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■ **Reductive Coupling** |*Hot Paper*|

Reductive Coupling of (Fluoro)pyridines by Linear 3d-Metal(I) Silylamides of Cr–Co: A Tale of C−C Bond Formation, C−F Bond Cleavage and a Pyridyl Radical Anion

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Abstract: Herein, we disclose the facile reduction of pyridine (and its derivatives) by linear 3d-metal(I) silylamides (M=Cr–Co). This reaction resulted in intermolecular C−C coupling to give dinuclear metal(II) complexes bearing a bridging 4,4′-di-hydrobipyridyl ligand. For iron, we demonstrated that the C−C coupling is reversible in solution, either directly or by reaction with substrates, via a presumed monomeric metal(II) complex bearing a pyridyl radical anion. In the course of this investigation, we also observed that the dinuclear metal(II) complex incorporating iron facilitated the isomerisation of 1,4-cyclohexadiene to 1,3-cyclohexadiene as well as equimolar amounts of benzene and cyclohexene. Further-more, we synthesised and structurally characterised a non-3d-metal-bound pyridyl radical anion. The reactions of the silylamides with perfluoropyridine led to C−F bond cleavage with the formation of metal(II) fluoride complexes of manganese, iron and cobalt along with the homocoupling or reductive degradation of the substrate. In the case of cobalt, the use of lesser fluorinated pyridines led to C−F bond cleavage but no homocoupling. Overall, in this paper we provide insights into the multifaceted behaviour of simple (fluoro)pyridines in the presence of moderately to highly reducing metal complexes.

Introduction

Polypyridines such as bipyridine or phenanthroline are a versatile class of donor ligands.[1,2] It has been shown that they can be reduced in the coordination sphere of a metal, often in a reversible fashion.[3] This also holds true for monopyridine-based ligands in which the pyridine is part of a larger conjugated system (e.g., mono- or diiminopyridines).[4–7] The redox non-innocent behaviour of such ligands has been exploited in numerous cases in (photo)redox chemistry as well as in bond and small-molecule activation.[2,5–8] As a further consequence of the reduction of polypyridines, especially by highly reducing actinide or divalent rare-earth metal complexes, the metal-bound radical anions formed can react by intra- or intermolecular C−C coupling.[9] In a few instances, the C−C bond forma-

tion was shown to be reversible, thereby revealing that the electron is formally stored not in the polypyridine as a radical anion, but within the formed bond,[10] a phenomenon also observed in other nitrogen-based ligands.[11]

The reduction of the parent pyridine is considerably less common due to its higher cathodic potential of −2.7 V (vs. SCE,[12] approx. −3.1 V vs. Fc/Fc+). A few examples of metal-mediated 1e− reduction and coupling of pyridine are known and rely on the highly reducing capabilities of low-valent rare-earth metal complexes of scandium, thulium and samarium as well as thorium.[13] Examples of reductive coupling of pyridine by d-block transition-metal complexes are restricted to titanium(II) synthons[14] and the iron(I) nacnac system (nacnac= N,N′−2,6-diisopropylphenyl-β-diketiminate) of Holland and co-workers (Figure 1).[15,16] They also observed the reversibility of C−C bond formation in solution, with the pyridine ligand of the monomeric iron–pyridine species bearing partial radical anion character.

Recently, we reported on the linear 3d-metal(I) hexamethyl-disilazanides [K(18c6)][M^I(NR$_2$)$_2$] (M=Cr–Co; 18c6=18-crown-6; R=SiMe$_3$).[17,18] Despite the easily accessible metal ion, these silylamide complexes are surprisingly inert towards Lewis bases such as phosphines and N-heterocyclic carbenes (NHCs).[19] This contrasts with the usual Lewis acidic behaviour of other low-coordinate metal(I) compounds,[20,21] and became obvious in the reaction of [K(18c6)][Fe^I(NR$_2$)$_2$] with an ethylene-bridged diphosphine, in which coordination to the ethylene backbone and not the phosphines was preferred.[19] Given this background, we started to explore the behaviour of metal(I) silyl-

