

Synthesis and structural characterisation of divalent transition metal complexes containing an unsymmetrical benzamidinate ligand†

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The unsymmetrical benzamidinate ligand $[\text{PhC}(\text{NSiMe}_3)(\text{NAr})]^-$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), denoted L^- , and its lithium derivative $[\text{LiL}(\text{TMEDA})]$ (**1**) ($\text{TMEDA} = N,N,N',N'$ -tetramethylethylenediamine) have been prepared. Treatment of **1** with MCl_2 ($\text{M} = \text{Mn}, \text{Co}, \text{Fe}$ or Ni) afforded the corresponding divalent transition metal benzamidinates with interesting molecular structures. The reaction of two equivalents of **1** with MnCl_2 or CoCl_2 afforded the centrosymmetric binuclear complexes $[(\text{ML}_2)_2 \cdot (\text{TMEDA})]$ ($\text{M} = \text{Mn}$ **2**, Co **5**). On the other hand, the reaction of FeCl_2 with **1**, in an appropriate stoichiometric ratio, led to the mononuclear mono(benzamidinate) $[\text{FeL}(\text{Cl})(\text{TMEDA})]$ (**3**) and the bis(benzamidinate) $[\text{FeL}_2(\text{TMEDA})]$ (**4**) complexes. The addition of two equivalents of **1** to NiCl_2 yielded the mononuclear $[\text{NiL}_2]$ (**6**). X-Ray crystallography revealed that the κ^2 -benzamidinate ligand L^- is bonded to the metal centre of these complexes in an unsymmetrical fashion. The TMEDA ligand in **2–5** exhibits different coordination modes. It acts as a chelating ligand in **3**, as a monodentate ligand in **4**, and as an unusual N,N' -bridging ligand in **2** and **5**.

Introduction

Over the past decades, considerable research efforts have been devoted to the development of various ancillary ligands as alternatives to cyclopentadienyl ligands in organometallic chemistry. Accordingly, the studies of alkoxy, amido and amidinato ligands have attracted much interest. Amidinate ligands of the type $[\text{RC}(\text{NR}')_2]^-$ ($\text{R}, \text{R}' = \text{H}, \text{alkyl}, \text{aryl}$ or SiMe_3) have proven to be versatile in supporting a wide range of main group, transition metal, and f element compounds.^{1–20} They offer a greater potential in ligand design (and thus a modification of the reactivities of their corresponding metal complexes) over the Cp ligands by virtue of their different steric and electronic properties due to the different substituents R and R'. Although the chemistry of early transition metal amidinates is well-developed, that of low-valent late transition metal derivatives has received relatively less attention.^{1,2,4,5,12,13e,13i,14,18–20}

Currently, we are interested in the chemistry of metal complexes supported by sterically demanding amido^{21–23} and amidinato ligands.^{23,24} By treating the lithium anilide $[\text{Li}\{\text{N}(\text{SiMe}_3)(\text{Ar})\}(\text{TMEDA})]^{25}$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\text{TMEDA} = N,N,N',N'$ -tetramethylethylenediamine) with benzonitrile, we have successfully isolated the lithium benzamidinate $[\text{Li}\{\text{PhC}(\text{NSiMe}_3)(\text{NAr})\}(\text{TMEDA})]$. The new unsymmetrical ligand has been shown to be versatile in supporting a number of main group and transition metal complexes with intriguing molecular structures.^{23,24} Herein we report the preparation and molecular structures of a series of divalent transition metal benzamidinate complexes derived from $[\text{PhC}(\text{NSiMe}_3)(\text{NAr})]^-$ (L^-) namely the binuclear $\text{Mn}(\text{II})$ and $\text{Co}(\text{II})$ benzamidinates $[(\text{ML}_2)_2 \cdot (\text{TMEDA})]$ ($\text{M} = \text{Mn}$ **2**, Co **5**), the mononuclear $\text{Fe}(\text{II})$ benzamidinate chloride $[\text{FeL}(\text{Cl})(\text{TMEDA})]$ (**3**) and the $\text{Fe}(\text{II})$ bis(benzamidinate) $[\text{FeL}_2(\text{TMEDA})]$ (**4**), and the

mononuclear $\text{Ni}(\text{II})$ derivative $[\text{NiL}_2]$ (**6**). Common to these complexes is the κ^2 coordination of the benzamidinate ligand L^- . The TMEDA ligand in **2–5** shows different coordination behaviour, namely as a chelating ligand in **3**, a monodentate ligand in **4** and a rare N,N' -bridging ligand in **2** and **5**.

Experimental

General procedures

All reactions were carried out under a purified nitrogen atmosphere using modified Schlenk techniques. Solvents were dried over and distilled from calcium hydride (hexane) or sodium benzophenone (diethyl ether, THF, and toluene), and degassed twice by freeze-thaw cycles before use. Anhydrous metal(II) chlorides were purchased from Aldrich and used as received. Benzonitrile was dried over and distilled from phosphorus pentoxide. The lithium anilide $[\text{Li}\{\text{N}(\text{SiMe}_3)(\text{Ar})\}(\text{TMEDA})]$ was prepared according to published procedures.²⁵

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts were referenced to residual solvent protons at $\delta = 7.15$ for C_6D_6 . EI mass spectra were taken from solid state samples using a ThermoFinnigan MAT 95 XL mass spectrometer. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by MEDAC Ltd., Brunel University, UK. Magnetic moments were measured in benzene solutions at 300 K by the Evans method²⁶ using a JEOL 60 MHz NMR spectrometer. Cyclic voltammetry was carried out by using a BAS CV-50W Voltammetric Analyzer. The electrochemical cell used in our studies consisted of a platinum ball working electrode, a silver wire reference electrode, and a platinum foil auxiliary electrode. All sample solutions were prepared in CH_2Cl_2 with $(\text{Bu}_4\text{N})(\text{PF}_6)$ (0.15 M) as the supporting electrolyte. Chemical potentials were internally referenced to the $\text{FeCp}_2^+/\text{FeCp}_2$ redox couple.

† Electronic supplementary information (ESI) available: inclination angles in complexes **1–6**. See <http://www.rsc.org/suppdata/nj/b3/b303527a/>

Syntheses

[LiL(TMEDA)] (1). To a solution of C_6H_5CN (1.5 mL, 14.7 mmol) in diethyl ether (30 mL) at $0^\circ C$ was slowly added a yellow solution of $[Li\{N(SiMe_3)(Ar)\}(TMEDA)]$ (4.63 g, 14.7 mmol) in diethyl ether (20 mL). The reaction mixture was stirred at room temperature for 12 h to give an orange solution, which was filtered through celite and then concentrated to *ca.* 10 mL under reduced pressure. Crystallisation at ambient temperature afforded compound **1** as colourless crystals. The product was washed with hexane and dried *in vacuo* (4.56 g, 10.9 mmol, 74%), mp $116\text{--}118^\circ C$. 1H NMR (300.13 MHz, C_6D_6): δ 7.36–7.38 (m, 2 H, $C_6H_5Me_2$), 6.98–7.04 (m, 4 H, C_6H_5), 6.87–6.92 (m, 1 H, C_6H_5), 6.77 (t, $J = 7.5$ Hz, 1 H, $C_6H_5Me_2$), 2.39 (s, 6 H, $C_6H_5Me_2$), 1.99 (s, 12 H, NMe_2), 1.77 (s, 4 H, NCH_2), 0.12 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 173.6, 151.6, 144.2, 130.8, 127.2, 126.8, 126.7, 122.1, 120.8, 56.6, 45.6, 19.9, 3.48. EI-MS (70 eV): m/z (%) 296 (22) $[L]^+$, 281 (11) $[L - Me]^+$, 208 (8) $[L - NSiMe_3]^+$, 176 (33) $[L - NAr]^+$, 73 (71) $[SiMe_3]^+$. Anal. found: C, 69.10; H, 9.48; N, 13.51%; calcd for $C_{24}H_{39}N_4LiSi$: C, 68.86; H, 9.39; N, 13.38%.

