Heteroleptic, two-coordinate $[\text{M(NHC)}\{\text{N(SiMe}_3\}_2]\}$ (M = Co, Fe) complexes: synthesis, reactivity and magnetism rationalized by an unexpected metal oxidation state†‡

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The linear, two-coordinate and isostructural heteroleptic $[\text{M(Pr)}\{\text{N(SiMe}_3\}_2]\}$ ($\text{Pr} = \text{1,3-bis(diisopropylphenyl)}$-imidazol-2-ylidine), formally $\text{M}^1$ complexes (M = Co, Fe) were obtained by the reduction of $[\text{M(Pr)}\text{Cl}\{\text{N(SiMe}_3\}_2]\}$ with $\text{KC}_8$, or $[\text{Co(Pr)}\{\text{N(SiMe}_3\}_2\}_2]\$ with $\text{mes}^*\text{PH}_2$, $\text{mes}^* = 2,4,6-$tris(trisopropylsilylethylidene)mesityl. The magnetism of $3$ and $4$ implies $\text{Co}^2$ and $\text{Fe}^3$ centres coupled to one ligand-delocalized electron, in line with XPS and XANES data; the ac susceptibility of $4$ detected a pronounced frequency dependence due to slow magnetization relaxation. Reduction of $[\text{Fe(Pr)}\text{Cl}\{\text{N(SiMe}_3\}_2\}]$ with excess $\text{KC}_8$ in toluene gave the heteronuclear ‘inverse-sandwich’ Fe–K complex $7$, featuring $\eta^6$-toluene sandwiched between one $\text{Fe}^0$ and one $\text{K}^+$ centre.

Introduction

Two-coordinate complexes of $\text{d}^n$ metals ($n < 10$) remain rare and challenging synthetic targets, calling for fine sterically and electronic ligand tuning, although the first example was structurally characterized in 1985. Their study constitutes a topical area due to their electronic structures (open-shells with diverse spin multiplicities), interesting magnetic properties (e.g. high magnetic moments, ‘single ion magnet’ (SIM) behaviour), and stoichiometric and catalytic reactivity. Insightful modelling of ‘base metal’ catalysts is linked to the mapping of the reactivity of complexes with low coordination numbers.

With the aim to rationally access linear two-coordinate complexes with particularly interesting magnetic properties, bulky ligands have been used. In general, departure from the exactly linear geometry due to intra- or inter-molecular interactions or other ligand effects has a deleterious effect on the desirably high unquenched orbital magnetism. Thus, alkyl $[\text{C(SiMe}_3\}_2]$, e.g. in $[\text{M}[\text{C(SiMe}_3\}_2]]_2$ (ref. 13), is a single ion magnet (SIM) behaviour, and to a lesser extent $\text{Cr}_{9,10}$ $\text{Mn}_{10,11}$ and $\text{V}_{11}$ two-coordinate linear or quasi-linear homoleptic terphenyls, alkoxides and thiocyanates have also been described. Neutral homoleptic complexes with the ubiquitous $[\text{M(SiMe}_3\}_2]$ form dimers in the solid state or in solution through amido bridging, due to the insufficient steric bulk of the ligand but the anion $[\text{Fe][N(SiMe}_3\}_2]_2]$ (ref. 13) is mononuclear and linear. Lately, mononuclear, 2-coordinate homoleptic complexes of $\text{Fe}_{9,10}^2\text{Co}_{11,12}^2\text{Mn}_{16}^2$ and $\text{Cr}_{17}^2$ with the $\text{cAAC}$ (CAAC = cyclic AlkylAmino Carbene), and cationic complexes with imidazol-2-ylidene ligands have also been reported.
Notwithstanding these synthetic successes, there is only a limited number of linear heteroleptic 2-coordinate complexes $A_{19}$, $B_{4}^{a,c,e,f,20}$ $a$, $c$, $e$, $f$, $20$ $C_{21}$ and $D_{22}$ with 3d $(n < 10)$ metals (Scheme 1). Heteroleptic 3-coordinate NHC amido species have recently been appearing more often.$^{23}$

Herein, we describe the stable, formally 12 and 11 valence electron, virtually linear, 2-coordinate, charge-neutral heteroleptic complexes $[M(IPr)\{N(SiMe_3)2\}]$ ($IPr = \text{N, N}'$-bis(di-iso-propylphenyl)imidazol-2-ylidene, $M = \text{Co (3), Fe (4)}$), respectively, and their remarkable magnetic behaviour; we propose an original, functional model for the interpretation of the latter, supported by probing the oxidation state of the metals with XPS and XANES techniques. We also include some preliminary reactivity studies of 3 and 4.