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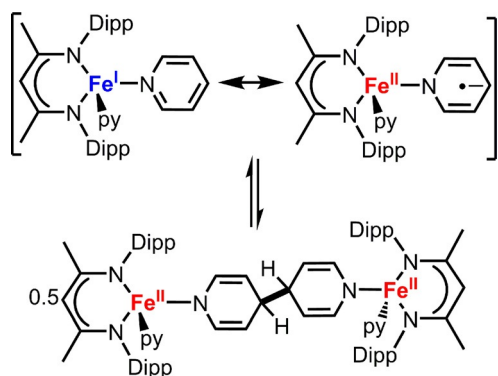
Figure 1. Reversible C—C bond formation in an iron–pyridine complex (py = pyridine).[16]

Scheme 1. Reactions of metal(I) silylamides with pyridines (R = SiMe₃, py = pyridine, phpy = 2-phenylpyridine, lut = 2,6-dimethylpyridine, 18c6 = 18-crown-6, n.d. = yield not determined).

amides towards substrates that, to a certain extent, can be reduced (e.g., 2,2'-bipyridine).[22,23]

Here, we report on the reaction of 3d-metal(I) complexes (M=Cr–Co) with pyridine and selected derivatives. This led in the cases of chromium, manganese and iron to the reductive C—C coupling of the substrate and formation of binuclear metal(II) complexes, which were isolated and characterised. For iron it was demonstrated that the C—C coupling was reversible. Furthermore, a pyridyl radical anion free of 3d-metal coordination was identified by X-ray diffraction analysis as well as by UV/Vis spectroscopy. Employing perfluoropyridine as the substrate led to instantaneous C—F bond cleavage and the formation of rare trigonal metal(II) fluorides of manganese, iron and cobalt as well as the homocoupling or reductive degradation of the substrate. In the case of cobalt, the use of lesser fluorinated pyridines led to C—F bond cleavage but no homocoupling.

Results and Discussion

The respective metal(I) silylamides [K(18c6)][Mᴵ(NR₂)₂] (M=Cr–Co), either isolated (Fe and Co) or synthesised in situ (Cr and Mn),[17,18] were treated with one equivalent of pyridine (py) in Et₂O. This resulted in an immediate colour change for iron (green-brown→light yellow), manganese (dark violet→light yellow) and chromium (red-orange→bright orange), whereas for cobalt no conversion was observed. The reaction mixtures were filtered, layered with pentane and stored at −35 °C. After a few days, crystalline samples of complexes **1** (Crpy) and **3a** (Fepy; Scheme 1) were obtained in moderate yields. Compound **2a** (Mnpy) could not be isolated in an analytically pure form due to the parallel formation of the manganese(II) trisamide [Mnᴵᴵ(NR₂)₃]⁻, the decomposition product of the labile [Mnᴵ(NR₂)₂]⁻ starting compound.[17] Solid-state analysis of compounds **1**, **2a** and **3a** (Figure 2) revealed the formation of dinuclear dianions. In these structures, the two metal ions are bridged by 4,4'-dihydrobipyridyl, which stems from the formal dimerisation of the elusive metal–pyridine adduct at the 4-position of the pyridine. The bond metrics of the bipyridyl ligand revealed a loss of aromaticity with now localised single and double bonds (Table 1). For **2a** and **3a**, the coordination
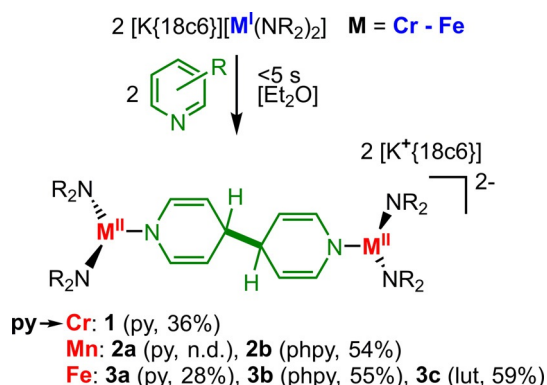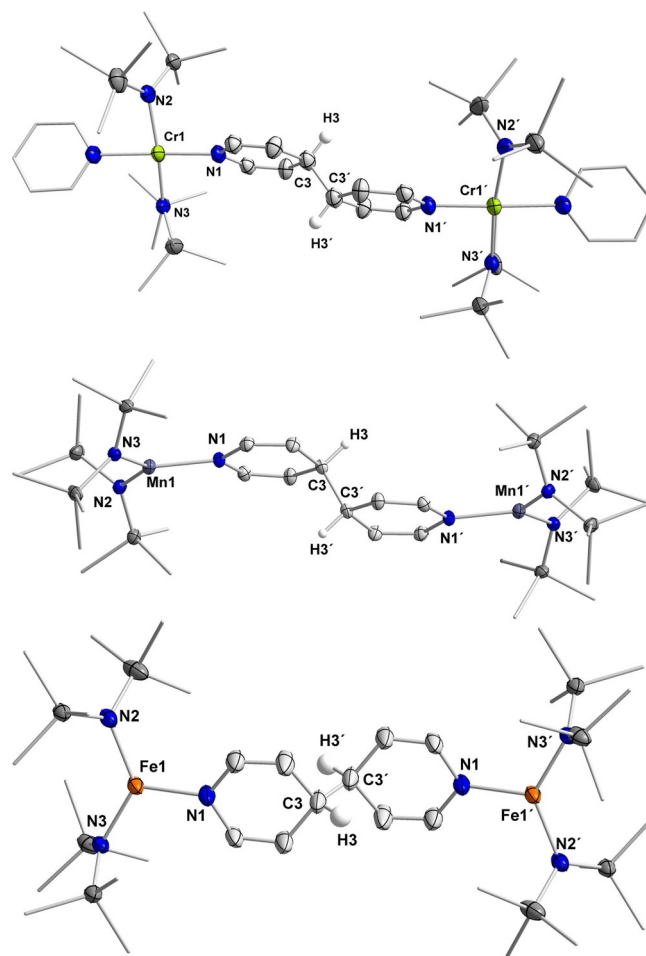

