t -$ Bu^t, 42%).

Di-*tert*-butoxo(2,2-dimethylhydrazido)(η-methylcyclopenta-dienyl)niobium 5. The compound LiOBu^t (120 mg, 1.5 mmol)

was dissolved in thf (20 cm^3) and added rapidly at room temperature with stirring to a solution of [$Nb(\eta$-$C_5H_4Me)$-$Cl_2(NNMe_2)$] (224 mg, 0.74 mmol) in thf (20 cm^3). The solution instantly changed from deep red to pale yellow. It was stirred for 30 min and volatiles were then removed under reduced pressure. Pentane (5 cm^3) was added and then removed under reduced pressure to ensure complete precipitation of LiCl. The mixture was extracted in pentane $(3 \times 20$ cm^3) and filtered through Celite. Volatiles were removed under reduced pressure to yield a red oil which was pure according to NMR spectroscopy. Yield 237 mg (85%) (Found: C, 49.05; H, 8.25; N, 9.35. $C_{16}H_{31}N_2NbO_2$ requires C, 51.05; H, 8.3; N, 7.45%). NMR (C_6D_6): ^1H (300 MHz), δ 6.20 (vt, $J_{HH} = 2.6$, 2 H, $C_5H_4CH_3$), 5.76 (vt , $J_{HH} = 2.6$ Hz, 2 H, $C_5H_4CH_3$), 2.54 [s, 6 H, $NN(CH_3)_2$], 2.10 (s, 3 H, $C_5H_4CH_3$) and 1.39 [s, 18 H, $OC(CH_3)_3$]; ^{13}C-$\{^1H\}$ (125.7 MHz), δ 107.2 ($C_5H_4CH_3$), 106.6 ($C_5H_4CH_3$), 48.0 [$NN(CH_3)_2$], 31.4 [$OC(CH_3)_3$] and 14.8 ($C_5H_4CH_3$). Mass spectrum: *m/z* 378 (M^+, 77), 363 ($M -$ Me, 5), 320 ($M - NNMe_2$, 16), 305 ($M -$ OBu^t, 3), 265 ($M - NNMe_2 -$ Bu^t, 91), 248 ($M - NNMe_2 -$ OBu^t, 46) and 57 (Bu^t, 100%).

Bromo(*tert*-butoxo)(2,2-dimethylhydrazido)(η-methylcyclo-pentadienyl)niobium 6. A sample of [$Nb(\eta$-$C_5H_4Me)(OBu^t)_2$-$(NNMe_2)$] **5** was prepared from compound **2** (475 mg, 1.58 mmol) and LiOBu^t (255 mg, 3.19 mmol) in thf (30 cm^3). To this solution was added SiMe$_3$Br (0.5 cm^3, 3.8 mmol) and the solution was then stirred for 1 h. Volatiles were removed under reduced pressure to afford a red oil which was extracted with pentane to give the required compound as a red oil; this was pure according to ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopy. Yield 0.192 g (40%). Accurate analytical data were not obtained. NMR (CD_2Cl_2): ^1H (300 MHz), δ 6.35 (m, 1 H, $C_5H_4CH_3$), 6.25 (m, 1 H, $C_5H_4CH_3$), 6.05 (m, 2 H, $C_5H_4CH_3$), 2.84 [s, 6 H, $NN(CH_3)_2$], 2.16 (s, 3 H, $C_5H_4CH_3$) and 1.32 [s, 9 H, $C(CH_3)_3$]; ^{13}C-$\{^1H\}$ (75.5 MHz), δ 128.3 ($C_5H_4CH_3$, quaternary), 111.7 ($C_5H_4CH_3$), 108.5 ($C_5H_4CH_3$), 107.6 ($C_5H_4CH_3$), 106.6 ($C_5H_4CH_3$), 81.1 [$C(CH_3)_3$], 46.7 [$NN(CH_3)_2$], 31.6 [$C(CH_3)_3$] and 14.9 ($C_5H_4CH_3$). Mass spectrum (fragments based on ^{79}Br): *m/z* 382 (M^+, 36), 326 ($M -$ C$_4$H$_8$, 100) and 268 ($M -$ C$_4$H$_8 -$ NNMe$_2$, 56%).