**Results and discussion**

**Synthesis of 3 and 4**

Reduction of $[\text{Co(Imes)}\{N(SiMe_3)2\}Cl]$ ($\text{Imes} = \text{1,3-bis(mesityl)-imidazol-2-ylidene}$) with KC$_8$ and of $[\text{Co(Imes)}\{N(SiMe_3)2\}2]$ with mes*PH$_2$ yielded $\text{Co}^{\text{II}}$ centres coordinated to one anionic imido and one radical anionic IPr. However, detailed comparison of the $M$–CNHC bond distances in 3 and 4 with those in known two-coordinate homoleptic complexes, as well as other two-coordinate analogues (Scheme 1) was inconclusive. Correlation of the metrical data with a metal oxidation state was hampered by the scarcity of relevant identically substituted, two-coordinate complexes in different oxidation states, and the disparate

**Scheme 1** Heteroleptic two-coordinate complexes of 3d metals.

**Scheme 2** Syntheses of the complexes described herein.
trans-influence of the NHC and amido donor types. In the known heteroleptic [Fe[N(SiMe$_3$)$_2$]$_2$]$^+$, [Fe(cyIDep)$_2$]$^+$ and [Fe(cAAC)$_2$]$^+$, cyIDep = 1,3-bis(2',6'-diethylphenyl)-4,5-(CH$_2$)$_2$-imidazol-2-ylidene (all assigned as Fe I complexes), the dis-
orbitals of the NHC and amido donor types. In addition, the M–N and M–C$_{NHC}$ distances in 3 and 4 are significantly shorter than those in the three-coordinate [M$^0$(IPr)[N(SiMe$_3$)$_2$]$_2$] (M = Fe, Co). Nevertheless, the Fe–C$_{NHC}$ distance in 4 is virtually identical to that in the heteroleptic C (Scheme 1), in which Fe$^0$ was implicated. In both 3 and 4 the heterocyclic rings are virtually planar (max. displacement from the mean 5-membered ring plane 0.002 Å); planar is also the environment of the amido N-atoms. In view of the lack of structural or computational data on plausible imidazole-2-ylidene radical anions$^{26}$ and the previous discussion, it is futile to argue for metrical (ligand) oxidation states$^{29}$ in 3 and 4. Close in energy, open-shell electronic structures may be attainable under specific conditions (temperature, solvent etc.) by fine ligand tuning, which may also potentially lead to ligand(s) noninnocence. Lastly, in the crystals of 3 and 4 there are no close contacts of the molecules with nearby atoms, implying sufficient electronic stabilization of the two-coordinate structures and the minimal role of steric and/or dispersion forces serving this purpose. In the crystalline solids the metal centres are at ca. 9.485 and 9.471 Å apart, respectively (self-dilute).