Figure 2. Molecular structures of compounds **1** (top), **2a** (middle) and **3a** (bottom). Hydrogen atoms have been omitted for clarity and ellipsoids are shown at the 50% probability level. The [K(18c6)]⁺ cations are not shown.

sphere of each metal(II) ion is completed by the two silylamide ligands, giving each metal a trigonal coordination geometry. In the case of the chromium compound **1**, an additional, unreduced pyridine ligand coordinates to the metal ion, leading to a square-planar coordination environment (τ'_4 parameter of 0.26). This supports the notion of divalent compounds, as chro-

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Table 1. Selected structural metrics for the complex anions of compounds **1**–**3c**.

Compd	1 (Crpy)	2a (Mnpy)	2b (Mnphpy)	3a (Fepy)	3b (Fephpy)	3c (Felut)
Bond length [Å]						
M—N1(py)	2.057(3)	2.053(1)	2.053(7)	1.990(3)	2.008(3)	1.966(4)
M—N2(hmds)	2.090(3)	2.045(1)	2.073(7)	1.959(3)	1.969(3)	1.972(4)
M—N3(hmds)	2.095(2)	2.047(1)	2.041(6)	1.960(3)	1.959(3)	1.971(4)
N1—C1	1.372(3)	1.385(2)	1.399(1)	1.404(5)	1.393(5)	1.407(5)
N1—C5	1.376(3)	1.394(2)	1.397(1)	1.371(5)	1.394(5)	1.406(6)
C1—C2	1.348(3)	1.345(2)	1.331(1)	1.337(6)	1.331(6)	1.337(6)
C3—C3′	1.558(5)	1.568(3)	1.550(2)	1.548(1)	1.569(8)	1.588(6)
C4—C5	1.339(3)	1.339(2)	1.346(1)	1.345(6)	1.360(6)	1.338(6)
Bond angles [°]						
N1-M-N2	175.23(8)	114.70(5)	110.60(3)	116.90(1)	110.86(1)	116.8(2)
N2-M-N3	171.58(7)	125.31(5)	124.90(3)	127.41(1)	121.08(1)	128.1(2)

mium(II) compounds prefer such a complex geometry.[24] The additional pyridine coordination and resulting ligand field stabilisation effects of a d^4 configuration in a square-planar coordination might explain why chromium facilitates pyridine reduction whereas cobalt does not, despite having similar reduction potentials ($E_{ox} = -1.47$ V for Co and -1.30 V for Cr vs. Fc/Fc$^+$).[17]

