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Reactions of Cp(NAr)$NbMe_2$ with H_2 and $HSiMe_2Cl$. Molecular structure of [CpNb(μ-NAr)Me]$_2$ (Ar = 2,6-$C_6H_3^iPr_2$)

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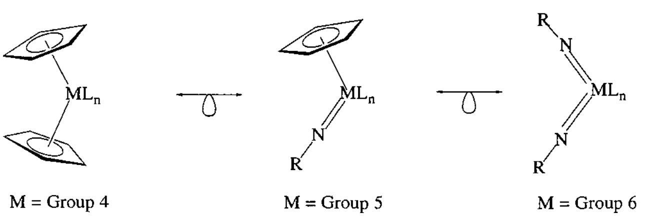
Abstract

Reactions of Cp(NAr)$NbMe_2$ with H_2 and $HSiMe_2Cl$ are described. With H_2 (1 atm) an apparent σ-bond metathesis process is accompanied by reduction to form the binuclear, metal–metal bonded species [CpNb(μ-NAr)Me]$_2$ (Nb–Nb = 2.6852(4) Å). With $HSiMe_2Cl$ (excess) Cp(NAr)NbMeCl is obtained in quantitative yield. © 2001 Elsevier Science B.V. All rights reserved.

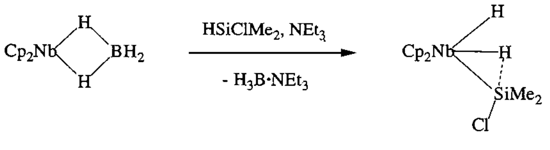
Keywords: Niobium; σ-Bond metathesis; X-ray diffraction; Metal–metal bond; Cyclopentadienyl

1. Introduction

The isolobal analogy between the imide di-anion (NR^{2-}) and the cyclopentadienide mono-anion ($C_5R_5^-$) is a very useful concept for the development of a metallocene-like chemistry in the framework of the cyclopentadienyl-imido and bis(imido) ligand sets [1–3]. For example, this analogy brings together the following series of compounds where L_n = bis(phosphine), di-alkyl, benzyne, carbene, etc. [4]:



One of the relatively recent achievements in Group 4 metallocene chemistry has been the development of σ-bond metathesis reactions [5]. Surprisingly, only one example of this process for isolobal Group 5 cyclopentadienyl-imido compounds of the type Cp(NR)M(L_n) (M = Group 5 metal) is known [6], although this reaction has a potential for the preparation of the rare imido-supported hydride- and silyl-substituted compounds. Hydridosilyl compounds are of current interest, and we have shown recently that such compounds can have non-classical interligand interactions between the H and Si ligands, as in $Cp_2NbH_2(SiMe_2Cl)$ (**A**) below [7].



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Prompted by the isolobal relationships outlined above we recently extended our studies of non-classical interligand interactions between H and Si ligands to cyclopentadienyl-imido compounds. Thus, reaction of Cp(NAr)M$(PMe_3)_2$ (M = Nb or Ta; Ar = 2,6-$C_6H_3^iPr_2$) with $HSiMe_2Cl$ gave two dramatically different products depending on the identity of M [7f]:

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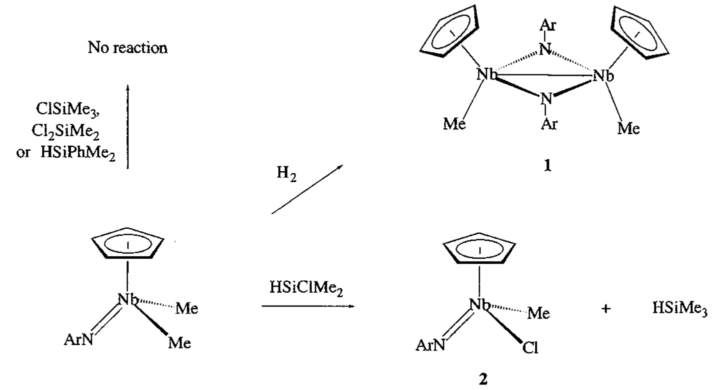
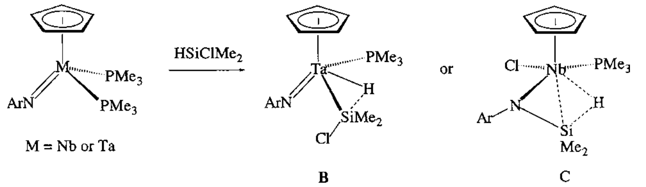


Scheme 1. Reactions of Cp(NAr)NMe$_2$ with H$_2$ and HSiMe$_2$Cl.