(η-Cyclopentadienyl)(2,2-dimethylhydrazido)bis(dimethyl-amido)niobium 7. The compound LiNMe$_2$ (110 mg, 2.16 mmol) was dissolved in thf (20 cm^3) and added over the course of 5 min at room temperature with stirring to [$Nb(\eta$-$C_5H_5)Cl_2$-$(NNMe_2)$] (299 mg, 1.04 mmol) in thf (20 cm^3). The mixture was stirred for 2.5 h and volatiles were then removed under reduced pressure. Pentane (5 cm^3) was added and then removed *in vacuo* to ensure the complete precipitation of LiCl. The mixture was then extracted in pentane $(3 \times 20$ cm^3) and filtered. Volatiles were removed under reduced pressure to yield a red oil which was pure according to NMR spectroscopy. Attempts at vacuum sublimation (100 °C, 10^{-2} mmHg) resulted in decomposition of the product. Yield 221 mg (70%). Accurate analytical data were not obtained. NMR (C_6D_6): ^1H (300 MHz), δ 5.96 (s, 5 H, C_5H_5), 3.26 [s, 12 H, $N(CH_3)_2$] and 2.53 [s, 6 H, $NN(CH_3)_2$]; ^{13}C-$\{^1H\}$ (125.7 MHz), δ 105.7 (C_5H_5), 53.0 [$N(CH_3)_2$] and 48.0 [$NN(CH_3)_2$]. Mass spectrum: *m/z* 304 (M^+, 100), 260 ($M -$ NMe$_2$, 4), 244 ($M -$ NNMe$_2$, 33), 214 [Nb-$(C_5H_5)(NMe_2)_2$, 55], 186 [Nb$(C_5H_5)N_2$, 27], 172 [Nb$(C_5H_5)N$, 27], 158 [Nb(C_5H_5), 40] and 44 (NMe$_2$, 18%).

(η-Cyclopentadienyl)(2,2-dimethylhydrazido)bis(2-methyl-2-phenylpropyl)niobium 8. The compound Mg(CH$_2$CMe$_2$Ph)Cl (3 cm^3 of a 1.33 mol dm^{-3} solution in thf, 4 mmol) was added with stirring at room temperature to a solution of [Nb(η-$C_5H_5)Cl_2(NNMe_2)$] (0.484 g, 1.68 mmol) in thf (40 cm^3). The solution was stirred for 72 h, over the course of which it became pale orange. The volatiles were then removed under reduced

pressure to afford a red oil which was extracted in pentane (3×20 cm^3). On standing overnight a grey precipitate formed, presumably of MgCl$_2$, so the volatiles were again removed under reduced pressure and the oil extracted a second time into pentane. Removal of this pentane afforded the compound as a red oil. Yield 0.683 g (84%). Accurate analytical data were not obtained. NMR (CD$_2$Cl$_2$): ^{1}H (300 MHz), δ 7.32 (m, C$_6$H$_5$), 7.25 (m, C$_6$H$_5$), 7.12 (m, C$_6$H$_5$), 5.70 (s, 5 H, C$_5$H$_5$), 2.73 [s, 6 H, NN(CH$_3$)$_2$], 2.42 [d, 2 H, $J_{HH} = 11.4$, CH$_2$], 1.45 [s, 6 H, C(CH$_3$)$_2$], 1.42 [s, 6 H, C(CH$_3$)$_2$] and -0.15 (d, 2 H, $J_{HH} = 11.4$ Hz, CH$_2$); ^{13}C-{^{1}H} (75.5 MHz), δ 154.0 (C$_6$H$_5$, quaternary), 127.8 (C$_6$H$_5$), 125.7 (C$_6$H$_5$), 124.9 (C$_6$H$_5$), 105.6 (C$_5$H$_5$), 81.7 (br, CH$_2$), 48.2 [NN(CH$_3$)$_2$], 41.8 [C(CH$_3$)$_2$] and 33.4 [C(CH$_3$)$_2$]. Mass spectrum: m/z 485 (M^+, 0.5), 351 ($M -$ CH$_2$CMe$_2$Ph, 1) and 120 (CMe$_2$Ph, 100%).