The M—N$_{hmds}$ bond lengths decrease from chromium (2.09 Å) to iron (1.96 Å), which reflects the general trend of ion radius contraction when going along the 3d-metal series. The same trend is observed for the M—N$_{py}$ bond lengths (2.06 Å for Cr to 1.99 Å for Fe), which are in the general range found for metal-bound amides. Next, we sought to gain insights into the factors that govern the C—C bond coupling as well as the presumed intermediate metal-bound pyridyl radical anions (such as [M^{II}(NR$_2$)$_2$(py$^{·-}$)]$^-$. If the 4-position of pyridine is blocked (e.g., by tBu or NMe$_2$), no dimerisation or even simple coordination was evidenced by ^{1}H NMR spectroscopy and recrystallisation of the starting compounds. This is in contrast with the observations made by Holland and co-workers[15,16] (Figure 1). To rule out simple steric effects, K{18c6}[Fe(NR$_2$)$_2$] was treated

with 3,5-lutidine (lut), which also gave a dimeric 4,4′-dihydrobipyridyl complex (**3c**; Figure 3). Next, we employed 2-phenylpyridine (phpy), in an attempt to stabilise the radical character over a larger aromatic system and thus favour the formation of a monomeric complex bearing a pyridyl radical anion. This led again to dimeric systems for manganese (**2b**) and iron (**3b**). The bond lengths and bond angles of these complexes do not differ significantly from the pyridine complexes described above. These findings indicate that simple substrate coordination and reduction are unfavoured and have to be followed by substrate dimerisation to give isolable pyridine-containing compounds. Intriguingly, during the synthesis of **2b**, a-pale-yellow compound, a bright-blue solution was obtained, which hinted at the presence of a radical anion. Upon careful crystallisation, small amounts of brownish violet crystals were observed as a by-product of **2b**. X-ray diffraction analysis revealed the formation of compound **4** (Figure 3) in which a 2-phenylpyridine unit is sandwiched between two [K(18c6)]$^+$ cations with a [M^{II}(NR$_2$)$_3$]$^-$ counter anion. The potassium cations are pulled out of the plane defined by the oxygen atoms of the crown ethers and are oriented towards the 2-phenylpyri-
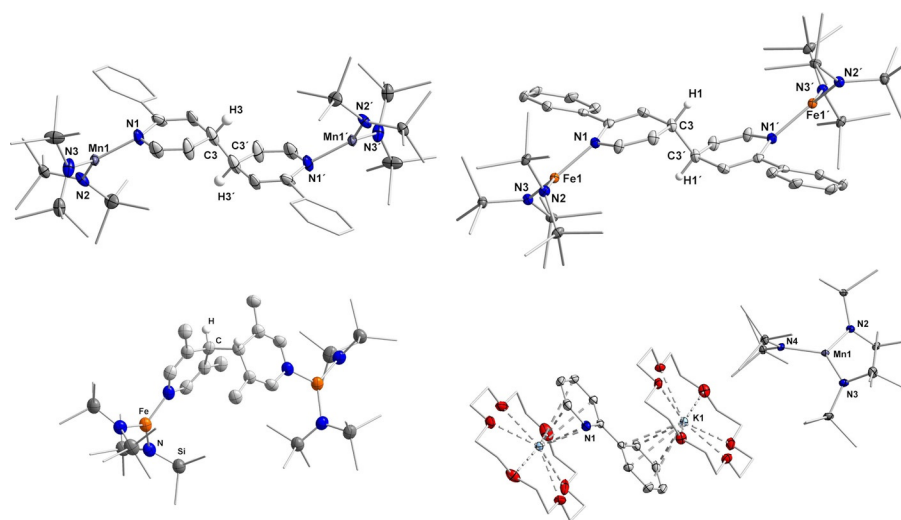

Figure 3. Molecular structures of compounds **2b** (top left), **3b** (top right), **3c** (bottom left), and **4** (bottom right). Hydrogen atoms have been omitted for clarity and ellipsoids are shown at the 50% probability level. The [K(18c6)]$^+$ cations are shown for only compound **4**.