[(MnL₂)₂·(TMEDA)] (2). To a stirred suspension of $MnCl_2$ (0.21 g, 1.67 mmol) in diethyl ether (20 mL) at $0^\circ C$ was slowly added a solution of $[LiL(TMEDA)]$ (**1**) (1.41 g, 3.37 mmol) in diethyl ether (10 mL). The reaction mixture was stirred at room temperature for 12 h. All the volatiles were removed under reduced pressure and the residue was extracted with toluene (30 mL). The extract was concentrated to *ca.* 8 mL to afford the title compound as colourless crystals (0.72 g, 0.51 mmol, 61%), mp $158\text{--}160^\circ C$ (dec.), $\mu_{eff} = 3.59 \mu_B$ per Mn atom. EI-MS (70 eV): m/z (%) 644 (12) $[MnL_2]^+$, 629 (10) $[MnL_2 - Me]^+$, 351 (6) $[MnL]^+$, 296 (95) $[L]^+$. Anal. found: C, 67.37; H, 7.76; N, 9.45%; calcd for $C_{78}H_{108}Mn_2N_{10}Si_4$: C, 66.54; H, 7.73; N, 9.95%.

[FeL(Cl)(TMEDA)] (3). A slurry of $FeCl_2$ (0.34 g, 2.68 mmol) in diethyl ether (10 mL) was cooled to $-78^\circ C$. To this was added dropwise a solution of **1** (1.12 g, 2.68 mmol) in the same solvent (20 mL). After stirring at $-78^\circ C$ for 20 min, the solution was allowed to warm slowly to room temperature and stirred for a further period of 12 h. All the volatiles were then removed *in vacuo* and the residue was extracted with toluene (30 mL). The yellowish-brown solution was filtered and then concentrated to *ca.* 3 mL. Allowing the solution to stand at ambient temperature for one day gave compound **3** as yellow crystals (0.78 g, 1.55 mmol, 58%). The product was washed three times with hexane and dried *in vacuo*, mp $100\text{--}102^\circ C$ (dec.), $\mu_{eff} = 5.13 \mu_B$. EI-MS (70 eV): m/z (%) 296 (50) $[L]^+$, 281 (40) $[L - Me]^+$, 224 (84) $[L - SiMe_3]^+$, 207 (96) $[L - NSiMe_3]^+$. Anal. found: C, 56.75; H, 7.83; N, 11.28%; calcd for $C_{24}H_{39}FeN_4SiCl$: C, 57.31; H, 7.81; N, 11.13%.

[FeL₂(TMEDA)] (4). To a suspension of $FeCl_2$ (0.44 g, 3.47 mmol) in diethyl ether (20 mL) at $0^\circ C$ was added dropwise a solution of **1** (2.91 g, 6.94 mmol) in the same solvent (10 mL). The reaction mixture was stirred at room temperature for 12 h to afford an olive-green solution. The solution was filtered and concentrated to *ca.* 3 mL to give the title compound as yellow crystals (1.85 g, 2.43 mmol, 70%). The product was washed three times with hexane and dried *in vacuo*, mp $118\text{--}120^\circ C$ (dec.), $\mu_{eff} = 4.96 \mu_B$. EI-MS (70 eV): m/z (%) 646 (18) $[FeL_2]^+$, 631 (19) $[FeL_2 - Me]^+$, 296 (98) $[L]^+$. Anal. found: C, 65.61; H, 8.29; N, 11.19%; calcd for $C_{42}H_{62}FeN_4Si_2$: C, 66.11; H, 8.19; N, 11.01%.

[(CoL₂)₂·(TMEDA)] (5). A solution of **1** (2.06 g, 4.92 mmol) in diethyl ether (10 mL) was added slowly to a slurry of $CoCl_2$ (0.32 g, 2.46 mmol) in diethyl ether (20 mL) at $0^\circ C$. Upon

stirring at room temperature for 12 h, a blue solution with a grey precipitate was obtained. The solution was filtered through celite and then concentrated to *ca.* 3 mL. Allowing the solution to stand at ambient temperature for one day gave compound **5** as dark blue crystals (1.95 g, 1.38 mmol, 56%). The compound was washed with hexane three times and dried *in vacuo*, mp $69\text{--}71^\circ C$, $\mu_{eff} = 3.40 \mu_B$ per Co atom. EI-MS (70 eV): m/z (%) 648 (12) $[CoL_2]^+$, 633 (10) $[CoL_2 - Me]^+$, 351 (6) $[CoL]^+$, 296 (96) $[L]^+$. Anal. found: C, 66.75; H, 7.71; N, 9.38%; calcd for $C_{78}H_{108}Co_2N_{10}Si_4$: C, 66.16; H, 7.69; N, 9.89%.

[NiL₂] (6). To a slurry of $NiCl_2$ (0.42 g, 3.24 mmol) in diethyl ether (20 mL) at $0^\circ C$ was added dropwise a solution of **1** (2.71 g, 6.48 mmol) in diethyl ether (10 mL). The reaction mixture was warmed slowly to room temperature and stirred for 12 h. All the volatiles were removed under reduced pressure and the residue was extracted with toluene (30 mL) and then filtered through celite. The filtrate was concentrated to *ca.* 3 mL. Compound **6** was obtained as purple crystals after allowing the solution to stand at ambient temperature (1.46 g, 2.24 mmol, 69%). The product was washed three times with hexane and dried *in vacuo*, mp $193\text{--}195^\circ C$ (dec.). 1H NMR (300.13 MHz, C_6D_6): δ 7.57–7.53 (m, 10 H, $C_6H_5Me_2$ and C_6H_5), 7.18–7.16 (m, 6 H, $C_6H_5Me_2$), 3.29 (s, 12 H, $C_6H_5Me_2$), 0.23 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 143.2, 137.9, 135.0, 130.1, 128.5, 128.0, 127.6, 125.2, 20.4, 2.3. EI-MS (70 eV): m/z (%) 649 (6) $[M]^+$, 354 (3) $[NiL]^+$, 296 (100) $[L]^+$, 281 (62) $[L - Me]^+$. Anal. found: C, 65.94; H, 7.11; N, 8.73%; calcd for $C_{36}H_{46}N_4NiSi_2$: C, 66.56; H, 7.14; N, 8.62%.

X-Ray crystallography

Single-crystals of complexes **1–6** suitable for crystallographic studies were mounted in glass capillaries and sealed under nitrogen. Details of crystal parameters, data collection and structural refinement are summarised in Table 1. Data were collected on a Bruker SMART CCD diffractometer at 293 K using graphite-monochromated $Mo\text{--}K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct phase determination using the computer program SHELX-97 on an IBM compatible personal computer and refined by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms.²⁷ Hydrogen atoms were introduced in their idealised positions and included in structure factor calculations with assigned isotropic temperature factors.²⁸

CCDC reference numbers 192352–55 and 207044–45. See <http://www.rsc.org/suppdata/nj/b3/b303527a/> for crystallographic files in CIF or other electronic format.