(2,2-Dimethylhydrazido)(η-methylcyclopentadienyl)bis(2-methyl-2-phenylpropyl)niobium 9.

The compound Mg(CH$_2$-CMe$_2$Ph)Cl (2.5 cm^3 of a 1.33 mol dm^{-3} solution in thf, 3.3 mmol) was added with stirring at room temperature to a solution of [Nb(η-C$_5$H$_4$Me)Cl$_2$(NNMe$_2$)] (0.400 g, 1.33 mmol) in thf (40 cm^3). The solution rapidly became pale orange and was stirred for 11 d. The volatiles were removed under reduced pressure to afford a red oil which was dissolved in pentane to ensure complete precipitation of MgCl$_2$. After filtration the volatiles were again removed under reduced pressure and the oil extracted into pentane (3×20 cm^3). Removal of this pentane afforded the required compound as a red oil. Yield 0.58 g (88%) (Found: C, 64.7; H, 7.55; N, 4.55. C$_{28}$H$_{39}$N$_2$Nb requires C, 67.85; H, 7.75; N, 5.65%). NMR (CD$_2$Cl$_2$): ^{1}H (300 MHz), δ 7.31 (m, C$_6$H$_5$), 7.22 (m, C$_6$H$_5$), 7.08 (m, C$_6$H$_5$), 5.50 (vt, 2 H, C$_5$H$_4$CH$_3$), 5.41 (vt, 2 H, C$_5$H$_4$CH$_3$), 2.72 [s, 6 H, NN(CH$_3$)$_2$], 2.31 (d, 2 H, $J_{HH} = 9$, CH$_2$), 2.02 (s, 3 H, C$_5$H$_4$CH_3), 1.45 [s, 6 H, C(CH_3)$_2$], 1.40 [s, 6 H, C(CH_3)$_2$] and -0.15 (d, 2 H, $J_{HH} = 9$ Hz, CH$_2$); ^{13}C-{^{1}H} (75.5 MHz), δ 154.1 (C$_6$H$_5$, quaternary), 127.8 (C$_6$H$_5$), 125.7 (C$_6$H$_5$), 124.9 (C$_6$H$_5$), 107.9 (C_5H$_4$CH$_3$), 101.9 (C_5H$_4$CH$_3$), 82.3 (br, CH$_2$), 48.24 [NN(CH$_3$)$_2$], 41.7 [C(CH$_3$)$_2$], 33.3 [C(CH$_3$)$_2$] and 14.4 (C$_5$H$_4$$CH_3$). Mass spectrum: m/z 497 (M^+, 2), 365 ($M -$ CH$_2$CMe$_2$Ph, 4) and 120 (CMe$_2$Ph, 48%). IR: $\tilde{\nu}_{max}$/cm^{-1} 2829, 1586, 1405 and 1224.

(η-Cyclopentadienyl)(2,2-dimethylhydrazido)bis(trimethyl-silylmethyl)niobium 10.