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dine. The shortest K$^+$···C distance (ca. 3.05 Å) is slightly shorter than those of reported interactions between [K(18c8)]$^+$ cations and reduced aromatic hydrocarbons.[25] Together with the almost coplanar orientation of the two aromatic rings (2.7(4)°), which contrasts with the slightly twisted orientation of 2-phenylpyridine units (10–20°),[26] this suggests the presence of a pyridyl radical anion and delocalisation of the radical anion character. This becomes more evident when looking at the C—C bond lengths within and between the two aromatic rings of the 2-phenylpyridine unit (Scheme 2). The inter-ring C—C bond length is 1.429(4) Å, which is markedly shorter than comparable bonds of 2-phenylpyridine units, which range between 1.47 and 1.50 Å. Furthermore, the C—C bonds within the aromatic rings vary between 1.373(4) and 1.434(4) Å, which is consistent with those of related potassium bipyridyl radical anion complexes.[27,28] Reports on structurally characterised pyridyl radical anions are rare, due to their clear tendency to dimerise, as already shown above and in the seminal report of Anderson in 1870, followed by others.[29]
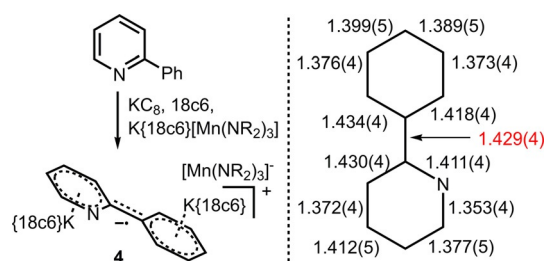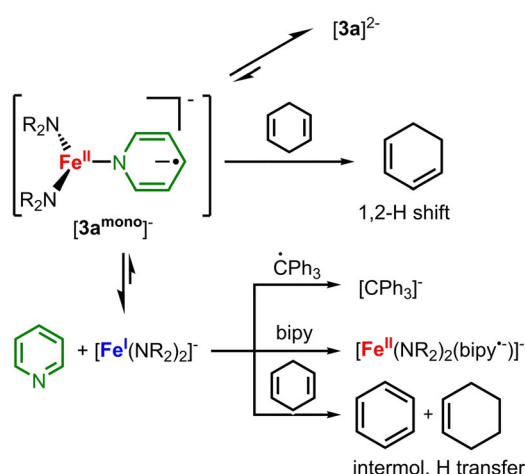

Scheme 2. Left: reduction of 2-phenylpyridine in the presence of [K(18c6)][Mn(NR$_2$)$_3$]. Right: bond metrics for the phpy radical anion.

Only in recent years could pyridine-based radical anions be isolated by using boron-based substituents.[30] The presence of the [Mn(NR$_2$)$_3$]$^-$ counter ion indicates that the formation of **4** is probably a result of the parallel decomposition of the manganese(I) starting complex [Mn(NR$_2$)$_2$]$^-$.[17] Indeed, the independent reduction of phpy with KC$_8$ in the presence of 18c6 and the manganese(II) trisamide [K(18c6)][Mn(NR$_2$)$_3$] gave a dark-blue solution from which larger amounts of **4** were obtained (Scheme 2). The product was extremely sensitive and decomposed quickly upon attempted isolation, and has so far eluded further characterisation.

Interestingly, the formation of the pyridyl radical anion [2-phpy]$^{•-}$ was not observed in the absence of the manganese trisamide and the provided additional [K(18c6)]$^+$ cation. This indicates that the sandwich-like structure seen in **4** helps to stabilise the radical anion [2-phpy]$^{•-}$. In situ UV/Vis spectroscopic analysis of mixtures containing **4** revealed two broad, overlapping absorption maxima at 560 and 590 nm. Their positions are similar to those of the related 2,2′-bipyridyl radical anion (540 and 576 nm) and can be assigned to intramolecular π→π* transitions.[22,27] Having acquired the UV/Vis spectroscopic signature of the 2-phenylpyridyl radical anion, the respective dimeric pyridine complexes were re-examined accordingly at room and low temperatures (−80 °C), in an attempt to

