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Syntheses, crystal structures and properties of four iron and cobalt complexes bearing 1,3,5-triazapentadienyl ligands

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

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ABSTRACT

Addition reactions of $MN(R)SiMe_3$ (R = Ph or $SiMe_3$, M = Li or Na) to 2 equivalents of α-hydrogen-free 1-piperidinecarbonitrile generated $[M\{N(R)C(R')NC(R')N(SiMe_3)\}]_2$ [(**1a**), R = $SiMe_3$, R′ = 1-piperidino, M = Li; (**1b**), R = Ph, R′ = 1-piperidino, M = Li; (**1c**), R = Ph, R′ = 1-piperidino, M = Na] which further reacted with MCl_2 (M = Fe, Co) to give $M[\{N(SiMe_3)C(R')\}_2N]_2$ [R′ = 1-piperidino, M = Fe (**2**); Co (**3**)] and $M[N(Ph)C(R')NC(R')N(SiMe_3)]_2$ [R′ = 1-piperidino, M = Fe (**4**); Co (**5**)], respectively. In each of the crystalline complexes **2**–**5** the MNCNCN rings are planar. The Fe and Co centers in **2**–**5** feature a tetrahedral environment in *N, N*′-1,5-chelated fashion. The molecular structures of **2**–**5** are presented. Furthermore, the thermal properties of the four complexes have been investigated.

1. Introduction

The five-atom 1,3,5-triazapentadienyl anions with NCNCN backbone, as potential supporting ligands for main and transition metal compounds have drawn increasing attention due to their structural features and synthesis considerations [1–5]. The electron-donating ligands not only coordinate to a wide range of metal ions but show a rich variety of coordination modes. This class of ligands is of easy accessibility and amenable to substituent variation, which allows for tuning of their steric and electronic properties, and for improving the reactivities and properties of their metal complexes [6].

The majority of previous publications have dealt with the families of perfluoroalkyl-substituted 1,3,5-triazapentadienyl ligands and their metal complexes [7,8]. The related 1,3,5-triazaheptatrienyl and 1,3,5,7-tetraazaheptatrienyl complexes [9,10] have also been documented. Currently, some of 2,4-*N,N*′-disubstituted 1,3,5-triazapentadienyl ligands have been structurally chracterized and their chemistry explored [11,12]. The ligand backbone NCNCN can adopt a U- or W-shaped configuration, and the presence of NR_2 functions would make it planar, sp^2 hybridized with the lone pair residing in a p orbital for overlap with the conjugated NCNCN moiety. At present, they are limited to some structurally characterized examples. In addition, studies on the properties of 1,3,5-triazapentadienyl metal complexes are rare.

We now report the synthesis of series of homoleptic iron and cobalt 2,4-*N,N*′-disubstituted 1,3,5-triazapentadienyl complexes $M[\{N(SiMe_3)C(R')\}_2N]_2$ [R′ = 1-piperidino, M = Fe (**2**); Co (**3**)] and $M[N(Ph)C(R')NC(R')N(SiMe_3)]_2$ [R′ = 1-piperidino, M = Fe (**4**); Co (**5**)]. We made these compounds because we thought they would be interesting in their coordination chemistry, spectral features, thermal stabilities and some potential applications [13–17]. The four complexes were characterized by elemental analysis, IR, UV–Vis spectra and thermogravimetric analyses and further characterized by single-crystal X-ray diffraction. The Fe and Co centers in **2**–**5** feature a tetrahedral environment in *N,N*′-1,5-chelated fashion, being agreement with Werner's theory of coordination.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources and dried prior to use. Deuterated solvents $CDCl_3$ were dried over activated molecular sieves (4 Å) and vacuum transferred before use. Diethyl ether was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Anhydrous metal chlorides were purchased from Aldrich and used as received. Glassware was oven-dried at 150 °C overnight. IR spectra (KBr pellets, cm^{-1}) were recorded with a SHIMADZU FTIR8400S spectrometer. TG measurements were performed on a Netzsch STA 409PC differential thermal analyzer.

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Table 1
Crystal and refinement data for **2**–**5**.

Compound	2	3	4	5
Formula	$C_{36}H_{76}FeN_{10}Si_4$	$C_{36}H_{76}CoN_{10}Si_4$	$C_{42}H_{68}FeN_{10}Si_2$	$C_{42}H_{68}CoN_{10}Si_2$
M	817.28	820.36	825.09	828.17
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$C2/c$ (No. 15)	$Pbcn$ (No. 60)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
a (Å)	17.572(5)	16.692(7)	10.865(15)	10.938(2)
b (Å)	18.086(7)	16.555(6)	11.940(14)	11.961(2)
c (Å)	16.375(5)	17.320(7)	19.95(3)	20.113(4)
α (°)	90.00	90.00	72.64(11)	107.221(2)
β (°)	111.81(3)	90.00	75.99(10)	92.649(3)
γ (°)	90.00	90.00	69.73(13)	110.900(2)
U (Å^3)	4831(3)	4786(3)	2289(5)	2313.8(7)
Z	4	4	2	2
T (K)	293(2)	223(2)	213(2)	293(2)
Absorption coefficient (mm^{-1})	0.446	0.494	0.422	0.463
Unique reflections (R_{int})	4219, 0.0280	4134, 0.0504	7691, 0.0293	7834, 0.0247
Reflections with $I > 2\sigma(I)$	3482	3174	6463	6093
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.0446, 0.1256	0.0409, 0.1086	0.0824, 0.2365	0.0625, 0.1755
R indices (all data) R_1, wR_2	0.0550, 0.1495	0.0598, 0.1379	0.0995, 0.2707	0.0802, 0.2101

Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

*2.2. Synthesis of the complexes **2**–**5***

*2.2.1. Synthesis of Fe[{N(SiMe$_3$)C(R′)}$_2$N]$_2$ (R′ = 1-piperidino) (**2**)*

1-Piperidinecarbonitrile (0.45 ml, 3.88 mmol) was added to a solution of LiN(SiMe$_3$)$_2$ (0.33 g, 1.97 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $FeCl_2$ (0.14 g, 1.10 mmol) was added by solid addition at −78 °C. The resulting yellow mixture was warmed to *ca.* 25 °C and stirred overnight, then filtered. The filtrate was concentrated *in vacuo to ca.* 15 cm^3 and stored at −25 °C yielding yellow crystals of **2** (0.49 g, 61%). Mp 100 °C (decomp.). *Anal.* Calc. for $C_{36}H_{76}FeN_{10}Si_4$: C, 52.91; H, 9.73; N, 17.14. Found: C, 53.36; H, 9.83; N, 16.86%. IR (KBr, cm^{-1}): 2939, 2831, 1521, 1429, 1352, 1309, 1236, 1207, 1093, 1027, 970, 894, 842, 756. UV–Vis (THF): $\lambda_{max,nm} = 241$.

*2.2.2. Synthesis of Co[{N(SiMe$_3$)C(R′)}$_2$N]$_2$ (R′ = 1-piperidino) (**3**)*

1-Piperidinecarbonitrile (0.64 ml, 5.50 mmol) was added to a solution of LiN(SiMe$_3$)$_2$ (0.46 g, 2.75 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $CoCl_2$ (0.18 g, 1.39 mmol) was added at −78 °C. The resulting purple mixture was warmed to *ca.* 25 °C and stirred overnight, then filtered. The filtrate was concentrated to give red crystals of **3** (0.44 g, 39%). Mp 121 °C (decomp.). *Anal.* Calc. for $C_{36}H_{76}CoN_{10}Si_4$: C, 52.71; H, 9.34; N, 17.07. Found: C, 53.22; H, 9.68; N, 17.05%. IR (KBr, cm^{-1}): 2943, 2835, 1535, 1431, 1355, 1309, 1234, 1207, 1095, 1027, 970, 898, 844, 757. UV–Vis (THF): $\lambda_{max,nm} = 235$.

*2.2.3. Synthesis of Fe[N(Ph)C(R′)NC(R′)N(SiMe$_3$)]$_2$ (R′ = 1-piperidino) (**4**)*

1-Piperidinecarbonitrile (0.69 mL, 5.96 mmol) was added to a solution of PhN(Li)SiMe$_3$ (0.51 g, 2.98 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $FeCl_2$ (0.19 g, 1.50 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 24 h, filtered, and the filtrate was concentrated in vacuo to *ca.* 20 cm^3 and cooled at −78 °C for 1 d, yielding yellow crystals of **4** (0.86 g, 70%). Mp 158 °C (decomp.). *Anal.* Calc. for $C_{42}H_{68}FeN_{10}Si_2$: C, 61.14; H, 8.31; N, 16.98. Found: C, 60.88; H, 8.76; N, 17.18%. IR (KBr, cm^{-1}): 2933, 2827, 1512, 1429, 1369, 1294, 1242, 1213, 1093, 1027, 972, 887, 837, 756. UV–Vis (THF): $\lambda_{max,nm} = 282$.

*2.2.4. Synthesis of Co[N(Ph)C(R′)NC(R′)N(SiMe$_3$)]$_2$ (R′ = 1-piperidino) (**5**)*

1-Piperidinecarbonitrile (0.59 ml, 5.10 mmol) was added to a solution of PhN(Na)SiMe$_3$ (0.48 g, 2.56 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $CoCl_2$ (0.17 g, 1.31 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 24 h, filtered, and the filtrate was concentrated *in vacuo* to *ca.* 20 cm^3 and cooled at −25 °C for 1 d, yielding red crystals of **5** (0.52 g, 49%). Mp: 144 °C (decomp.). *Anal.* Calc. for $C_{42}H_{68}CoN_{10}Si_2$: C, 60.91; H, 8.28; N, 16.91. Found: C, 60.44; H, 8.78; N, 16.36%. IR (KBr, cm^{-1}): 2933, 2852, 1515, 1433, 1371, 1242, 1213, 1093, 1027, 973, 838, 756. UV–Vis (THF): $\lambda_{max,nm} = 279$.

2.3. X-ray crystallographic determination

Single crystals of **2**–**5** suitable for X-ray diffraction studies were obtained by recrystallization of compounds from Et_2O. Data collection was performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer at 293(2), 247(2), 223(2) or 213(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. A total of *N* reflections was collected by using ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [18]. The structure was solved by direct method (SHELXS-97) [19]. Then the remaining non-hydrogen atoms were obtained from the successive difference fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using a riding mode. (SHELXTL) [20]. Crystal data and details of data collection and refinements for **2**–**5** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and structural descriptions of complexes

The lithium or sodium reagent MN(Ph)SiMe$_3$ was prepared according to the literature procedures [11,21–24]. The lithium amide LiN(SiMe$_3$)$_2$ was easily accessible via the lithiation of 1,1,1,3,3,3-hexamethyldisilazane with LiBu^n in hexane [11]. Treatment of the above lithium or sodium salt with 2 equivalents of α-hydrogen-free 1-piperidinecarbonitrile generated [M{N(R)C(R′)NC(R′)N(SiMe$_3$)}]$_2$ [(**1a**), R = SiMe$_3$, R′ = 1-piperidino, M = Li; (**1b**), R = Ph, R′ = 1-piperidino, M = Li; (**1c**), R = Ph, R′ = 1-piperidino, M = Na). The formation of the 1,3,5-triazapentadienyl ligands