The compound Li(CH$_2$SiMe$_3$) (1.4 cm^3 of a 1 mol dm^{-3} solution in pentane, 1.4 mmol) was added with stirring at room temperature to a solution of [Nb(η-C$_5$H$_5$)-Cl$_2$(NNMe$_2$)] (0.197 g, 0.68 mmol) in thf (20 cm^3). The solution was stirred for 1 h and the volatiles were then removed under reduced pressure to afford a red oil which was extracted in pentane (3×10 cm^3). Removal of this pentane afforded a red oil which was pure by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy. Yield 0.240 g (89%). Analytical data were not obtained. NMR (CD$_2$Cl$_2$): ^{1}H (300 MHz), δ 6.07 (s, 5 H, C$_5$H$_5$), 2.77 [s, 6 H, NN(CH$_3$)$_2$], 1.22 (d, 2 H, $J_{HH} = 9.8$, CH$_2$), 0.02 [s, 18 H, Si(CH$_3$)$_3$] and -0.13 (d, 2 H, $J_{HH} = 9.8$ Hz, CH$_2$); ^{13}C-{^{1}H} (75.5 MHz), δ 105.9 (C$_5$H$_5$), 50.3 (br, CH$_2$), 48.6 [NN(CH$_3$)$_2$] and 2.3 [Si(CH$_3$)$_3$]. Mass spectrum: m/z 391 (M^+, 13), 376 ($M -$ Me, 1), 304 ($M -$ CH$_2$SiMe$_3$, 1), 158 (C$_5$H$_5$Nb, 23) and 73 (SiMe$_3$, 100%).

cis-Dichloro(η-cyclopentadienyl)(2,2-dimethylhydrazido)-(trimethyl phosphite)niobium 11.

The compound [Nb(η-C$_5$H$_5$)-Cl$_2$(NNMe$_2$)] (0.200 g, 0.69 mmol) was dissolved in toluene (20 cm^3) and placed in one arm of a thick walled glass H-cell which had a sinter-glass frit dividing the two halves of the cell. A mixture of P(OMe)$_3$ (ca. 2 cm^3) and toluene (10 cm^3) was introduced into the other side and cooled to -78 °C. The whole apparatus was then left under nitrogen to warm up overnight, during which time large deep ruby red crystals formed. The supernatant liquid was decanted and the solid washed in a toluene–P(OMe)$_3$ mixture. The solid was then dried in vacuo. A

second crop of smaller crystals separated from the washings overnight. Yield 215 mg (75%) (Found: C, 29.2; H, 4.85; Cl, 17.45; N, 6.95. C$_{10}$H$_{20}$Cl$_2$N$_2$NbO$_3$P requires C, 29.2; H, 4.9; Cl, 17.2; N, 6.8%). NMR (CD$_2$Cl$_2$): ^{1}H (300 MHz), all peaks were broad, δ 6.22 (s, 5 H, C$_5$H$_5$), 3.78 (d, 9 H, $J_{PH} = 10$ Hz, P(OCH$_3$)$_3$) and 3.05 [s, 6 H, NN(CH$_3$)$_2$]; ^{13}C-{^{1}H} (125.7 MHz), δ 108.61 (br, C$_5$H$_5$), 45.76 [NN(CH$_3$)$_2$], P(OCH$_3$)$_3$ resonance obscured under the CD$_2$Cl$_2$ resonances; ^{31}P-{^{1}H} (202.34 MHz), δ 222 [br, P(OMe)$_3$]. Mass spectrum: m/z 413 (M^+, 4), 287 [$M -$ P(OMe)$_3$, 4], 229 [$M -$ P(OMe)$_3$ $-$ NNMe$_2$, 34], 124 [P(OMe)$_3$, 25], 109 [PO(OMe)$_2$, 39], 93 [P(OMe)$_2$, 66], 62 (POMe, 9) and 15 (Me, 100%).

cis-Dichloro(η-cyclopentadienyl)(2,2-dimethylhydrazido)-(trimethylphosphine)niobium 12 and trans-chloro(η-cyclopenta-dienyl)(2,2-dimethylhydrazido)bis(trimethylphosphine)niobium chloride 13.