detect the possible presence of their monomeric forms, which would likely consist of a metal(II)-bound radical anion. However, the corresponding absorption bands were not observed.
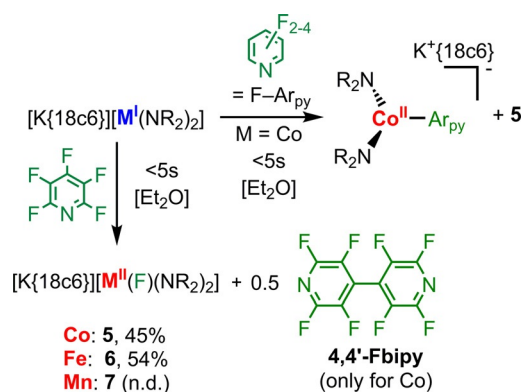
To gain additional insights into the solution behaviour of the pyridine complexes, we studied their ^{1}H NMR spectroscopic features. The ^{1}H NMR spectra of the chromium (**1** (Crpy) and manganese (**2 a** (Mnpy) and **2 b** (Mnphpy)) complexes in [D$_8$]THF showed very broad and uninformative signals due to the highly paramagnetic character of the compounds. The iron complex **3 a** showed a proton signal attributed to the SiMe$_3$ units at −4.50 ppm, which corresponds well with the signals of other anionic trigonal iron(II) silylamide complexes bearing an anionic ligand.[31] Complex **3 a** (Fepy) also showed a further three signals at 12.5, 15.7 and 198.6 ppm arising from the pyridine ligand. Thus, the signals belonging to the pyridyl unit could only be observed through the in situ formation of **3 a** using five equivalents of pyridine, which indicates an equilibrium of **3 a** with the starting iron(I) complex. Such an equilibrium became obvious in the cases of the isolated compounds **3 b** (Fephpy) and **3 c** (Felut), as their ^{1}H NMR spectra showed mostly the initial iron(I) complex [Fe(NR$_2$)$_2$]$^-$, the corresponding free pyridine and minor signals tentatively attributed to the provided **3 b** and **3 c**, respectively. The addition of 2-phenylpyridine and 3,5-lutidine, respectively, led to a slight shift in the equilibrium in solution towards **3 b** or **3 c**, but also effected the decomposition to [Fe(NR$_2$)$_3$]$^-$. Given these observations, we explored whether the reductive C—C bond formation is also reversible in the case of **3 a**, and whether an intermediary monomeric pyridyl radical anion species, such as [**3 a**^{mono}]$^{•-}$, might be present (Scheme 3). The treatment of **3 a** with 2,2′-bipyridine (bipy) led to the partial formation of the known bipyridyl complex [Fe(NR$_2$)$_2$(bipy$^{•-}$)]$^-$, showing that the dimerisation of pyridine is indeed reversible, however, with concomitant decomposition (see Figure S30 in the Supporting Information).[22] Next, we used the trityl radical $^•$CPh$_3$ (Gomberg dimer) to trap the elusive pyridyl radical anion. This resulted in an instantaneous colour change of the solution to blood red, which eventually was attributed to the formation of small amounts of the triphenylmethanide anion. The anion was therefore a result of the reaction of the trityl radical anion with the iron(I) starting complex [K(18c6)][Fe(NR$_2$)$_2$], as corroborated by an independent reaction (see Figures S43–S45). Intriguingly, the treatment of **3 a** with 1,4-cyclohexadiene (1,4-CHD), to prove the presence of the pyridyl radical anion by hydrogen-atom abstraction, gave rise to 1,3-cyclohexadiene (1,3-CHD) as well as benzene and equimolar amounts of cyclohexene, as evidenced by ^{1}H NMR spectroscopy (see Figures S31 and S32). The impact of pyridine on free [Fe(NR$_2$)$_2$]$^-$ was also investigated and indeed showed the complete transfer hydrogenation of 1,4-CHD to benzene and cyclohexene over the course of 12 h (see Figures S33S–S35). No 1,3-CHD was observed in this case. The mechanisms of the two transformations, double-bond migration and intermolecular hydrogen transfer are not clear at this point. Metal hydrides are usually proposed to form in these bond isomerisation reactions,[32] however, no evidence for this has yet been obtained in this system. An alternative mechanistic possibility is bond isomerisation by reversible hydrogen atom

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Scheme 3. Chemical investigation of the reversibility of the formation of [**3a**]$^{2-}$ via the proposed monomeric form [**3a^{mono}**]$^-$ to the starting iron(I) complex [Fe^I{N(SiMe$_3$)$_2$}$_2$]$^-$ and pyridine. The [K(18c6)]$^+$ cations are not shown.