**Magnetic studies of 3 and 4**

The interpretation of the SQUID magnetometry data of solid samples of 3 and 4 may imply remarkable electronic structures. The static field (dc) susceptibility data (as $\chi_{m}\times T$ vs. $T$ at 0.1 T and $M_m$ vs. $B$ at 2.0 K) are presented in Fig. 2. For 3, the room-temperature value of $\chi_{m}=4.88$ cm$^3$ K mol$^{-1}$ (corresponding to $\mu_{eff}=6.25\mu_B$) is very high. Upon cooling, $\chi_{m}$ increases to 4.99 cm$^3$ K mol$^{-1}$ at 170 K, then decreases to 4.92 cm$^3$ K mol$^{-1}$ at 12 K, and finally drops to 4.65 cm$^3$ K mol$^{-1}$ at 2.0 K. At this temperature, $M_m$ shows saturation at ca. 3.4N$_B$ above $B \approx 2$ T. The room temperature value of $\mu_{eff}=6.25\mu_B$ is even higher than the free-ion value (for 3d$^9$: $L=3$, $S=1$, $J=4$, $g_J=5/4$, $\mu_{eff}\approx \chi(1+11/12)\mu_B=5.59\mu_B$), which constitutes the upper limit for high spin 3d$^9$ mononuclear complexes, thus ruling out the scenario of 3 as a Co$^2$ high-spin complex. Similarly, for 4, $\chi_{m}T$ is 4.37 cm$^3$ K mol$^{-1}$ at 290 K (corresponding to $\mu_{eff}=5.91\mu_B$). It increases to 4.85 cm$^3$ K mol$^{-1}$ at 75 K, and then decreases to 3.67 cm$^3$ K mol$^{-1}$ at 2.0 K, where $M_m$ is linear in $B$ up to 1 T and reaches 2.8N$_B$ at 5 T. The room temperature value of $\mu_{eff}=5.91\mu_B$ is also unusually high for a high spin 3d$^7$ Fe$^1$ configuration, but smaller than the
free-ion value ($L = 3$, $S = 3/2$, $J = 9/2$, $g_J = 4/3$, $\mu_{\text{eff}} \approx 6.63 \mu_B$). Interestingly, $\mu_{\text{eff}}$ values reported in the literature for the majority of linear CoI and FeI complexes are significantly smaller, while very few complexes of linear FeII centres exhibit similarly high values have been described. Measurements under various magnetic fields at 290 K did not reveal any ferromagnetic impurities (see Fig. S7†), corroborating the high intrinsic $\mu_{\text{eff}}$ values.

To account for the observed values, we reasoned that 3 may be characterized by either a 3d$^4$4s$^1$ configuration in a quintet state ($S = 2$), or by a configuration resulting from the transfer of one electron from the CoI to the ligand periphery, i.e. localized at one of the ligands or delocalized over the $\pi$ system of the complex. Analogous considerations for 4 may lead to a 3d$^6$4s$^1$ configuration in a sextet state ($S = 5/2$), or one electron transferred from FeI to one of the ligands, more likely the NHC. Consequently, three different electronic configuration scenarios have been investigated: (i) a single M$^+$ centre (3d$^6$, $M = \text{Co}^+$: $N = 8$; $M = \text{Fe}^+$: $N = 7$); (ii) a single M$^0$ centre (3d$^{N−1}$) representing the upper limit for a high spin 3d$^6$ electron configuration, with free ion values: $L = 2$, $S = 2$, $J = 4$, $g_J = 3/2$, $\mu_{\text{eff}} \approx 6.71 \mu_B$, to explore the unlikely possibility of decomposition; (iii) a single M$^0$ (3d$^{N−1}$) centre interacting with one electron ($S = 1/2$) via Heisenberg–Dirac–Van Vleck exchange coupling that is (de)localized over the ligand/complex (referred hereafter to as the ‘M$^+ + e^−$’ scenario). In the latter case, maximum $\mu_{\text{eff}} \approx 6.86 \mu_B$, and $\mu_{\text{eff}} \approx 6.93 \mu_B$ corresponding to “3d$^7 + e^−”$ and “3d$^6 + e^−”, respectively, could be envisaged.

Considering the $C_{\text{soc}}$ ligand field symmetry to be in line with the linear heteroleptic nature of 3 and 4, we employed the ‘full’ model Hamiltonian implemented in CONDOR 2.0.30 The corresponding Hamiltonian, neglecting contributions resulting in constant shifts of the total energy, is defined as:

$$
\hat{H} = \sum_{j=1}^N e^2 + \sum_{j=1}^N \zeta(r_j) \mathbf{\hat{I}}_j \cdot \mathbf{\hat{s}}_j + \sum_{i=1}^{N_{\text{M}}} \left\{ B_0 \mathbf{C}_0^2(i) + B_0^4 \mathbf{C}_0^4(i) \right\} 
+ \sum_{i=1}^{N_{\text{M}}} \mu_B \left( \mathbf{k} \mathbf{I}_i + g_I \mathbf{S}_i \right) \cdot \mathbf{B} \left( -2J \right) \sum_{i=1}^{N_{\text{M}}} \mathbf{S}_i \cdot \mathbf{S}_c
$$

where all operators, but the Heisenberg operator $\hat{H}_{\text{ex}}$, describe the various single-ion contributions ($\hat{H}_{\text{soc}}$: interelectronic repulsion, $\hat{H}_{\text{so}}$: spin–orbit coupling, $\hat{H}_{\text{lf}}$: ligand field effects theory framework, $\hat{H}_{\text{mag}}$: Zeeman effect of an external magnetic field). $\hat{H}_{\text{ex}}$ is parameterized by the Racah parameters $B$ and $C$, $\hat{H}_{\text{soc}}$ by the one-electron spin–orbit coupling parameter $\kappa$ and the orbital reduction factor $\kappa$. The $C_0^2 \equiv \sqrt{4\pi/(2k + 1)}Y_0^k$ in $\hat{H}_{\text{lf}}$ denote the relevant spherical tensors for a given ligand field symmetry and are directly related to the spherical harmonics $Y_0^k$. $B_0^{k}$ are the (real) ligand field parameters in the Wybourne notation. The sum index $i$ runs over all $N_{\text{M}}$ valence electrons of the corresponding metal center.

The least-squares fits for the scenarios (i) and (ii) did not yield even remotely acceptable solutions (including considerations of free ions, and physically unlikely parameters, see Fig. S8‡ for a selection of resulting fits). In contrast, the “M$^+ + e^−$” scenario indeed reproduced the temperature-dependent susceptibility data ($\chi' = 1.0\%$; Fig. 2 and Table S6†). We note that for 3, inclusion of the field-dependent magnetization data at 2.0 K (Fig. 2a, inset) reduces the overall fit quality ($\chi' = 7.7\%$). Fitting solely the $M_m$ vs. $B$ data would point (ii) as the preferred scenario, but then the $\chi_m$ vs. $T$ curve would not be reproduced at all (Fig. S8c†). By employing the “M$^+ + e^−$” scenario for 4, the least-squares fit yields a reasonable $\chi' = 2.8\%$ (1.8% when excluding $M_m$ vs. $B$ data). The single ion contribution of the M$^0$ centre is highlighted in Fig. 2 for both complexes.

The scenario “M$^+ + e^−$” yields small, antiferromagnetic exchange energies $J = −0.1$ cm$^{-1}$ (3) and −0.5 cm$^{-1}$ (4). These results indicate that the additional electron should be assigned to the ligands. Such parameters imply formal triplet (3) or quartet (4) ground states with respect to the whole molecule. We note that DFT calculations of 3 and 4 also support triplet and quartet electronic ground states, respectively; however, at the DFT theory level, only minimal spin delocalization on the ligand is predicted (see the EST‡ for details).

Since the Heisenberg–Dirac–Van Vleck exchange formalism refers to localized electrons, an unpaired electron localized on a ligand atom is expected to induce a strong exchange interaction. In contrast, within the limitations of the model, the small magnitudes of $J$ hint at (at least partially) delocalized electrons for which various effects, e.g. electron transfer, might compensate each other, yielding a small effective net value. Thus, the fits also reflect the inherent limitations of ligand field theory, where electrons localized at the metal interact with an electrostatic ligand field potential, neglecting further dynamic aspects generated by e.g. the conjugation of the $\pi$ system.