The compound [Nb(η-C$_5$H$_5$)Cl$_2$(NNMe$_2$)] (0.10 g, 0.34 mmol) was dissolved in toluene (20 cm^3) and the solution was filtered into one side of a thick walled glass H-cell which had a sinter-glass frit dividing the two sides of the cell. The apparatus was then evacuated and PMe$_3$ (3 cm^3) was condensed into the other side of the H-cell. Nitrogen gas was admitted, the apparatus was sealed and allowed to warm to room temperature. Yellow crystals of compounds **12** and **13** formed and were filtered off, washed in toluene and dried in vacuo. Yield 96 mg (72%, based on the assumption the composition is **1**·1.2PMe$_3$) (Found: C, 34.95; H, 6.75; Cl, 16.9; N, 6.3. **1**·1.8PMe$_3$, that is a 2:3 mixture of compounds **12** and **13**, requires C, 35.15; H, 6.45; Cl, 16.75; N, 6.6%). The NMR assignments were confirmed by a C–H correlation experiment. Compound **12**: NMR (CD$_2$Cl$_2$), ^{1}H (300 MHz), δ 6.05 (d, $^3J_{PH} = 3$, 5 H, C$_5$H$_5$), 3.02 [d, 6 H, $^5J_{HH} = 1$, NN(CH$_3$)$_2$], 1.53 [d, $^2J_{PH} = 9$, 9 H, P(CH$_3$)$_3$]; ^{13}C-{^{1}H} (125.7 MHz), δ 107.5 (C$_5$H$_5$), 46.1 [NN(CH$_3$)$_2$] and 14.8 [d, $^1J_{PC} = 26$ Hz, P(CH$_3$)$_3$]; ^{31}P-{^{1}H} (202.34 MHz), δ 10.1. Compound **13**: ^{1}H, δ 6.09 (t, $^3J_{PH} = 2.1$, 5 H, C$_5$H$_5$), 3.16 [t, $^3J_{PH} = 1.2$, 6 H, NN(CH$_3$)$_2$], 1.56 [t, $^2J_{PH} = 4.5$, 18 H, P(CH$_3$)$_3$]; ^{13}C-{^{1}H}, δ 105.0 (C$_5$H$_5$), 46.6 [NN(CH$_3$)$_2$] and 15.09 [vt, $^1J_{PC} \approx {^3}J_{PC} = 12.5$ Hz, P(CH$_3$)$_3$]; ^{31}P-{^{1}H}, δ 3.3. Mass spectrum: m/z 364 (M^+, 2), 288 ($M -$ PMe$_3$, 13), 229 ($M -$ PMe$_3$ $-$ NNMe$_2$, 34), 76 (PMe$_3$, 99) and 61 (PMe$_2$, 100%).

cis-Dichloro(η-methylcyclopentadienyl)(2,2-dimethyl-hydrazido)(trimethylphosphine)niobium 14 and trans-chloro-(η-methylcyclopentadienyl)(2,2-dimethylhydrazido)bis(trimethyl-phosphine)niobium chloride 15a.