Scheme 4. Synthesis of the three-coordinate fluorido complexes **5, 6** and **7** from [M{N(SiMe$_3$)$_2$}$_2$]$^-$ and perfluoropyridine, and reaction of [Co{N(SiMe$_3$)$_2$}$_2$]$^-$ with partially fluorinated pyridines.
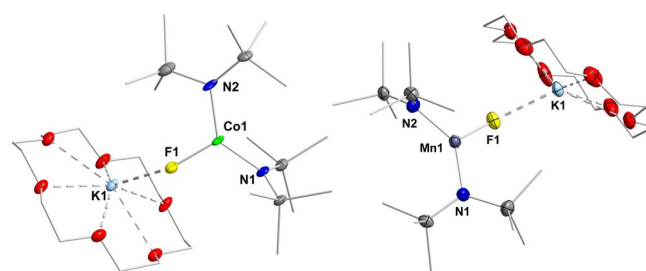

Figure 4. Molecular structures of compounds **5** (left) and **7** (right). Hydrogen atoms have been omitted for clarity and ellipsoids are shown at the 50% probability level. Only one of the three molecules in the asymmetric units of **5** and **7** is shown. Selected bond lengths [Å] and distances [°] for **5**: Co–F1 1.885(4), Co–N1 1.938(4), Co–N2 1.935(4), K–F1 2.588(4), N1-Co-N2 133.2(2), N1-Co-F1 111.8(2), N2-Co-F1 114.3(2); for **7**: Mn–F1 1.946(3), Mn–N1 2.048(4), Mn–N2 2.048(4), K–F1 2.609(3), N1-Mn-N2 129.8(2), N1-Mn-F1 113.6(2), N2-Mn-F1 116.6(2).

abstraction, which was proposed for the transformation of 1,4-CHD to 1,3-CHD in the presence of an iron nitride.[33] Such behaviour is plausible for the pyridine complex **3a**, or to be more precise, for its presumed monomeric radical anion form [**3a^{mono}**]$^-$, and might thus hint at its existence. All these results combined suggest that the coordination and dimerisation of pyridine in **3a** are reversible in solution, with the equilibrium overwhelmingly on the side of **3a**. In terms of reactivity, both the iron(I) starting compound [Fe^I(NR$_2$)$_2$]$^-$ as well as an elusive monomeric pyridyl radical anion complex are responsible for the observed reactivity of **3a**.

Having established the reductive coupling of pyridines by using the metal(I) silylamides of chromium, manganese and iron, we turned back to cobalt. As reported above, the cobalt(I) complex [K(18c6)][Co(NR$_2$)$_2$] did not interact with the examined pyridines, which we attributed to its relatively low reduction potential. Thus, the significantly more electron-deficient perfluoropyridine (C$_6$F$_5$N, PFP) was employed to facilitate pyridine reduction (Scheme 4). Indeed, its reaction with [K(18c6)][Co(NR$_2$)$_2$] led to an instantaneous change of colour from pale to intense green. In situ ^{1}H NMR analysis showed the formation of only one paramagnetic species ($\delta_{SiMe3} = -15.20$ ppm), which was subsequently identified as a rare low-coordinate cobalt(II) fluoride ([K(18c6)][Co(F)(NR$_2$)$_2$] (**5**), Figure 4 right).[21] The fate of the employed PFP was revealed by in situ ^{19}F NMR spectroscopy through the detection of considerable amounts of 4,4′-octafluorobipyridine (4,4′-Fbipy).[34] 4,4′-Fbipy is an uncommon perfluoro derivative of 4,4′-bipyridine and its synthesis can be achieved by copper-mediated cross coupling using zinc organyls under forcing conditions,[35] the reaction of PFB with hexaethyltriamidophosphite[34] or the unselective electrochemical reduction of PFB.[36] Given our previous observation of the C–F bond cleavage of fluorobenzene by the iron(I) compound [K(18c6)][Fe(NR$_2$)$_2$] to yield a fluoroiron(II) and an aryliron(II) complex,[31] we speculated on a related mechanism in the present case. However, the reaction of PFP with two equivalents of