The in-phase $\chi_m'$ and out-of-phase $\chi_m''$ components of the magnetic ac susceptibility data as a function of temperature (Fig. S9 (3) and S10‡ (4)) show out-of-phase signals for 4, up to ca. 15 K (<1000 Hz) but not for 3. The $\chi_m'$ vs. $\chi_m''$ data (Fig. 2c) were analysed in terms of the generalized Debye expression (solid lines). The dependence of the magnetic relaxation time $\tau$ on $T_n$ is shown in Fig. 2d as the Arrhenius plot. The distribution of relaxation times $\alpha$ (0.04–0.17, mean value 0.12) suggests the existence of multiple relaxation pathways. Notably, the semi-logarithmic Arrhenius plot exhibits two quasi-linear segments between 3.0–5.5 K and 8.5–14 K. Fitting these to the Arrhenius expression $\tau = \tau_0 \exp(U_{\text{eff}}/(k_BT))$ (attempt time $\tau_0$, effective energy barrier $U_{\text{eff}}$, Boltzmann constant $k_B$) yields $\tau_0 = (3.23 \pm 0.03) \times 10^{-4} \text{ s}$, $U_{\text{eff}} = (0.89 \pm 0.03) \text{ cm}^{-1}$ for 3.0–5.5 K, and $\tau_0 = (1.64 \pm 0.80) \times 10^{-6} \text{ s}$, $U_{\text{eff}} = (31.0 \pm 3.1) \text{ cm}^{-1}$ for 8.5–14 K. Whereas the latter parameters are at the upper limit for typical Orbach relaxation in single ion magnets (SIM), the first is not, thus potentially describing a different process. Note that the effective energy barrier is of the same order as the exchange coupling parameter $J$. The first process might be thus linked to the potential exchange interaction of the Fe centre and the delocalized electron. We therefore
considered two different models for fitting the entire temperature range (2.0–14 K): (a) quantum tunnelling, Orbach and Raman relaxation processes \( (\tau^{-1} = B + \tau_{0,1}^{-1}\exp[-U_{\text{eff}}/(k_B T)] + C/T^6) \), and (b) quantum tunnelling, Orbach relaxation process and another Arrhenius-type relaxation process \( (\tau^{-1} = B + \tau_{0,2}^{-1}\exp[-U_{\text{eff},2}/(k_B T)] + \tau_{0,3}^{-1}\exp[-U_{\text{eff},3}/(k_B T)]) \). Least-squares fits to (a) (Fig. 2 and S11) blue dashed line) yield \( B = (1352 \pm 152) \text{s}^{-1}, \tau_{0,1} = (4.56 \pm 0.17) \times 10^{-4} \text{s}^{-1}, U_{\text{eff}} = (2.55 \pm 0.52) \text{cm}^{-1}, C = (2.88 \pm 3.35) \times 10^{-5} \text{s}^{-1} \text{K}^{-6} \), and \( n = 8.02 \pm 0.53 \). Model (b) (Fig. 2 and S11) red line) results in \( B = (1547 \pm 87) \text{s}^{-1}, \tau_{0,1} = (1.01 \pm 0.45) \times 10^{-7} \text{s}, U_{\text{eff},1} = (56.6 \pm 3.1) \text{cm}^{-1}, \tau_{0,2} = (4.03 \pm 0.25) \times 10^{-4} \text{s}, \text{and } U_{\text{eff},2} = (3.59 \pm 0.50) \text{cm}^{-1} \). The fit parameters of (a) describe a system characterized by quantum tunnelling (B) and Raman (C) relaxation processes close to Kramers systems (\( n = 9 \)), and a process which is not a typical SIM-type Orbach relaxation. Note that there are several other relaxation processes\(^{22}\) compared to the suggested exchange interaction, which are characterized by an Arrhenius law, e.g. the sum process. Model (b) essentially replaces Raman relaxation by Orbach relaxation, while the other fit parameters are almost unchanged. Due to a slightly better goodness-of-fit, the occurrence of an Orbach relaxation process typical of SIMs and fit parameters in the range for similar compounds,\(^{34,35}\) the SIM characteristics of 4 are better characterized by model (b) than (a), although the nature of the second Arrhenius-type process could not be fully resolved. We note that the magnetization relaxation dynamics of linear Co\(^{2+}\) compounds seem to be very sensitive to the ligand field, as was also observed by Meng et al.,\(^{18a}\) which may also be related to the electron delocalization implied in the \( \text{M}^{II} + e^- \text{"} \) scenario.