Results and discussion

Syntheses

The lithium reagent $[LiL(TMEDA)]$ (**1**) is easily accessible *via* the reaction of $[Li\{N(SiMe_3)(Ar)\}(TMEDA)]$ ($Ar = 2,6\text{-}Me_2\text{-}C_6H_3$) with benzonitrile in diethyl ether. The lithium anilide $[Li\{N(SiMe_3)(Ar)\}(TMEDA)]$ was prepared according to a modified literature procedure.²⁵ As shown in Scheme 1, lithiation of 2,6-dimethylaniline with $LiBu^t$ in diethyl ether, followed by quenching of the resulting solution with one equivalent of trimethylsilyl chloride, gave the silylated aniline $[HN(SiMe_3)\text{--}(Ar)]$. Subsequent lithiation of $[HN(SiMe_3)(Ar)]$ with $LiBu^t$, in the presence of TMEDA, gave the corresponding lithium anilide $[Li\{N(SiMe_3)(Ar)\}(TMEDA)]$. Reaction of the lithium anilide with one equivalent of benzonitrile afforded the lithium benzamidinate **1** as colourless crystals in 74% yield. The reaction of $[Li\{N(SiMe_3)(Ar)\}(TMEDA)]$ with benzonitrile involves a direct insertion of the amido ligand

Table 1 Crystallographic data for complexes **1–6**

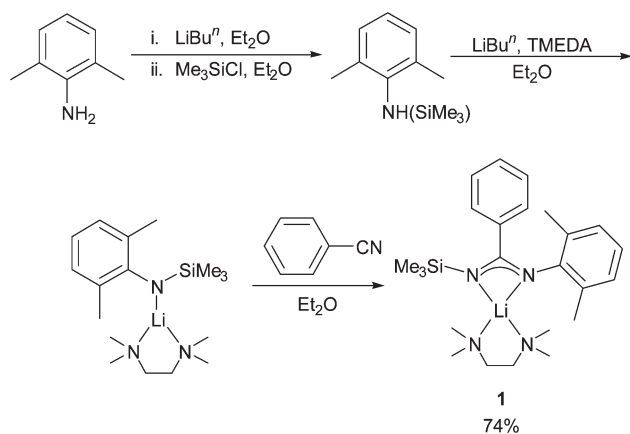
	1	2 ·C ₆ H ₅ CH ₃	3	4	5	6
Molecular formula	C ₂₄ H ₃₉ LiN ₄ Si	C ₇₈ H ₁₀₈ Mn ₂ N ₁₀ Si ₄ ·C ₇ H ₈	C ₂₄ H ₃₉ ClFeN ₄ Si	C ₄₂ H ₆₂ FeN ₆ Si ₂	C ₇₈ H ₁₀₈ Co ₂ N ₁₀ Si ₄	C ₃₆ H ₄₆ N ₄ NiSi ₂
Molecular weight	418.62	1500.12	502.98	763.01	1415.96	649.66
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
<i>a</i> /Å	8.2152(8)	32.691(5)	7.9613(8)	10.414(4)	10.9563(9)	12.3641(9)
<i>b</i> /Å	25.198(2)	13.883(2)	10.053(1)	18.633(7)	11.6745(9)	12.4981(9)
<i>c</i> /Å	13.140(1)	20.286(3)	18.026(2)	23.860(9)	17.633(1)	14.485(1)
α /°	90	90	92.056(2)	90	108.250(2)	97.980(1)
β /°	93.696(2)	106.162(4)	98.285(2)	93.964(8)	104.354(2)	109.071(2)
γ /°	90	90	101.881(2)	90	95.475(2)	114.916(1)
<i>Z</i>	4	4	2	4	1	2
<i>U</i> /Å ³	2714.5(4)	8843(2)	1393.9(2)	4619(3)	2038.1(3)	1816.0(2)
Reflections collected	18 162	29 380	9892	26 108	13 501	12 250
Unique data measured	6527	10 738	6618	11 011	9622	8591
Obs. data [<i>I</i> ≥ 2σ(<i>I</i>)]	2794	4078	3894	5889	6064	6473
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)] ^a	0.0478	0.0530	0.0424	0.0503	0.0465	0.0404
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)] ^a	0.1213	0.1206	0.0923	0.1340	0.1172	0.1161
<i>R</i> ₁ (all data) ^a	0.1258	0.1635	0.0853	0.1026	0.0802	0.0560
<i>wR</i> ₂ (all data) ^a	0.1496	0.1511	0.1083	0.1540	0.1312	0.1241
<i>R</i> _{int}	0.0503	0.0808	0.0225	0.0379	0.0215	0.0134

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$$

[N(SiMe₃)(Ar)][−] into the −C≡N functionality, followed by a 1,3-silyl migration.

The transition metal derivatives **2–6** were readily prepared by treating **1** with the corresponding metal dichloride in the appropriate stoichiometric ratio (Scheme 2). The binuclear Mn(II) and Co(II) benzamidinate complexes [(ML₂)₂·(TMEDA)] (M = Mn **2**, Co **5**), isolated as colourless and dark blue crystals, respectively, were synthesised by treating the appropriate metal dichloride with two equivalents of **1** in diethyl ether. In contrast, an analogous reaction of NiCl₂ with **1** gave the mononuclear [NiL₂] (**6**) as purple crystals. For the Fe(II) derivatives, treatment of anhydrous FeCl₂ with one molar equivalent of **1** in diethyl ether at −78 °C yielded the mono(benzamidinate) complex [FeL(Cl)(TMEDA)] (**3**), whereas the addition of two equivalents of **1** to FeCl₂ at 0 °C followed by stirring at room temperature for 12 h gave the bis(benzamidinate) derivative [FeL₂(TMEDA)] (**4**). Both complexes **3** and **4** were isolated as yellow crystals. It is noteworthy that mono(amidinate) complexes of transition metals are rare. Complex **3** may be considered as an intermediate compound during the course of reaction to the corresponding bis(benzamidinate) **4**. Thus, the preparation of **3** requires a strict and proper control of reaction stoichiometry and conditions.

Complexes **2–6** were isolated as highly air-sensitive compounds. They are readily soluble in diethyl ether, THF and toluene, but only sparingly soluble in saturated hydrocarbons.