Here we report on complimentary comparative studies of the reactions of Cp(NAr)NbMe$_2$ with H$_2$, HSiMe$_2$Cl and related substrates.

2. Results and discussion

Long before the isolobal analogy between the Cp$_2$Zr and Cp(NR)Ta fragments was recognised, Bercaw et al. [6] reported the reaction of the 16 valence electron compound Cp(N^{t}Bu)TaMe$_2$ with dihydrogen (4 atm.) in the presence of PMe$_3$ to give Cp(N^{t}Bu)Ta(PMe$_3$)(H)$_2$. This slow (11 days) reaction occurs at 80°C and apparently proceeds via σ-bond metathesis.

We have found (Scheme 1) that the 16 valence electron, d^0 compound Cp(NAr)NbMe$_2$ reacts smoothly at room temperature with H$_2$ to give quantitatively the diamagnetic, binuclear compound [CpNb(μ-NAr)Me]$_2$ (**1**). The compound **1** was characterised by CHN combustion analysis and NMR spectroscopy. Its dinuclear formulation was confirmed by an X-ray structure determination (see below). The formation of **1** most likely proceeds via a σ-bond metathesis reaction. The probable intermediate, Cp(NAr)NbMeH, has not been directly observed and the mechanism of its transformation into **1** is unknown. The compound **1** is stable to further transformations and does not react further under prolonged exposure to H$_2$ (1 atm.) nor does it react with PMe$_3$ at 50°C. The ^{1}H NMR spectrum of **1** displays singlets for the Cp and Me ligands at 5.70 and 0.17 ppm, respectively, and two sets of signals for the two non-equivalent *iso*-propyl groups. This non-equivalence implies that there is restricted rotation around the N–Ar bond on the NMR timescale, presumably due to the bulkiness of the Ar substituent.

The molecular structure of **1** is shown in Fig. 1, crystal and data collection parameters are listed in Table 1, and selected bond distances and angles are given in Table 2. A number of crystallographically characterised compounds with two bridging imido groups between transition metals have been reported previously [8]. Those most closely related to **1** are of the type [CpM(μ-NR)X]$_2$, where X are terminal chloro- or oxo-groups [9]. Two other examples of binuclear niobium compounds with two μ-imido bridges [10a] and one example with bridging hydrazido groups are known [10b]. The methyl groups in **1** are in mutually *cis* positions with respect to the Nb$_2$(μ-N)$_2$ unit, the N(1)–Nb(1)–C(2″) and N(1A)–Nb(1)–C(2″) bond angles being 109.70(9) and 106.80(9)°, respectively. Such a

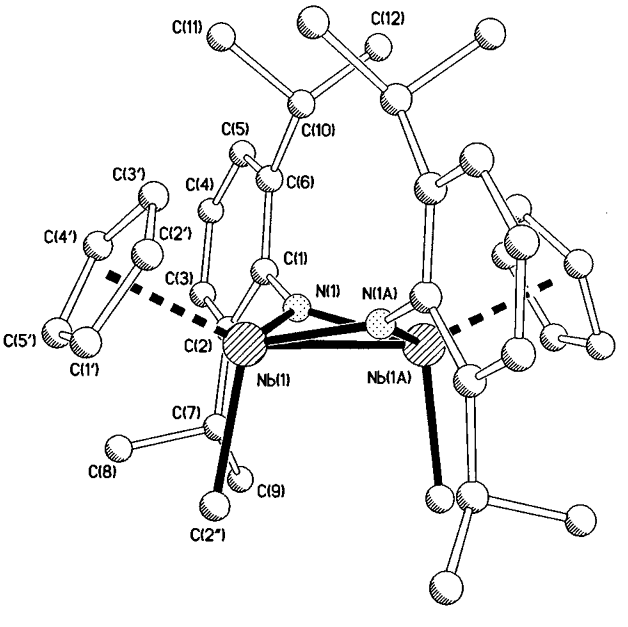


Fig. 1. Ball and stick plot of [CpNb(μ-NAr)Me]$_2$ (**1**). Hydrogen atoms are omitted for clarity. Atoms carrying the suffix ‘A’ are related to their counterparts by the symmetry operator [$-x$, y, $-z+1/2$].