**XPS, EXAFS and XANES studies of 3 and 4**

The \( \text{M}^{II} + e^- \text{"} \) scenario was corroborated by the XPS spectra of 3 and 4 (see Fig. S12 and S13 and Table S7\(^{1/2}\) for binding energies). The spectrum of 3 showed well-resolved 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks (780.7 and 796.4 eV, respectively) in support of Co\(^{II}\) in a soft environment.\(^{33}\) Strong satellite peaks at 785.7 and 802.1 eV arose from the shake-up transitions of the core photoelectron to metal d and ligand valence levels.\(^{34,35}\) Their intensity increases with the spin of the metal and the covalency of the metal–ligand bond.\(^{34,35}\) Overall, the data are consistent with 3 featuring a high-spin Co\(^{II}\).

The structural analysis of 3 with Co K-edge EXAFS spectroscopy agreed with the crystal structure data (see ES1\(^{11}\)). Remarkably, and in agreement with XPS, the Co K-edge XANES revealed an overall charge of +2 on the Co, with the pre-edge features nicely supporting the linear structure. The Co K-edge XANES of 3, in comparison to some representative Co\(^{II}\) and Co\(^{III}\) compounds, is given in Fig. 3 (the first derivatives of the XANES are given in Fig. S14\(^{1}\)). Although the XANES is known to be dependent on the metal oxidation state (charge) as well as the nature of the ligands and the coordination geometry, Fig. 3 suggests that 3 represents an overall Co\(^{3+}\) complex. The first pre-edge feature as seen for 3 can be assigned to pd hybridization, making the dipole forbidden s-to-d transition slightly visible, and the second pre-edge feature originates from hybridization of the Co-p and Co-d (with C-p mostly, and little mixing from N-p, as indicated by simulations (see Fig. S15 in ESI\(^{1}\))). The high intensity of the second pre-edge is due to the empty character of the orbital, which is indicative of the linear Co. The simulations also suggest the channel of charge redistribution being the aromatic part (i.e. NHC) of the molecule.

The XPS spectrum of 4 is less well resolved but globally similar to that of 3. The 2p\(_{3/2}\) peak is unsymmetrical with a tail on the high-energy side and a broad feature, which is due to the presence of a satellite peak partly overlapping with the 2p\(_{3/2}\); the 2p\(_{1/2}\) peak behaves similarly. A deconvolution using a Gaussian/Lorentzian admixture allows distinguishing both components (Table S7\(^{1}\)). The energies of the 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks and their satellites are consistent with a Fe\(^{II}\) centre.\(^{29,36}\) The small intensity of the satellite peaks does not support a high-spin Fe, however, due to the small energy difference between the 2p peaks and their satellites, the intensities of the latter are strongly dependent on the deconvolution mode and base line correction.

**Preliminary reactivity studies related to 3 and 4**

Reactivity experiments showed that the IPr ligand in 3 and 4 can be displaced by SIPr or IAd, leading to equilibrium mixtures of 3 and 4 and the heteroleptic, 2-coordinate SIPr or IAd analogues, respectively (inferred by \(^{1}\)H NMR monitoring). Furthermore, the reaction of 4 with Ph–Cl or Me\(_3\)SiCH\(_2\)–Cl led to mixtures, in which 2Cl is the major paramagnetic component (by comparison of the \(^{1}\)H NMR spectra with authentic samples). Finally, 3 and 4 react with weak organic protic reagents: for example, the reaction of 3 with mesNH\(_2\), mes = mesityl, 2,4,6-trimethylphenyl, gave after aminolysis of the Co–N(SiMe\(_3\))\(_2\) bond the paramagnetic 6 as red crystals (Scheme 2 and Fig. 4),\(^{1}\) which was characterized crystallographically. In the centrosymmetric binuclear 6, each Co is coordinated by one IPr and the symmetrically bridging primary mesitylaldo ligands (mesNH). The Co(N\(_2\))\(_2\) core is planar with intermetallic separation of 2.5765(4) \(\text{Å} \), supporting the interaction between the Co centres (\( \Sigma_{\text{cov, rad}} = 2.52 \text{ Å} \)), while the bridging mesityla-
mido ligand adopts a distorted tetrahedral geometry at the N atom, presumably due to steric reasons and the presence of the intermetallic interaction.