**Scheme 1**

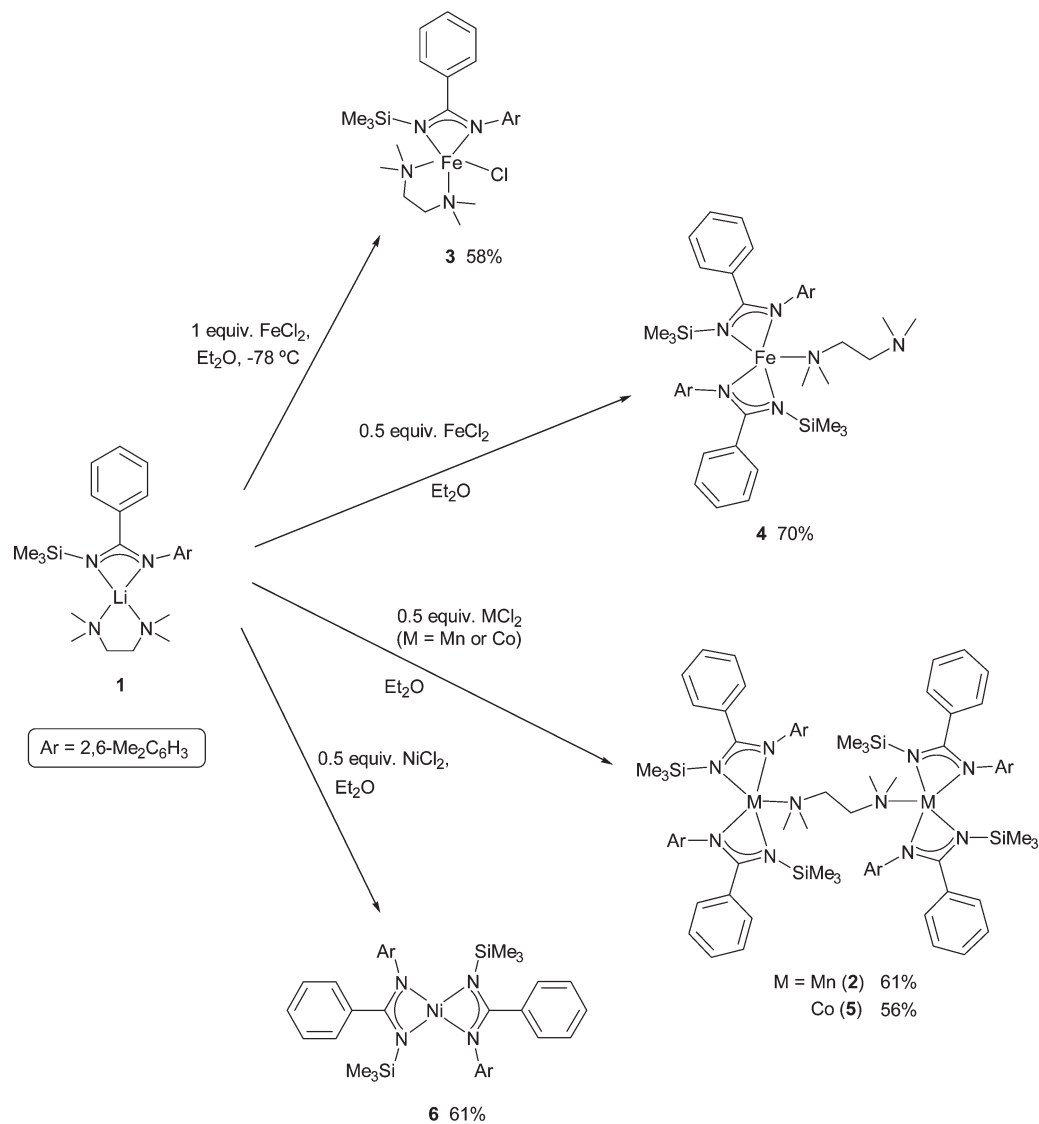
Whilst complexes **2–5** are paramagnetic species (*vide infra*), the nickel derivative **6** is a diamagnetic compound. The ¹H and ¹³C NMR spectra of **6** elicit one single set of signals, which are assignable to a pair of equivalent L[−] ligands. No paramagnetic shifts were observed in the NMR spectra, suggesting that the compound adopts a diamagnetic 16-electron configuration with a pseudo-square-planar geometry in solution.

It is believed that the TMEDA ligand provides coordination saturation to the metal centres, which contributes to the stability of the present complexes **2–5**. Interestingly, the TMEDA ligand shows three different coordination modes in these complexes: it acts as a bidentate *N,N'*-chelating ligand in **3**, a monodentate ligand in **4**, and an unusual *N,N'*-bridging ligand in **2** and **5**. In general, the coordination number of a metal complex is determined by the bulky nature of the supporting ligands around the metal centre. An increase in steric encumbrance around a metal centre generally results in a lowering of its coordination number. Since complex **3** is sterically less crowded (as compared to **2**, **4** and **5**), the TMEDA ligand can coordinate to its metal centre in the commonly observed *N,N'*-chelating fashion. On the other hand, the presence of an additional benzamidinate ligand around each metal centre in **2**, **4** and **5** prohibits the TMEDA from binding in a chelating mode. The unusual *N,N'*-bridging TMEDA ligand in complexes **2** and **5** is noteworthy. A few examples of this unusual coordination mode of TMEDA have been reported for some main group metal hydrides, alkyls, and amides,²⁹ but are rarely observed in transition metal chemistry.³⁰ Recently, we have reported a binuclear cobalt(II) amido compound that contains an unusual bridging TMEDA ligand.^{22c}

X-Ray crystal structures

Crystals of complexes **1–6** suitable for X-ray diffraction studies were obtained from toluene. The molecular structures of **1–6** with the atom numbering schemes are depicted in Figs. 1–6, respectively. Selected bond distances and angles of the compounds are listed in Tables 2–7.

The crystal structures of **1–6** reveal that each L[−] ligand is bonded to the metal centre as a bidentate, four-electron donor ligand. This leads to the formation of a highly strained four-member M–N–C–N metallacycle. The bonding parameters within each benzamidinate ligand are normal. The amidinate N–C–N backbone consists of almost identical N–C distances



Scheme 2

(see Tables 2–7), which are close to the average value of the observed $\text{N}=\text{C}$ [1.302(7) Å] and $\text{N}-\text{C}$ [1.360(8) Å] bonds reported for other amidines.³¹ The Ph and Ar substituents of the L^- ligand are not co-planar with the plane of the $\text{N}-\text{C}-\text{N}$ motif (see Table S1 in the electronic supplementary information†). Moreover, the $\text{C}-\text{C}$ distances between the Ph ring and

the central carbon atom of the $\text{N}-\text{C}-\text{N}$ moiety [1.492(3)–1.512(3) Å], as well as the $\text{C}-\text{N}$ distances between the Ar substituent and the $\text{N}_{\text{amidinate}}$ atom [1.414(2)–1.434(4) Å] are typical for $\text{C}_{\text{sp}2}-\text{C}_{\text{sp}2}$ and $\text{C}_{\text{sp}2}-\text{N}_{\text{sp}2}$ single bond distances,

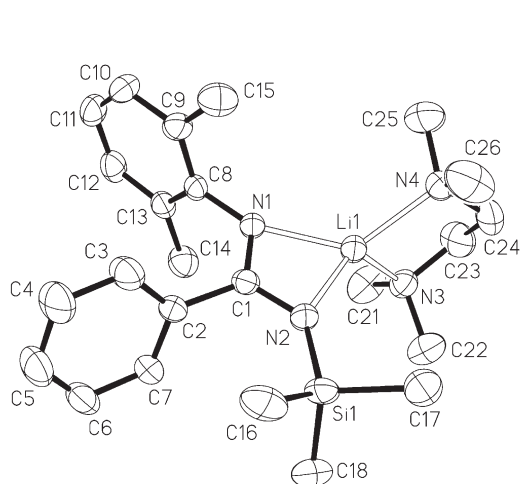


Fig. 1 Molecular structure of $[\text{LiL}(\text{TMEDA})]$ (**1**) (30% thermal ellipsoids) with the atomic labelling scheme.

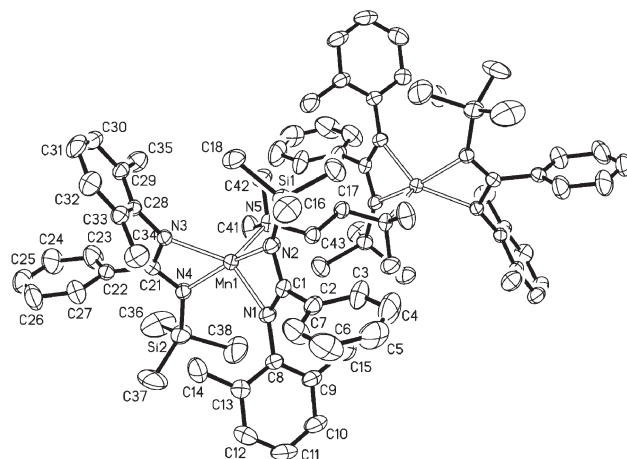


Fig. 2 Molecular structure of the centrosymmetric $[(\text{MnL}_2)_2 \cdot (\text{TMEDA})] \cdot \text{C}_7\text{H}_8$ (**2**· C_7H_8) (30% thermal ellipsoids) with the atomic labelling scheme. The solvated toluene molecule is omitted for clarity.