Table 1
Crystal data and processing parameters for $[CpNb(\mu\text{-}NAr)Me]_2$

Experimental formula	$C_{18}H_{25}NNb$
Formula weight	348.30
Temperature (K)	150.0(2)
Wavelength (Å)	0.71073
Crystal	Dark-red brick
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	16.9342(9)
b (Å)	9.9950(5)
c (Å)	20.3469(11)
β (°)	107.782(4)
V (Å^3)	3279.3(3)
Z	8
D_{calc} (Mg m^{-3})	1.411
Absorption coefficient (mm^{-1})	0.725
F(000)	1448
Range for data collection	$2.10<\theta<26.00$
Reflections collected	10,068
Independent reflections	3217
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.091
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0252$, $wR_2=0.0536$
R indices (all data)	$R_1=0.0332$, $wR_2=0.0561$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.392 and −0.334

Table 2
Selected bond lengths (Å) and angles (°) for $[CpNb(\mu\text{-}NAr)Me]_2$ (**1**) [a]

Nb(1)–N(1)	1.9991(17)	Nb(1)–C(2′)	2.450(2)
Nb(1)–N(1A)	2.0128(18)	Nb(1)–C(3′)	2.388(2)
Nb(1)–Nb(1A)	2.6852(4)	Nb(1)–C(4′)	2.448(2)
Nb(1)–C(2″)	2.213(3)	Nb(1)–C(5′)	2.518(2)
Nb(1)–C(1′)	2.513(2)	N(1)–C(1)	1.426(3)
Nb(1)–Cp_{cent}	2.151		
N(1)–Nb(1)–N(1A)	91.35(7)	N(1A)–Nb(1)–Nb(1A)	47.77(5)
N(1)–Nb(1)–Nb(1A)	48.20(5)	Nb(1)–N(1)–Nb(1A)	84.03(7)
N(1A)–Nb(1)–C(2″)	106.80(9)	C(2″)–Nb(1)–Nb(1A)	99.95(8)
N(1)–Nb(1)–C(2″)	109.70(9)	Cp_{cent}–Nb(1)–Nb(1A)	154.7
Cp_{cent}–Nb(1)–N(1)	120.0	Cp_{cent}–Nb(1)–N(1A)	122.6
Cp_{cent}–Nb(1)–C(2″)	105.3		

[a] Atoms carrying the suffix ‘A’ are related to their counterpart by the symmetry operator $[-x, y, -z+1/2]$. Cp_{cent} refers to the computed centroid for the cyclopentadienyl ring carbons.

disposition of the methyl group leaves no co-ordination site for a possible hydride ligand, thus confirming its absence from the ^{1}H NMR spectrum of **1** and establishing the presence of two Nb(IV) centres. The Nb–Me bond length of 2.213(3) Å is noticeably shorter than the Ta–Me bond length of 2.246(12) Å in $Cp_2Ta(CH_2)Me$, [11] and Nb–Et bonds in $Cp_2Nb(Et)(\eta^2\text{-}MeCCMe)$ (2.311(11) Å) [12] and $Cp_2Nb(Et)(\eta^2\text{-}C_2H_4)$ (2.316(8) Å) [13]. The Nb(1)–N(1) and Nb(1)–N(1A) bond distances of 1.999(2) and 2.013(2) Å, respectively, lie within the range of corresponding bonds in the imido and hydrazido derivatives cited above (range 1.96(1)–2.14(3) Å) [10]. The N(1)–Nb(1)–N(1A) bond angle of 91.35(7)° is unexceptional, whereas the Nb(1)–N(1)–Nb(1A) bond angle of 84.03(7)° is somewhat smaller than in related niobocene systems (range 61–95(1) and 87–95(1)°, respectively). The small Nb(1)–Nb(1A) bond length of 2.6852(4) Å unequivocally establishes the presence of a direct metal–metal single bond and accounts for the diamagnetism of the compound. This bond length is significantly less than those in niobocene-derived bis(imido)-bridged derivatives (2.834(5) and 2.921(1) Å) [10a] and in other dinuclear compounds of niobium (range 3.001–3.136 (3) Å) [8,10b,14].

Reaction of $Cp(NAr)NbMe_2$ with $HSiMe_2Cl$ at room temperature quantitatively affords the previously described compound Cp(NAr)NbMeCl (**2**) [15] with concomitant formation of $HSiMe_3$ (which was observed by ^{1}H NMR when the reaction between $Cp(NAr)NbMe_2$ and $HSiMe_2Cl$ was carried out in benzene-d_6). Only one Me group in $Cp(NAr)NbMe_2$ is replaced by Cl even after prolonged reaction with an excess of silane. In contrast, $Cp(NAr)NbMe_2$ reacts neither with $ClSiMe_3$ nor with Cl_2SiMe_2, demonstrating the importance of steric factors. Analogously, addition of $HSiMe_2Cl$ to the oily product of the reaction of $Cp(N^tBu)NbCl_2$ with two equivalents of MeLi (presumably $Cp(N^tBu)NbMe_2$)[4] gives the known and previously described $Cp(N^tBu)NbMeCl$ as the main component of the reaction mixture. Previously, chlorine for alkyl group exchange has been observed in reactions of zirconocene metallocyclopropanes with chlorosilanes [16]. To our surprise, no reaction was observed between $Cp(NAr)NbMe_2$ and $HSiMe_2Ph$ or even with H_2SiMe_2, whereas addition of $BH_3{\cdot}THF$ to a pentane solution of $Cp(NAr)NbMe_2$ lead to immediate gas evolution and formation of a mixture of compounds. By way of comparison, reactions of the isolobal Group 4 dimethyl metallocenes with primary silanes are known to produce organopolysilanes, whereas secondary silanes are catalytically oligomerised into tetraorganodisilanes [17].