Reduction of 2CI with excess KC₈ in toluene afforded low yields of the yellow-green, paramagnetic 7 which could only be characterized crystallographically (Fig. 5).† It is a centrosymmetric, ‘inverse-sandwich’ tetranuclear heterometallic dimer, each monomer containing a η⁶-toluene sandwiched between one Fe⁰ (16e⁻) and one K⁺ centre; the two monomers are connected by two bridging –N(SiMe₃)₂ ligands ligated to the K cations.

Complex 7 is a rare example of the Fe–NHC η⁶-arene complex;37,38 [Fe⁰(IPr)[diene]] species were also recently described.39 Interestingly, it could not be obtained by the reduction of 4 in toluene. It is also worth pointing out that mechanistically the formation of 7 is remarkable. The sole source of K is the reducing KC₈ and of –N(SiMe₃)₂ the 2CI featuring a direct Fe–N(SiMe₃)₂ bond. The formation of 7 may involve a consecutive insertion of the K(toluene) fragment into the Fe–N(SiMe₃)₂ of a transient [IPrFe⁰(N(SiMe₃)₂)]⁺ with or without prior coordination to the metal; [IPrFe⁰(N(SiMe₃)₂)]⁺ is a plausible initial product from the 2e⁻ reduction of 2CI. Fe–K assemblies have been recently studied with respect to Fe catalysed N₂ activation.40

**Conclusion**

In conclusion, we have developed methods for the synthesis of the heteroleptic two coordinate 3 and 4 using reductive strategies under well defined conditions. 3 and 4 constitute timely additions to the growing family of two-coordinate 3d-organo-metallics. The unexpected and remarkable finding related to 3 and 4, based on several lines of experimental evidence, is their high magnetic moments, which led to the proposition of an electronic structure model featuring MII centres and a delocalized electron on the ligand (e.g. IPr) based orbitals. This assignment renders the IPr as a radical anion and therefore electronically non-innocent by definition. Radical anionic NHCs (excluding good π-accepting cAAC) have been rarely established experimentally or invoked in the coordination chemistry of transition metals; for example, radical anions have been detected by ESR after the electrochemical reduction of the ‘Enders carbene’,41 more recently Apeloig demonstrated the duality of IPr adducts with paramagnetic organometallic species: reaction of IPr with the photochemically generated ‘singlet organometallic radical’ M[CO]₃ (M = Mn, Re) gave adducts, which were formulated as [(IPr⁻)Re[CO]₃]⁻ and [(IPr)[Mn][CO]₃] (i.e. a IPr stabilised organometallic radical) on the basis of EPR spectroscopy and calculations.28 Furthermore, cAAC NHC ligands being excellent π-acceptors have given rise to remarkable, stable 3d complexes in lower oxidation states, in which their electronic non-innocence and open-shell structures have been established.42 It is plausible that the higher energy of 3d metal orbitals in combination with the low coordination numbers and the weaker ligand fields may promote non-innocent NHC ligand behaviour in
the poor π-accepting IPr and related Arduengo-type NHCs, by
closer energy proximity of the metal and ligand orbitals. The
coordinated NHC non-innocence under these conditions may
also be relevant in catalysis with 3d metal NHC complexes,
where ‘underligated’ structures are postulated as common
intermediates. The topic of NHC (including Arduengo-type IPr
and cAAC) stabilized main group radicals and radical ions has
been recently reviewed.43

Although the experimental evidence for the nature of IPr in 3
and 4 is convincing, and DFT calculations support triplet
and quartet electronic ground states, respectively, minimal spin
delocalization on the ligand is predicted by this methodology
(see the ESI† for details); this may be a consequence of the well-
known limitations of this method with multi-reference
structures. Therefore high-level ab initio calculations are desirable to
provide a better insight into the electronic structures of 3 and 4.

