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## Metal atom chemistry as a direct pathway to access homoleptic mono- and dinuclear isonitrile compounds of the iron triad Fe, Co, and Ni†

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The co-condensation of atomic metal vapors of iron, nickel and cobalt with toluene, followed by a direct reaction with isonitriles, between  $-30\text{ }^{\circ}\text{C}$  and  $-78\text{ }^{\circ}\text{C}$ , yields stable homoleptic metal isonitrile complexes. Complexes of Fe, Ni, and Co with DippNC (Dipp = 2,6- $(\text{CH}(\text{CH}_3)_2)_2\text{C}_6\text{H}_3$ ) and 4-fluorophenylisonitrile (4-FPI) are obtained in high yields using this method. This method offers an efficient and straightforward approach compared to previously reported syntheses.

### Introduction

Isonitriles (CNRs), compared to carbon monoxide (CO), exhibit stronger  $\sigma$ -donating characteristics and weaker  $\pi$ -acceptor properties, with both effects contributing to bonding in (CNR)–metal complexes, as evidenced by structural and spectroscopic data.<sup>1,2</sup> The dipole moment of isonitriles is significantly higher than that of carbon monoxide ( $\mu_{\text{CNP}} = 3.4\text{ D}$ , with the negative end on the carbon atom and  $\mu_{\text{CO}} = 0.1\text{ D}$ ). Additionally, CNRs can substitute CO in transition metal complexes, as demonstrated by the substitution reaction of Ni(CO)<sub>4</sub> with four equivalents of phenyl isocyanide (PhNC), yielding Ni(PhNC)<sub>4</sub> and releasing four equivalents of CO.<sup>2</sup> Although CNRs can function as bridging ligands, this behavior is, however, relatively underdeveloped compared to the well-documented bridging characteristics of CO. Furthermore, metal isonitrile complexes form more readily in positive metal oxidation states +I and +II. Certain cationic complexes, such as  $[\text{V}(\text{CN}^t\text{Bu})_6]_2$  and  $[\text{M}(\text{CN-Xyl})_7]^+$  (M = Nb, Ta), have no CO

analogs. In contrast, lower or negative oxidation states (0,  $-I$ ) are less common.<sup>2</sup>

Moreover, isonitriles can be electronically and sterically modified by changing their organic substituents, making them interesting ligands for metal catalysis.<sup>3</sup> Isonitriles tend to form stable transition-state metal complexes and show unique properties, making them valuable candidates even for use in catalysis, materials science, and pharmaceuticals.<sup>1,4</sup> Due to their well-known stability and versatile reactivity, they are useful reagents in chemical reactions, like hydrogenations, polymerizations, and cross-coupling reactions.<sup>1</sup> In transition metal chemistry, homoleptic zerovalent metal isonitrile complexes act as Lewis bases. Therefore, they can interact with Lewis acidic ligands to cooperatively modulate the electronic structure on the metal center, facilitating unique reactions. As a result, they enhance reaction rates and selectivity in their reactions. In materials science, they contribute to the development of advanced materials like photosensitizers that function as potent photoreducing agents.<sup>5</sup> Additionally, their potential pharmaceutical applications are being explored, as they may lead to the development of new drugs and therapeutic agents.<sup>4</sup> The radioactive octahedral isonitrile complex  $[\text{}^{99\text{m}}\text{Tc}(\text{CN-CH}_2\text{CMe}_2\text{OMe})_6]^{2+}$  has already been utilized in cardiac imaging for radio diagnostic purposes since 1991.<sup>2</sup>

Conventional synthesis of these complexes involves the reaction of metal salts with the reducing agents of sodium/mercury amalgam (Na/Hg) or sodium naphthalide ( $\text{C}_{10}\text{H}_8\text{Na}$ ) in the presence of isonitriles.<sup>6,7</sup> However, their synthesis procedure can be challenging, time-consuming, and sometimes inefficient, particularly when complexes should be synthesized with sensitive ligands. Additionally, these reducing agents are toxic due to Hg and may produce larger amounts of naphthalene, which poses significant environmental concerns. So, various safety precautions are necessary. Separation of unwanted by-products from the desired complexes can also be challenging.<sup>8</sup> An alternative is to employ  $\text{KC}_8$  and sodium silicide as reducing agents. These solid reducing agents offer considerable advantages over conventional liquid reagents. The