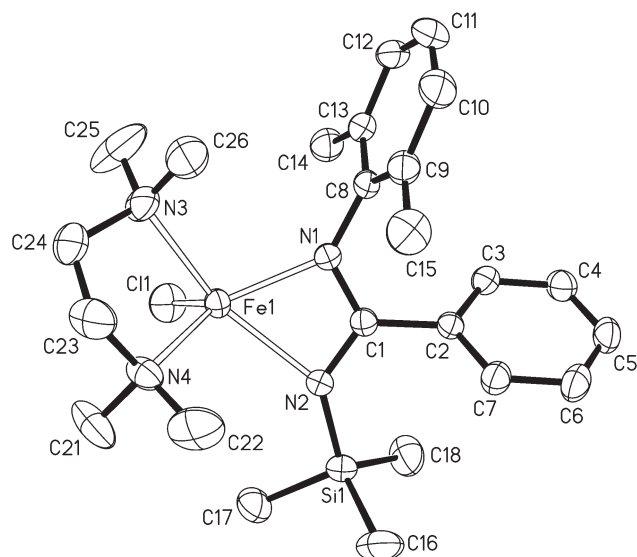


Fig. 3 Molecular structure of $[\text{FeL}(\text{Cl})(\text{TMEDA})]$ (**3**) (30% thermal ellipsoids) with the atomic labelling scheme.

respectively. All of these observations exclude the possibility of any conjugation between the amidinato N–C–N moiety and the Ph or Ar substituents. The observed Si–N_{amidinate} distances in **1–6**, ranging from 1.695(2)–1.741(1) Å, are comparable to those reported for other silylamido systems.³²

The lithium benzamidinate 1. Compound **1** crystallises in a monoclinic crystal system with space group $P2_1/n$. The mononuclear compound consists of a lithium cation bound by an κ^2 -benzamidinate anion and a chelating TMEDA ligand, resulting in a distorted tetrahedral environment around the metal centre. The unsymmetrical nature of the L^- ligand leads to a slightly unsymmetrical coordination of L^- to the lithium centre, as evidenced by the slightly different Li–N_{amidinate} distances of 2.009(3) and 2.032(3) Å in **1**. In addition to its inherently unsymmetrical nature, the unsymmetrical binding of the L^- ligand to the metal centre in **1** (and also in **2–6**, *vide infra*) may also be related to the steric and electronic properties of the SiMe_3 and Ar substituents attached to the amidinato nitrogens (Chart 1). Since the SiMe_3 group is sterically more demanding than the Ar substituent, the M–N(SiMe_3) bonds are longer as compared to the M–N(Ar) distances. In addition to steric considerations, an electronic effect is also expected to exert a substantial influence on the M–N bond distances.

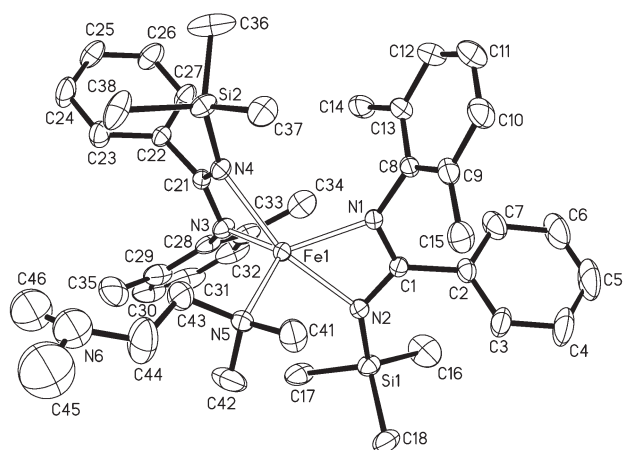


Fig. 4 Molecular structure of $[\text{FeL}_2(\text{TMEDA})]$ (**4**) (30% thermal ellipsoids) with the atomic labelling scheme. Disorder of the uncoordinated NMe_2 group of the TMEDA ligand is not shown for clarity.

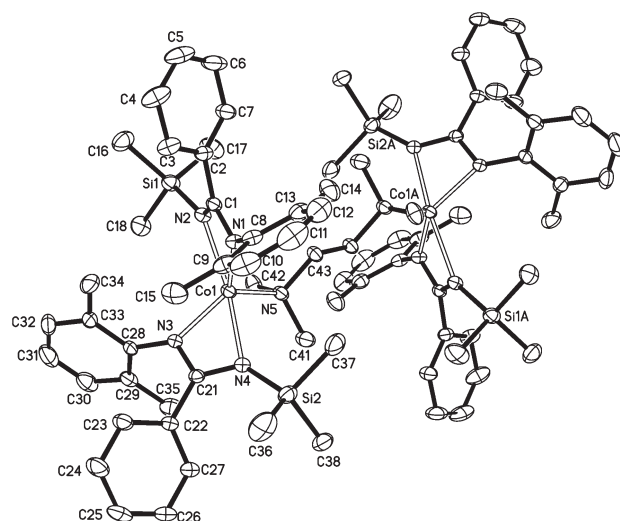


Fig. 5 Molecular structure of the centrosymmetric $[(\text{CoL}_2)_2 \cdot (\text{TMEDA})]$ (**5**) (30% thermal ellipsoids) with the atomic labelling scheme.

Apparently, the more electron-withdrawing Ar substituent may force the negative charge on L^- to locate mainly on the N atom bearing the Ar ring and, hence, a shorter M–N(Ar) distance may result. However, the almost identical C–N distances of the N–C–N moiety in each of the present complexes (see Tables 2–7) suggest that the electronic effect may not be the dominating factor in determining the unsymmetrical coordination mode of the L^- ligand in these complexes.

The Li–N_{amidinate} distances are comparable to those of 2.023 Å (ave.) reported for $[\text{Li}\{\text{PhC}(\text{NPh})_2\}(\text{TMEDA})]$ ³¹ and 1.997 Å (ave.) for, $[\text{Li}\{(2,6\text{-}(p\text{-Bu}'\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3)\text{C}(\text{NPr}')_2\}(\text{TMEDA})]$ ^{13h} but slightly shorter than those of 2.076(6)–2.188(6) Å in the monomeric $[\text{Li}\{\text{PhC}(\text{NPh})_2\}(\text{PMEDTA})]$ ³¹ and 2.144 Å (ave.) in the dimeric $[\text{Li}\{(p\text{-MeC}_6\text{H}_4)\text{C}(\text{NSiMe}_3)_2\}(\text{THF})_2]_2$.³³ The Li–N_{amidinate} distances in **1** are similar to the Li–N distances of 1.98(3)–2.03(3) Å reported for the isoelectronic lithium guanidinate $[\text{Li}\{(\text{NC}_6\text{H}_{11})_2\text{C}[\text{N}(\text{SiMe}_3)_2]\}_2]$.³⁴

The transition metal derivatives 2–6. The mononuclear complex $[\text{FeL}(\text{Cl})(\text{TMEDA})]$ (**3**) crystallises in the triclinic space group $P\bar{1}$, whilst the bis(benzamidinate) derivative

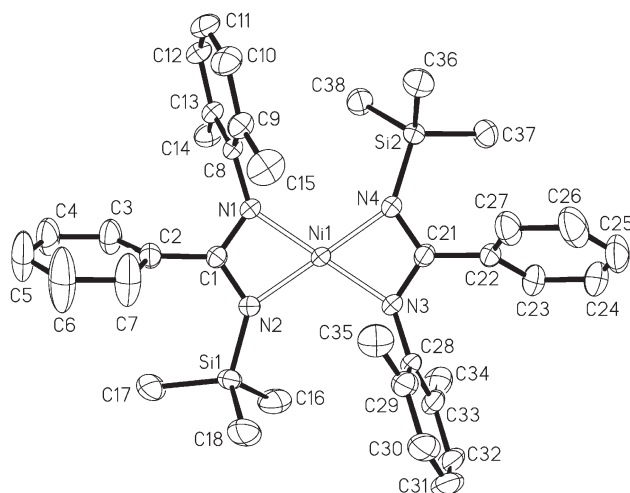


Fig. 6 Molecular structure of the centrosymmetric $[\text{NiL}_2]$ (**6**) (30% thermal ellipsoids) with the atomic labelling scheme.