Compounds **14** and **15a** were prepared in an analogous fashion to **12** and **13** using [Nb-(η-C$_5$H$_4$Me)Cl$_2$(NNMe$_2$)] (0.54 g, 1.8 mmol). Yield 270 mg (39%, based on the composition **2**·1.1PMe$_3$) (Found: C, 35.35; H, 6.2; Cl, 18.8; N, 7.55. **2**·1.1PMe$_3$, that is a 9:1 mixture of compounds **14** and **15a**, requires C, 35.3; H, 6.0; Cl, 18.45; N, 7.3%). The NMR assignments were confirmed by a C–H correlation experiment. Compound **14**: NMR (CD$_2$Cl$_2$), ^{1}H (500 MHz), δ 6.20 (m, 1 H, C$_5$H$_4$CH$_3$), 5.95 (m, 1 H, C$_5$H$_4$CH$_3$), 5.78 (m, 1 H, C$_5$H$_4$CH$_3$), 5.60 (m, 1 H, C$_5$H$_4$CH$_3$), 3.05 [d, $^5J_{PH} = 0.1$, 6 H, N(CH$_3$)$_2$], 2.25 (s, 3 H, C$_5$H$_4$CH_3) and 1.51 [d, $^2J_{PH} = 9.2$ Hz, 9 H, P(CH$_3$)$_3$]; ^{13}C-{^{1}H} (125.7 MHz), δ 111.8 (C_5H$_4$CH$_3$), 110.5 (C_5H$_4$CH$_3$), 101.7 (C_5H$_4$CH$_3$), 98.6 (C_5H$_4$CH$_3$), 46.6 [N(CH$_3$)$_2$], 15.0 [P(CH$_3$)$_3$] and 14.2 (C$_5$H$_4$$CH_3$); ^{31}P-{^{1}H} (202.34 MHz), δ 4.8. Compound **15**: NMR, ^{1}H, δ 5.86 (m, 2 H, C$_5$H$_4$CH$_3$), 5.65 (m, 2 H, C$_5$H$_4$CH$_3$), 3.20 [s, 6 H, N(CH$_3$)$_2$], 2.02 (s, 3 H, C$_5$H$_4$CH_3), 1.59 [vt, $^2J_{PH} \approx {^4}J_{PH} = 4.5$, 18 H, $2 \times$ P(CH$_3$)$_3$]; ^{13}C-{^{1}H}, δ 110.2 (C_5H$_4$CH$_3$), 96.0 (C_5H$_4$CH$_3$), 46.1 [N(CH$_3$)$_2$], 14.7 [vt, $^1J_{PC} \approx {^3}J_{PC} = 13.5$ Hz, P(CH$_3$)$_3$] and 15.2 (C$_5$H$_4$$CH_3$); ^{31}P-{^{1}H}, δ -0.1. Mass spectrum: m/z 301 (M^+ $-$ PMe$_3$, 58), 243 ($M -$ PMe$_3$ $-$ NNMe$_2$, 100), 76 (PMe$_3$, 41) and 61 (PMe$_2$, 59).

trans-Chloro(2,2-dimethylhydrazido)(η-methylcyclopenta-dienyl)bis(trimethylphosphine)niobium hexafluorophosphate 15b.

A mixture of [Nb(η-C$_5$H$_4$Me)Cl(NNMe$_2$)(PMe$_3$)$_2$]Cl and

Table 3 Crystallographic data* for complexes **1** and **11**

	1	**11**
Formula	$C_{14}H_{22}Cl_4N_4Nb_2$	$C_{10}H_{20}Cl_2N_2NbO_3P$
M	573.98	411.04
Space group	$P2_1/m$	$P2_1/c$
$a/Å$	8.904(9)	9.573(1)
$b/Å$	11.802(6)	11.4907(8)
$c/Å$	10.738(14)	15.685(2)
$\beta/°$	112.84(6)	106.18(1)
$U/Å^3$	1040.16	1657.17
$D_c/\text{Mg m}^{-3}$	1.833	1.64
μ/mm^{-1}	1.574	1.167
$\theta_{max}/°$	24	30.0
T_{min}, T_{max}	0.44, 1.00	
Scan type	ω	ω–2θ
Total data collected	2263	5833
Unique data	1723	4839
Observed data $[I > 3\sigma(I)]$	1209	3678
Merging R	0.057	0.023
Chebychev weighting coefficients	20.6, −11.9, 15.1	15.0, −9.20, 12.20
Number parameters refined	121	172
Minimum, maximum residual electron density/e $Å^{-3}$	−1.15, 2.05	−0.39, 0.94
R	0.072	0.029
R'	0.083	0.035

* Details in common: monoclinic; $Z = 4$; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}}$.