Experimental

General details on the synthetic methodologies for the new
complexes as well as improved synthetic methods for 1Cl and
2Cl can be found in the ESL.‡

[Co(IPr)[N(SiMe3)2]] (3), method A

A solution of [Co(IPr)[N(SiMe3)2]Cl] (1N) (1.00 g, 1.30 mmol)
and mes*PH2 (0.40 g, 1.43 mmol, 1.1 equiv.) in toluene
(20 cm3) was stirred at 45 °C for 3 days, when it changed
colour from green to orange-brown. If the starting material
was not completely consumed after this period (i.e. <90% con-
version by 1H NMR spectroscopy), more mes*PH2 (typically
0.10 g, 0.13 mmol, 10%) was added, and the reaction was con-
tinued for an additional period of 24 h. After completion,
the toluene was removed under reduced pressure and the residue
was extracted into ca. 20 cm3 pentane. The pentane solution
was concentrated to ca. 6–7 cm3 and cooled to −40 °C for 24 h
to yield yellow-orange plates of 3 that were isolated and dried
under vacuum. Yield: 0.55 g, 0.90 mmol, ca. 69%. Further concentra-
tion of the supernatant and cooling at −40 °C for 2 days
gave as a second crop a minor quantity of 3 contaminated with
a few green crystals of 1N; this crop was discarded. For
C13H23CoN3Si2, calculated (%): C 65.09, H 9.10, N 6.90; found (%): C 64.98, H 9.02, N 6.90. 1H-NMR (C6D6): δ 178.10 (2H,
DiPP aromatic), 79.10 (4H, DiPP aromatic), 12.56 (12H, CH
(CH3)2, in part masked by solvent), 15.24 (2H, CH(CH3)2),
−48.8 (4H, CH(CH3)2), −152.19 (12H, CH(CH3)2) ppm. The
1H-NMR spectrum in d8-THF remains unchanged.

Complex 6

To a solution of 3 (0.070 g, 0.12 mmol) in toluene (2 cm3) at
room temperature was added 2,4,6-trimethylaniline (mesNH2,
0.40 cm3 of 0.35 M toluene solution, 0.14 mmol). The reaction
mixture was stirred at 80 °C for 8 h and then after cooling to
room temperature was evaporated to dryness. The residue
was washed with cold pentane and redissolved in toluene (1 cm3),
the red solution was layered with pentane and allowed to diffuse
at −40 °C giving red crystals after one week. Yield: 0.045 g,
0.04 mmol, ca. 64% (based on Co). 1H-NMR (C6D6): δ 113.4 (6H),
85.1 (12H), 56.7 (4H), 45.7 (2H), 23.0 (4H), −3.9 (6H), −4.1
(three broad overlapping peaks 17H), −34.5 (two single peaks 1H
each), −56.7 (1H) ppm; in the diamagnetic region peaks assign-
able to free IPr (δ 1.24, 2.90, 6.58 ppm) could also be identified.
Magnetic susceptibility, CαDα: rt: 3.8 μαB (1.9 μαB per Co).

Complex 7

In a Young’s ampoule, a suspension of 2Cl (0.20 g, 0.31 mmol)
and KC8 (0.21 g, 1.55 mmol, 5 equiv.) in toluene (ca. 10 cm3)
was heated at 80 °C for 8 h. After cooling, the suspension was evaporated to dryness and the residue was dissolved in pentane (ca. 10 cm³), giving a yellow-green solution, which was concentrated under reduced pressure to ca. 5 cm³ and then evaporated slowly in a stream of nitrogen in a glove box to give yellow green crystals of 7. ¹H-NMR (C₆D₆): the following paramagnetic features of the spectrum are broad: δ, 23.90 (2H), 21.20 (2H), 2.9 (broad, toluene), −1.14 (24H two broad peaks), −4.10 (4H), −7.11 (6H, two broad overlapping peaks), −40.92 (2H) ppm; in addition there are signals in the diamagnetic region that are assignable to IPr (δ, 1.24, 2.90, 6.58) ppm. Satisfactory analytical data could not be obtained for this complex.

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Notes and references


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