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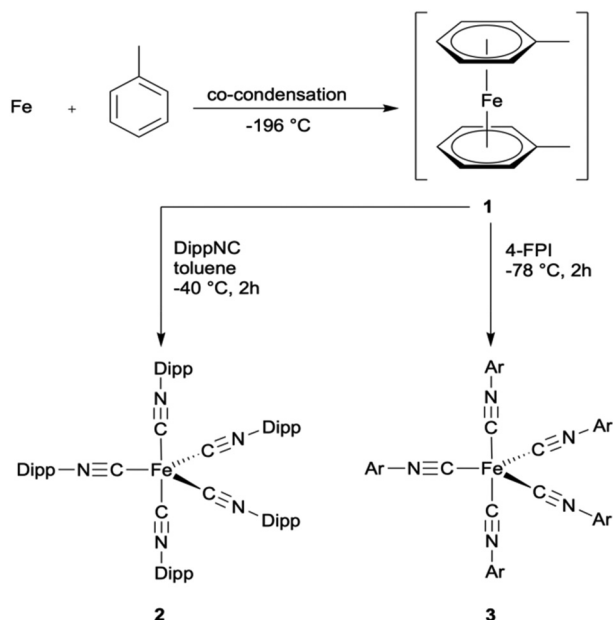
solid residues can be removed by filtration after the reaction, simplifying the workup process and minimizing exposure to hazardous substances.<sup>9</sup> It is feasible to synthesize homoleptic iron and nickel isonitrile complexes from nickel tetracarbonyl and iron pentacarbonyl. However, these methods present significant challenges, too. The use of both metal carbonyls is particularly hazardous due to their extreme toxicity. When employing iron pentacarbonyl, it is even difficult to achieve complete substitution of all CO ligands and obtain the homoleptic complexes in reasonable yields employing this substitutional process.<sup>10,11</sup> Alternatively, homoleptic nickel isonitrile complexes can be synthesized using [bis(1,5-cyclooctadiene)nickel(0)] and the corresponding isonitrile, offering a safe and controlled method for their preparation.<sup>12,13</sup>

In this context, we present a direct synthesis approach employing bare metal atoms generated under evaporation as an alternative route. It allows Fe, Ni, and Co atoms to react directly with isonitriles without requiring a reducing reagent. Importantly, the process is even shorter, more efficient, and can be conducted under milder conditions, without using hazardous chemicals and producing any by-products. Accordingly, it has the potential to be a substitute for conventional synthetic approaches to metal isonitrile compounds. We comprehensively describe the synthesis process, including the precise conditions and parameters optimized for maximum yield and purity. The characterization studies of the obtained products by NMR spectroscopy, IR spectroscopy, elemental analysis, and mass spectrometry (MS), as well as a single crystal structural analysis, confirm the structures and compositions of the complexes. A comparison with other methods is reported.

## Results and discussion

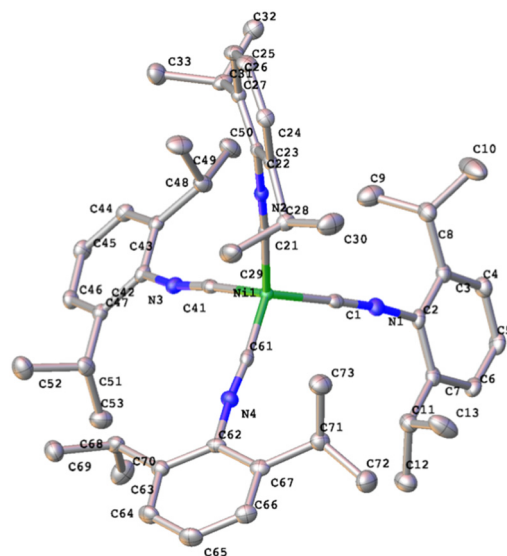
The reaction between 2,6-diisopropylphenylisonitrile and bis(toluene)iron(0) in toluene at  $-30\text{ }^{\circ}\text{C}$  forms the red crystalline complex  $\text{Fe}(\text{DippNC})_5$  in high yield. The reaction of bis(toluene)nickel(0) and bis(toluene)cobalt(0) with 2,6-diisopropylphenylisonitrile in toluene, respectively, results in the yellow crystalline complex  $\text{Ni}(\text{DippNC})_4$  and the brown dinuclear compound  $[\text{Co}(\text{DippNC})_4]_2$ , respectively. Red  $\text{Fe}(\text{4-FPI})_5$  and bright yellow  $\text{Ni}(\text{4-FPI})_4$  are the products of the reaction between the iron and nickel toluene sandwich compounds with 4-fluorophenylisonitrile, respectively. The latter are characterized by elemental analyses, mass spectroscopy, infrared spectroscopy, and  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. While the diisopropylphenylisonitrile compounds are temperature and air-stable, the two 4-fluorophenylisonitrile complexes are sensitive to air and water. As reaction intermediates in our synthetic approach, bis(toluene)metal ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) sandwich compounds are obtained. Due to the internal volume of the metal vapor reactor (6 L), a minimum of about 50 mL of solvent is technically required to effectively trap and disperse vaporized metal atoms. The available isonitrile ligands were insufficient to serve this role, making direct co-condensation