[K(18c6)][Co(NR$_2$)$_2$] did not lead to an NMR signal belonging to an arylcobalt(II) species [Co(R)(NR$_2$)$_2$] although full consumption of the employed cobalt(I) compound still occurred. In this case, 4,4′-Fbipy was absent, which indicates that the 4,4′-Fbipy formed might have reacted with the excess of the cobalt(I) complex. Next, pyridines with a lower degree of fluorination were briefly examined, namely 2-fluoropyridine, 2,4-difluoropyridine, 2,4,6-trifluoropyridine, 2,3,6-trifluoropyridine and 2,3,5,6-tetrafluoropyridine. Whereas no conversion was observed with 2-fluoropyridine, the reactions of the other pyridines with [K(18c6)][Co(NR$_2$)$_2$] led to the formation of cobalt(II) fluoride **5** (in yields of up to 45%) and a second, presumably organocobalt(II) species ([Co(R)(NR$_2$)$_2$]) with a C-bonded fluoropyridyl anion, as revealed by ^{1}H NMR analysis. The latter has so far not been isolated or structurally characterised, but the ^{1}H NMR signature of the respective SiMe$_3$ groups are similar to other three-coordinate (organo)cobalt(II) complexes with the same ligand set (R = 9,10-dihydroanthracenyl, xanthenyl or –NH*t*Bu).[37] No defluorinative C–C homocoupling of the substrate, which would have led to a purely organic product, was observed in any case.

This behaviour is in agreement with the above-mentioned study of the reactivity of [K(18c6)][Fe(NR$_2$)$_2$] towards organo-

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fluorides, also giving 1:1 mixtures of the iron(II) fluoride and an organoiron(II) complex.[31] Given the successful isolation of the cobalt fluoride complex **5** using PFP as the fluorinating agent, analogous reactions of PFP with [K(18c6)][Fe(NR$_2$)$_2$] and [K(18c6)][Mn(NR$_2$)$_2$] were also performed. For the former, the reaction gave a dark solution from which the known iron fluoride [K(18c6)][Fe(F)(NR$_2$)$_2$] (**6**)[31] was isolated in pure form. In this case, only traces of 4,4′-Fbipy as well as small amounts of FSiMe$_3$ were observed, which is likely attributable to the total degradation of perfluoropyridine by subsequent defluorination reactions, which also explains the blackish reaction mixture. Similar observations were made in the reaction of the manganese(I) silylamide [Mn{N(SiMe$_3$)$_2$}$_2$]$^-$, which yielded the first example of the low-coordinate manganese(II) fluoride [K(18c6)][Mn(F)(NR$_2$)$_2$] (**7**). In the solid state, the complex anions of compounds **5** and **7** exhibit a three-coordinate metal ion with a distorted trigonal-planar geometry (Figure 4). For the three complexes **5**–**7**, the M–N$_{hmds}$ bond lengths shorten from manganese (2.05 Å) to cobalt (1.94 Å). The same trend is observed for the M–F bonds (1.95 Å for Mn to 1.89 Å for Co). In the three structures **5**–**7**, the fluorine atom is directed towards the potassium atom of the cation.

Conclusion

We have presented here the facile reductive coupling of pyridines using the linear metal(I) silylamides [M{N(SiMe$_3$)$_2$}$_2$]$^-$ of chromium, manganese and iron, which led to dinuclear metal(II) complexes bridged by a 4,4′-dihydrobipyridyl ligand. This is especially remarkable in the case of chromium, as its reduction potential is about 2 V lower than that needed for the electrochemical reduction of pyridine. We have also provided structural evidence for the formation of a non-3d-metal-ligated pyridyl radical anion sandwiched between two [K(18c6)] units. For the dimeric 4,4′-dihydrobipyridyl iron complexes, we have shown that the C–C bond formation is reversible, and also demonstrated the iron(I)-mediated double-bond isomerisation of 1,4-cyclohexadiene by either by a proposed elusive monomeric iron pyridyl radical anion [Fe(py$^{•-}$)(NR$_2$)$_2$]$^-$ or the starting iron(I) complex [Fe(NR$_2$)$_2$]$^-$. With perfluoropyridine as substrate, cleavage of the *para*-C–F bond with the formation of rare metal(II) fluoride complexes was observed together with the C–C-coupling product perfluoro-4,4′-bipyridine or its subsequent degradation. The reactions of lesser fluorinated pyridines with the cobalt(I) silylamide [Co{N(SiMe$_3$)$_2$}$_2$]$^-$ led to a mixture of the metal(II) fluoride and the organometal(II) complex. Overall, we have shown the multifaceted behaviour of simple (fluoro)pyridines in the presence of reducing metal(I) complexes. Studies are continuing in our laboratory concerning the isolation and characterisation of pyridine and related radical anions, as well as the iron(I)-mediated bond isomerisation processes observed herein.

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Conflict of interest

The authors declare no conflict of interest.

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