3. Experimental

3.1. General

All manipulations were carried out using conventional Schlenk and dry-box techniques. Protio- and deutero-solvents were dried over appropriate agents and distilled prior to use. NMR samples of air- and moisture-sensitive compounds were prepared in a dry-box in 5 mm Wilmad tubes, equipped with a Young's Teflon valve. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity Plus 500 or Varian Mercury Vx300

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[4] An analogous oil is obtained under the action of MeMgBr on Cp(NBut)NbClMe (see Ref. [15]).

spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$ ppm) in δ (ppm) and coupling constants in Hertz. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional experiments as appropriate. $HSiMe_2Cl$ was purchased from Sigma–Aldrich and used as received. $Cp(NAr)NbMe_2$ was prepared according to the literature method [15].

*3.2. Preparation of [CpNb(μ-NAr)Me]$_2$ (**1**)*

A solution of $Cp(NAr)NbMe_2$ (0.415 g, 1.14 mmol) in pentane (7 ml) was placed under an atmosphere of H_2 (1 atm). The mixture was stirred for 2 h and then left for a further 14 h without stirring. Large, dark-red crystals of **1** formed. The supernatant was decanted and the crystals were washed with 1 ml of cold pentane. Volatiles were removed under reduced pressure from the combined fractions giving **1** in the form of dark red powder. The combined yield of **1** was quantitative.

^{1}H NMR (benzene-d_6): 5.73 (s, 5H, Cp), 2.65 (sept, $J = 6.8$ Hz, 1H, $C\underline{H}Me_2$), 2.44 (sept, $J = 6.8$ Hz, 1H, $C\underline{H}Me_2$), 1.14 (d, $J = 6.8$ Hz, 6 H, $CH\underline{Me_2}$), 1.09 (d, $J = 6.8$ Hz, 6H, $CH\underline{Me_2}$) 0.21, (s, 3H, NbMe). $^{13}C\{^1H\}$ NMR (benzene-d_6): 107.7 (Cp), 27.5 ($\underline{C}HMe_2$), 26.5 ($\underline{C}HMe_2$), 26.4 ($CH\underline{Me_2}$), 24.4 ($CH\underline{Me_2}$), 24.0 (NbMe). Anal. Found: C, 62.24; H, 7.40; N, 3.95. Calc. for $C_{12}H_{25}NNb$: C, 62.07; H, 7.52; N, 4.02%.

*3.3. Preparation of [Cp(NAr)NbMeCl] (**2**)*

$HSiMe_2Cl$ (0.8 ml, 7.2 mmol) was added to Cp(-NAr)$NbMe_2$ (0.501 g, 1.38 mmol) in pentane (8 ml). The mixture was kept in the dark for 3 days at room temperature during which time large dark crystals of **2** were formed. The supernatant was decanted and the crystals were washed with cold pentane (1 ml). The volatiles were removed under reduced pressure from the combined pentane fractions and a second crop of **2** was obtained. The combined yield of **2** was quantitative. The ^{1}H and ^{13}C NMR spectra of **2** prepared in this manner are analogous to those reported previously [15].

*3.4. X-ray structure determination of [CpNb(μ-NAr)Me]$_2$ (**1**)*

A crystal of **1** was covered with RS3000 perfluoropolyether oil and mounted on an Siemens SMART diffractometer at 50 K. Crystal data are given in Table 1 and bond lengths and bond angles in Table 2. The structure amplitudes for 3217 independent reflections were obtained after the usual Lorentz and polarization corrections. The structure was solved by direct methods [18] and refined by full-matrix least-squares procedures [19] using $(F_o^2 - F_c^2)^2$ as the function minimised. In the final cycles of refinement, all non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were found from Fourier difference maps and refined isotropically.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CDCC no. 154892. Copies of this information may be obtained free of charge from The Director, CDCC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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