Table 2 Selected bond distances (Å) and angles (°) for [LiL(TMEDA)] (1)

Li(1)–N(1)	2.032(3)	Li(1)–N(2)	2.009(3)
Li(1)–N(3)	2.112(4)	Li(1)–N(4)	2.102(4)
Li(1)–Cl(1)	2.348(4)	N(1)–C(1)	1.323(2)
N(2)–C(1)	1.328(2)	C(1)–C(2)	1.505(3)
N(1)–C(8)	1.414(2)	Si(1)–N(2)	1.695(2)
N(1)–Li(1)–N(2)	68.5(1)	N(3)–Li(1)–N(4)	87.3(1)
N(1)–Li(1)–N(3)	129.8(2)	N(1)–Li(1)–N(4)	127.6(2)
N(2)–Li(1)–N(3)	118.9(2)	N(2)–Li(1)–N(4)	130.4(2)
N(1)–C(1)–N(2)	118.2(2)	N(1)–C(1)–C(2)	121.3(2)
N(2)–C(1)–C(2)	120.5(2)	C(1)–N(1)–Li(1)	86.1(1)
C(1)–N(1)–C(8)	122.3(2)	C(8)–N(1)–Li(1)	151.2(2)
C(1)–N(2)–Li(1)	86.9(1)	C(1)–N(2)–Si(1)	133.0(1)
Si(1)–N(2)–Li(1)	140.1(1)		

[FeL₂(TMEDA)] (4) crystallises in the monoclinic space group *P*2₁/*n*. Both complexes display a distorted trigonal bipyramidal geometry. Complex 3 consists of a chloride ligand, a bidentate benzamidinate and a *N,N'*-chelating TMEDA. The chlorine atom Cl(1), the benzamidinate nitrogen N(1) and the amino nitrogen N(4) of the TMEDA constitute the trigonal plane (sum of bond angles around the Fe centre = 359.5°, °), whereas the nitrogen atoms N(2) and N(3) occupy the axial positions with N(2)–Fe(1)–N(3) = 153.54(9)°. For the bis(benzamidinate) complex 4, the Fe centre is chelated by two benzamidinate ligands and a monodentate TMEDA. Disorder of the uncoordinated NMe₂ terminus of the TMEDA ligand was observed (not shown in Fig. 3). The equatorial plane of the trigonal bipyramidal structure is composed of the benzamidinate nitrogens N(1), N(3) and the amino nitrogen N(5) from the TMEDA (sum of bond angles around the Fe centre = 360.0°). The axial positions are occupied by nitrogens N(2) and N(4) with N(2)–Fe(1)–N(4) = 159.76(8)°. Deviation of the N(2)–Fe(1)–N(3) angle in 3 and the corresponding N(2)–Fe(1)–N(4) angle in 4 from linearity may be ascribed to the small bite of the L[–] ligand.

The observed Fe–N_{amidinate} distances, which range from 2.083(2)–2.260(2) Å in 3 and 2.095(2)–2.240(2) Å in 4, reveal that L[–] binds unsymmetrically to the Fe(II) centre, with the Fe–N(SiMe₃) distances being longer than the Fe–N(Ar) distances. The N atom attached to the SiMe₃ group occupies the axial position, whilst the one bearing the Ar ring occupies the equatorial position. The Fe–N_{amidinate} distances of 3 and 4 are longer than the corresponding distances of 2.037 Å (ave.)

Table 3 Selected bond distances (Å) and angles (°) for [(MnL₂)₂(TMEDA)]·C₆H₅CH₃ (2·C₆H₅CH₃)

Mn(1)–N(1)	2.184(3)	Mn(1)–N(2)	2.223(3)
Mn(1)–N(3)	2.177(3)	Mn(1)–N(4)	2.211(2)
Mn(1)–N(5)	2.303(3)	N(1)–C(1)	1.329(4)
N(2)–C(1)	1.336(4)	C(1)–C(2)	1.496(4)
N(1)–C(8)	1.434(4)	N(2)–Si(1)	1.728(3)
N(3)–C(21)	1.341(4)	N(4)–C(21)	1.333(4)
C(21)–C(22)	1.496(4)	N(3)–C(28)	1.426(4)
N(4)–Si(2)	1.716(3)		
N(1)–Mn(1)–N(2)	61.58(9)	N(3)–Mn(1)–N(4)	61.97(9)
N(1)–Mn(1)–N(3)	135.9(1)	N(1)–Mn(1)–N(5)	115.8(1)
N(3)–Mn(1)–N(5)	108.4(1)	N(2)–Mn(1)–N(4)	162.1(1)
N(1)–C(1)–N(2)	115.6(3)	N(1)–C(1)–C(2)	122.2(3)
N(2)–C(1)–C(2)	122.1(3)	C(1)–N(1)–Mn(1)	92.3(2)
C(1)–N(1)–C(8)	122.4(3)	C(8)–N(1)–Mn(1)	144.5(2)
C(1)–N(2)–Mn(1)	90.4(2)	C(1)–N(2)–Si(1)	130.4(2)
Si(1)–N(2)–Mn(1)	138.6(2)	N(3)–C(21)–N(4)	115.3(3)
N(3)–C(21)–C(22)	121.0(3)	N(4)–C(21)–C(22)	123.7(3)
C(21)–N(3)–Mn(1)	91.9(2)	C(21)–N(3)–C(28)	122.3(3)
C(28)–N(3)–Mn(1)	145.4(2)	C(21)–N(4)–Mn(1)	90.6(2)
C(21)–N(4)–Si(2)	130.8(2)	Si(2)–N(4)–Mn(1)	136.6(2)

Table 4 Selected bond distances (Å) and angles (°) for [FeL(Cl)(TMEDA)] (3)

Fe(1)–N(1)	2.083(2)	Fe(1)–N(2)	2.260(2)
Fe(1)–N(3)	2.297(2)	Fe(1)–N(4)	2.204(2)
Fe(1)–Cl(1)	2.2766(8)	N(1)–C(1)	1.314(3)
N(2)–C(1)	1.325(3)	C(1)–C(2)	1.512(3)
N(1)–C(8)	1.428(3)	Si(1)–N(2)	1.722(2)
N(1)–Fe(1)–N(2)	61.87(7)	N(3)–Fe(1)–N(4)	78.58(9)
N(1)–Fe(1)–Cl(1)	120.92(6)	N(4)–Fe(1)–Cl(1)	112.74(7)
N(1)–Fe(1)–N(4)	125.83(8)	N(2)–Fe(1)–N(3)	153.54(9)
N(1)–C(1)–N(2)	116.0(2)	N(1)–C(1)–C(2)	121.5(2)
N(2)–C(1)–C(2)	122.5(2)	C(1)–N(1)–Fe(1)	95.1(1)
C(1)–N(1)–C(8)	123.8(2)	C(8)–N(1)–Fe(1)	141.1(2)
C(1)–N(2)–Fe(1)	87.0(1)	C(1)–N(2)–Si(1)	130.2(2)
Si(1)–N(2)–Fe(1)	139.9(1)		

reported for [Fe{FeC(NCy)₂}₂·0.25Et₂O]^{13e} and 2.020 Å (ave.) for [Fe{Bu^tC(NCy)₂}₂]²⁰. They are also longer than those of 1.997(8)–2.109(9) Å reported for the Fe(III) compound [Fe{PhC(NSiMe₃)₂}₂Cl]^{5b}.