$[Nb(\eta\text{-}C_5H_4Me)Cl_2(NNMe_2)(PMe_3)]$ (80 mg) from the previous reaction was dissolved in the minimum volume of thf (20 cm³) and PMe₃ (*ca.* 0.5 cm³) was condensed in at 77 K. The solution was allowed to warm to room temperature and filtered. A saturated solution of $[NH_4][PF_6]$ in thf was added (*ca.* 10 cm³ containing *ca.* 150 mg of $[NH_4][PF_6]$) whereupon a fine yellow precipitate formed. The solution was allowed to stand for 1 h to let the precipitate settle, then filtered and the residue washed in thf (3 × 5 cm³) and dried *in vacuo.* Yield 40 mg (27%) based on the assumption the starting material was largely compound **14** (Found: C, 29.2; H, 5.7; Cl, 6.45; N, 5.15; P, 15.45. $C_{14}H_{31}ClF_6N_2NbP_2$ requires C, 29.9; H, 5.55; Cl, 6.3; N, 5.0; P, 16.5%). NMR (CD_2Cl_2): ¹H (300 MHz), δ 6.02 (m, 2 H, $C_5H_4CH_3$), 5.49 (m, 2 H, $C_5H_4CH_3$), 3.13 [s, 6 H, $N(CH_3)_2$], 1.98 (s, 3 H, $C_5H_4CH_3$) and 1.51 [vt, $^2J_{PH} \approx {}^4J_{PH} = 4.5$, 18 H, $2 \times P(CH_3)_3$]; ¹³C-{¹H} (75.5 MHz), δ 109.6 ($C_5H_4CH_3$), 95.6 ($C_5H_4CH_3$), 46.3 [$N(CH_3)_2$], 14.7 [vt, $^1J_{PC} \approx {}^3J_{PC} = 13.5$, $P(CH_3)_3$] and 14.1 ($C_5H_4CH_3$); ³¹P-{¹H} (121.5 MHz), δ −0.3 (br s, PMe_3) and −147.3 (spt, $^1J_{PF} = 708$ Hz, PF_6^-).

Crystallography

A crystal of compound **1** of dimensions $0.1 \times 0.2 \times 0.2$ mm was mounted under nitrogen in a Lindemann tube. The data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ 0.710 69 Å) and indexed as monoclinic. The systematic absences were consistent with the space groups $P2_1$ and $P2_1/m$. Structure solution in both space groups clearly indicated the presence of mirror symmetry giving the final space group $P2_1/m$. The structure was solved using the CRYSTALS[39] package by direct methods (SIR 92).[40] Full-matrix least-squares refinement was performed and vibrational restraints, the DIFABS absorption correction[41] and a Chebychev weighting scheme applied.[42] Hydrogen atoms were placed geometrically yielding a final R value of 0.072. Unfortunately, the crystal quality was poor, with the surface showing extensive powdering. The effects of powdering were shown by the smearing out of the sharp reflections in the polaroid photograph of the crystal taken to check its crystallinity. In this case there was still enough intensity in the original peak for the crystal to be indexed. As a result however the reflection measurements have substantially larger estimated standard deviations (e.s.d.s) which caused problems in the refinement of the structure, requiring the application of vibrational restraints.

This resulted in a larger R value than desirable. Full crystallographic details are in Table 3.

A crystal of compound **11** of dimensions $0.34 \times 0.40 \times 0.47$ mm was mounted in a Lindemann tube and data were collected as above. The crystal was indexed as monoclinic. The systematic absences were consistent with the space group $P2_1/c$. Data were corrected for Lorentz-polarisation effects. The non-hydrogen atoms were located by Patterson and Fourier-difference syntheses. The hydrogen atoms were placed in calculated positions (C–H 1.0 Å and $U_{iso} = 1.25 U_{eq}$ of the adjacent atom) and were not included in the final cycles of refinement. The structure was refined using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The refinement was based on F.

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 186/413.

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