The centrosymmetric binuclear complexes [(ML₂)₂(TMEDA)] (2 and 5) are isostructural. The Mn(II) derivative, which crystallises in the monoclinic space group *C*2/*c*, was obtained in a solvated form with co-crystallised toluene in a molar ratio of 1:1, whereas no solvent of crystallisation was observed for the Co(II) derivative 5, which crystallises in the triclinic space group *P* $\bar{1}$. Each M(II) centre in the two complexes is bound by a pair of κ^2 -benzamidinate ligands, forming a {MN₄} moiety. Coordination by one amino nitrogen of the TMEDA ligand completes a distorted trigonal bipyramidal configuration around the metal centre. It is noteworthy that the TMEDA ligand in 2 and 5 links two {MN₄} moieties together by coordinating in an unusual *N,N'*-bridging mode. Similarly, the benzamidinate ligand L[–] coordinates to the M(II) centre of 2 and 5 in an unsymmetrical manner, leading to the unsymmetrical M–N_{amidinate} bond lengths of 2.177(3)–2.223(3) Å in 2 and 2.016(1)–2.246(1) Å in 5. The Mn–N_{amidinate} distances in 2 are comparable to the corresponding distances of 2.186(4)–2.219(4) Å for [Mn{PhC₆H₄C(NSiMe₃)₂}₂]⁴, 2.177(2)–2.348(2) Å for [Mn{HC(NCy)₂}₂(TMEDA)]¹⁸ and 2.155(2)–2.188(2) Å for the terminal amidinate ligands of the dimeric [Mn{HC(NCy)₂}₂{ μ -HC(NCy)₂}₂]¹⁸. However, they are slightly longer than those of 2.075(7)–2.096(7) Å for the sterically congested [Mn{(2,6-Mes₂C₆H₃)C(NPrⁱ)₂}₂]¹³ⁱ. The observed Co–N_{amidinate} distances in 5 are only marginally longer than

Table 5 Selected bond distances (Å) and angles (°) for [FeL₂(TMEDA)] (4)

Fe(1)–N(1)	2.095(2)	Fe(1)–N(2)	2.240(2)
Fe(1)–N(3)	2.109(2)	Fe(1)–N(4)	2.211(2)
Fe(1)–N(5)	2.181(2)	N(1)–C(1)	1.331(3)
N(2)–C(1)	1.330(3)	C(1)–C(2)	1.497(4)
N(1)–C(8)	1.434(3)	N(2)–Si(1)	1.727(2)
N(3)–C(21)	1.330(3)	N(4)–C(21)	1.331(3)
C(21)–C(22)	1.495(3)	N(3)–C(28)	1.440(3)
N(4)–Si(2)	1.728(2)		
N(1)–Fe(1)–N(2)	62.46(8)	N(3)–Fe(1)–N(4)	62.51(8)
N(1)–Fe(1)–N(3)	128.20(9)	N(1)–Fe(1)–N(5)	117.06(9)
N(3)–Fe(1)–N(5)	114.74(9)	N(2)–Fe(1)–N(4)	159.76(8)
N(1)–C(1)–N(2)	115.5(2)	N(1)–C(1)–C(2)	121.6(2)
N(2)–C(1)–C(2)	122.9(2)	C(1)–N(1)–Fe(1)	94.1(2)
C(1)–N(1)–C(8)	124.5(2)	C(8)–N(1)–Fe(1)	141.4(2)
C(1)–N(2)–Fe(1)	87.8(2)	C(1)–N(2)–Si(1)	131.1(2)
Si(1)–N(2)–Fe(1)	139.2(1)	N(3)–C(21)–N(4)	114.9(2)
N(3)–C(21)–C(22)	122.5(2)	N(4)–C(21)–C(22)	122.5(2)
C(21)–N(3)–Fe(1)	93.5(2)	C(21)–N(3)–C(28)	123.2(2)
C(28)–N(3)–Fe(1)	143.2(2)	C(21)–N(4)–Fe(1)	88.9(2)
C(21)–N(4)–Si(2)	130.3(2)	Si(2)–N(4)–Fe(1)	140.5(1)

Table 6 Selected bond distances (Å) and angles (°) for [(CoL₂)₂·(TMEDA)] (5)

Co(1)–N(1)	2.029(2)	Co(1)–N(2)	2.246(2)
Co(1)–N(3)	2.016(2)	Co(1)–N(4)	2.198(2)
Co(1)–N(5)	2.159(2)	N(1)–C(1)	1.327(3)
N(2)–C(1)	1.324(3)	C(1)–C(2)	1.504(3)
N(1)–C(8)	1.424(3)	N(2)–Si(1)	1.725(2)
N(3)–C(21)	1.329(3)	N(4)–C(21)	1.318(3)
C(21)–C(22)	1.500(3)	N(3)–C(28)	1.428(3)
N(4)–Si(2)	1.722(2)		
N(1)–Co(1)–N(2)	62.96(7)	N(3)–Co(1)–N(4)	63.66(7)
N(1)–Co(1)–N(3)	125.32(8)	N(1)–Co(1)–N(5)	121.41(7)
N(3)–Co(1)–N(5)	113.26(7)	N(2)–Co(1)–N(4)	163.76(7)
N(1)–C(1)–N(2)	115.4(2)	N(1)–C(1)–C(2)	122.2(2)
N(2)–C(1)–C(2)	122.5(2)	C(1)–N(1)–Co(1)	95.5(1)
C(1)–N(1)–C(8)	123.9(2)	C(8)–N(1)–Co(1)	140.6(2)
C(1)–N(2)–Co(1)	86.1(1)	C(1)–N(2)–Si(1)	130.3(2)
Si(1)–N(2)–Co(1)	141.9(1)	N(3)–C(21)–N(4)	114.6(2)
N(3)–C(21)–C(22)	121.9(2)	N(4)–C(21)–C(22)	123.3(2)
C(21)–N(3)–Co(1)	94.4(1)	C(21)–N(3)–C(28)	123.9(2)
C(28)–N(3)–Co(1)	141.6(2)	C(21)–N(4)–Co(1)	86.8(1)
C(21)–N(4)–Si(2)	134.4(2)	Si(2)–N(4)–Co(1)	137.7(1)

those of 2.006(4)–2.020(4) Å reported for [Co{FcC(NCy)₂Et₂O}],^{13e} and slightly longer than those of 1.973(4)–1.993(3) Å in [Co{(2,6-Mes₂C₆H₃)C(NPrⁱ)₂}]₂.¹³ⁱ

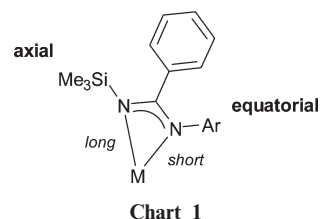
The mononuclear Ni(II) derivative **6** crystallises in the triclinic space group *P* $\bar{1}$. As shown in Fig. 6, the complex consists of an almost square-planar Ni(II) centre bound by a pair of trans-chelating L[–] ligands. This is in contrast with the closely related [Ni{PhC(NSiMe₃)₂}]₂,^{15c} and the bulky [Ni{(2,6-Mes₂C₆H₃)C(NPrⁱ)₂}]₂ derivatives,¹³ⁱ with both of the latter exhibiting a distorted tetrahedral structure. An unsymmetrical coordination of L[–] to the Ni(II) centre of **6** is also noted. The observed Ni–N_{amidinate} distances of 1.908(2)–1.945(2) Å in **6** are shorter than the corresponding bond lengths of 2.007(3)–2.016(4) Å in [Ni{PhC(NSiMe₃)₂}]₂.^{15c} They are slightly shorter than those of 1.969(3)–1.977(2) Å in [Ni{(2,6-Mes₂C₆H₃)C(NPrⁱ)₂}]₂,¹³ⁱ but marginally longer than those of 1.904(5) Å (ave.) in the binuclear Ni(II) complex of *N,N'*-di-*p*-tolylformamidinate [Ni₂{MeC(N(C₆H₄Me-*p*))₂}]₄.^{12g}

Mass spectrometry, magnetic susceptibility measurements, and cyclic voltammetry

Although the EI mass spectrum of the lithium derivative **1** only showed a fragmentation pattern due to the L[–] ligand, those of the binuclear complexes **2** and **5** displayed fragmentation

Table 7 Selected bond distances (Å) and angles (°) for [NiL₂] (6)

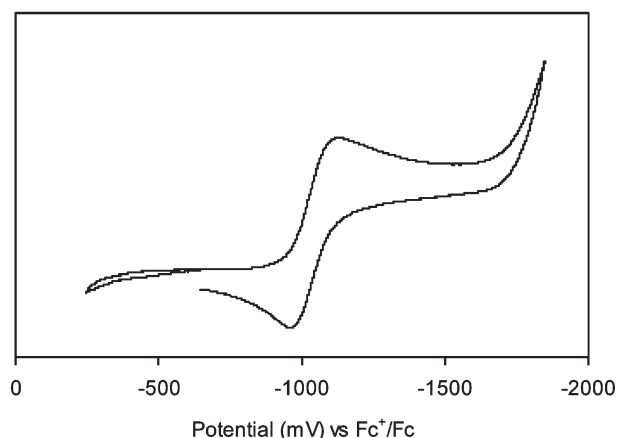
Ni(1)–N(1)	1.908(2)	Ni(1)–N(2)	1.945(2)
Ni(1)–N(3)	1.921(2)	Ni(1)–N(4)	1.937(2)
N(1)–C(1)	1.319(3)	N(2)–C(1)	1.329(2)
C(1)–C(2)	1.492(3)	N(1)–C(8)	1.426(2)
N(2)–Si(1)	1.734(2)	N(3)–C(21)	1.320(3)
N(4)–C(21)	1.330(2)	C(21)–C(22)	1.500(3)
N(3)–C(28)	1.430(3)	N(4)–Si(2)	1.741(2)
N(1)–Ni(1)–N(2)	68.93(7)	N(3)–Ni(1)–N(4)	69.09(7)
N(1)–Ni(1)–N(3)	173.70(8)	N(2)–Ni(1)–N(4)	176.39(8)
N(1)–C(1)–N(2)	110.9(2)	N(1)–C(1)–C(2)	123.9(2)
N(2)–C(1)–C(2)	125.2(2)	C(1)–N(1)–Ni(1)	90.4(1)
C(1)–N(1)–C(8)	124.9(2)	C(8)–N(1)–Ni(1)	137.9(1)
C(1)–N(2)–Ni(1)	88.6(1)	C(1)–N(2)–Si(1)	132.1(2)
Si(1)–N(2)–Ni(1)	139.2(1)	N(3)–C(21)–N(4)	111.3(2)
N(3)–C(21)–C(22)	123.7(2)	N(4)–C(21)–C(22)	124.8(2)
C(21)–N(3)–Ni(1)	89.5(1)	C(21)–N(3)–C(28)	123.4(2)
C(28)–N(3)–Ni(1)	138.6(1)	C(21)–N(4)–Ni(1)	88.5(1)
C(21)–N(4)–Si(2)	129.8(2)	Si(2)–N(4)–Ni(1)	141.6(1)

**Chart 1**

peaks associated with the mononuclear [ML₂]⁺ unit (*m/z* = 644 for **2**, 649 for **5**). For the mononuclear [FeL(Cl)(TMEDA)] (**3**), no molecular ion peak was observed, only the fragmentation pattern due to the L[–] ligand. The mass spectrum of [FeL₂(TMEDA)] (**4**) showed signals associated with the [FeL₂]⁺ species (*m/z* = 646) as well as its fragments. The Ni(II) derivative **6** is the only compound in the series that showed its molecular ion peak at *m/z* = 649 in its mass spectrum.

The magnetic moments of complexes **2–5** in benzene solutions at 300 K have been measured by the Evans NMR method.²⁶ The magnetic moment of 3.59 μ_B per Mn(II) ion for the binuclear complex **2** is much lower than the spin-only value expected for a high-spin d⁵ electronic configuration. Although a variable temperature magnetic susceptibility measurement for this compound is not available, it appears that a plausible mechanism for a Mn···Mn interaction may not be present in the compound. This may be supported by the solution magnetic moment of 3.40 μ_B per Co(II) ion for the analogous binuclear Co(II) derivative **5**, which suggests a high-spin d⁷ electronic configuration with three unpaired electrons for each Co(II) ion. On the basis of this information, the observed magnetic moment for each Mn(II) ion in **2** may be ascribed to a *S* = 3/2 quartet ground state.^{35,36} The respective magnetic moments of 5.13 and 4.96 μ_B for the Fe(II) derivatives **3** and **4** are consistent with the spin-only value of 4.90 μ_B for four unpaired electrons.

The redox properties of the present complexes in CH₂Cl₂ solutions have been studied by cyclic voltammetry. Although complexes **2**, **3** and **5** did not show any redox behaviour within the limits of solvent decomposition under the conditions of our studies, the Fe(II) bis(benzamidinate) **4** and the Ni(II) derivative **6** both exhibited cyclic voltammetric behaviour. The cyclic voltammogram of **4** (Fig. 7) shows a quasi-reversible reduction wave at *E*_{1/2} = –1.04 V (versus ferrocene) with Δ*E*_p = 162 mV. On the other hand, the cyclic voltammogram of **6** (Fig. 8) consists of two anodic processes, namely an initial quasi-reversible oxidation at *E*_{1/2} = 0.17 V (Δ*E*_p = 165 mV), followed by an irreversible oxidation at *E*_{pa} = 0.69 V. Since benzamidines

**Fig. 7** Cyclic voltammogram of **4** in a CH₂Cl₂ solution containing [Bu₄N][PF₆] (0.15 M). Scan rate: 50 mV s^{–1}.

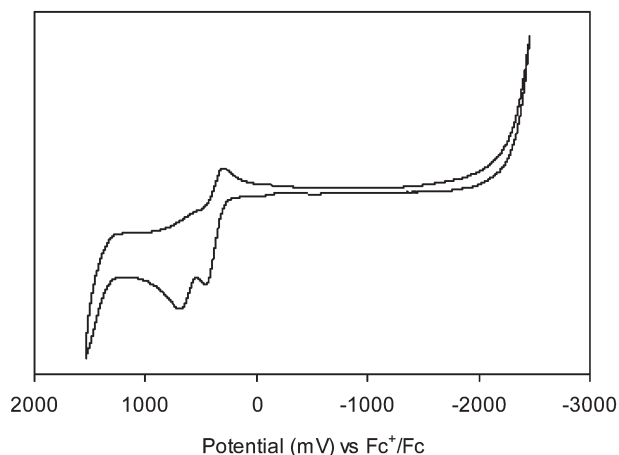


Fig. 8 Cyclic voltammogram of **6** in a CH_2Cl_2 solution containing $[\text{Bu}_4\text{N}][\text{PF}_6]$ (0.15 M). Scan rate: 100 mV s^{-1} .

are also known to be electrochemically active, assignments of the redox processes for **4** and **6** appear to be difficult in the present cases.

Acknowledgements

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