impractical. Therefore, well-defined bis(toluene)metal complexes were thus used as intermediates to trap the metal atoms for controlled ligand substitution under homogeneous conditions. Bis(arene)Fe, Co, and Ni complexes are electron non-precise ( $\text{Fe} = 20, \text{Co} = 21, \text{Ni} = 22$  valence electrons) and tend to decompose instantaneously at temperatures above  $-50\text{ }^{\circ}\text{C}$ , even in an excess of stabilizing toluene solvent.<sup>14,15</sup> The preparation of these reactive solutions requires precise control over experimental conditions to ensure the formation of stable solutions at these low temperatures. Chemically labile  $[(\eta^6\text{-toluene})\text{Fe}(\eta^4\text{-toluene})]$  (**1**) is electron precise ( $\text{Fe} = 18$  VE) and is presumably obtained from the direct co-condensation product of iron and toluene. However, it still remains unstable at temperatures well above  $-50\text{ }^{\circ}\text{C}$ .<sup>15</sup> On the other hand, the characteristics of these solutions can be used to synthesize hitherto unknown compounds. Typically, elemental iron is vaporized under vacuum ( $<10^{-3}$  torr) using resistive heating of a bulk iron sample, generating single iron atoms in the gas phase. The metal atoms are then captured into a frozen toluene layer at  $-196\text{ }^{\circ}\text{C}$ . As the frozen matrix warms up to  $-78\text{ }^{\circ}\text{C}$  and later to  $-50\text{ }^{\circ}\text{C}$ , a reaction between the metal atoms and toluene takes place, leading to the formation of reactive **1**. The  $\text{Fe}(0)$  center therein is stabilized by  $\pi$ -interactions with the toluene, making the compound soluble in organic solvents. The same procedure allows the synthesis of cobalt and nickel arene sandwich compounds serving as reactive Ni and Co metal precursors<sup>14</sup> for further reactions with isonitriles. The iron toluene sandwich compound undergoes autocatalytic decomposition slightly above  $-50\text{ }^{\circ}\text{C}$ , making a meticulous preparation procedure mandatory. Nevertheless, synthetic isolation techniques at that low temperature enable the storage and handling of these arene solutions, especially of **1**, without significant decomposition by standard Schlenk techniques below  $-50\text{ }^{\circ}\text{C}$ . Precursor **1** reacts with diisopropylphenylisocyanide or 4-fluorophenylisocyanide at  $-40\text{ }^{\circ}\text{C}$ , resulting in a color change from dark green to red for both reaction mixtures after two hours. As Scheme 1 shows, the formation of compounds **2** and **3** involved the complete substitution of two toluene ligands in **1**. While the co-condensation of iron with toluene produces metastable bis(toluene)iron (**1**), the co-condensation of nickel or cobalt atoms in the presence of toluene results in a finely dispersed suspension of metal atoms in toluene upon warming up to  $-78\text{ }^{\circ}\text{C}$ . This cannot be handled as described for **1** at that low temperature without significant decomposition. Instead, the isonitriles are immediately added to these suspensions at  $-78\text{ }^{\circ}\text{C}$  and the mixtures are stirred slowly to reach room temperature. It is crucial to add the ligand immediately after thawing the toluene matrix, typically still below  $-100\text{ }^{\circ}\text{C}$ , to initiate a reaction with the still intact Fe, Co, Ni sandwich compounds. Avoiding the ligand addition and letting the melted solution react further at  $T > -78\text{ }^{\circ}\text{C}$  results in autocatalytic decomposition of the toluene-solvated metal atoms and agglomeration of Ni and Co metal atoms to form metal clusters and fine metal particles, which are, however, unreactive towards the isonitriles. The color of the reaction mixture, while

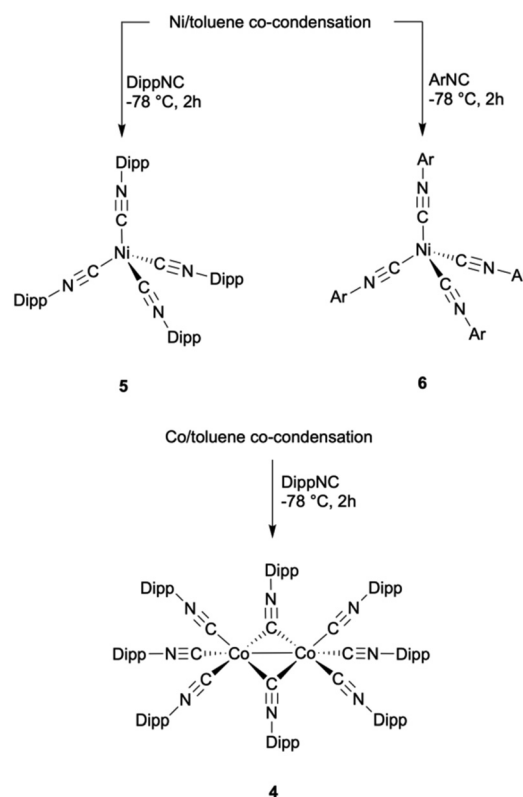


**Scheme 1** Synthesis of homoleptic  $\text{Fe}(\text{DippNC})_5$  (**2**) and  $\text{Fe}(\text{4-FPI})_5$  (**3**).

slowly warming from  $-78\text{ }^{\circ}\text{C}$  to ambient temperature, changes from black to yellow due to the formation of the nickel compounds, while the color of the obtained final reaction suspension of cobalt complexes is brown. After filtration and solvent removal at ambient temperature, the crude products were recrystallized from pentane. The reaction between cobalt atoms and 4-FPI was initially considered. However, we ultimately decided not to pursue this route due to specific safety and handling concerns associated with the ligand. During the synthesis of 4-FPI, we observed that the compound is extremely malodorous, with a strong, persistent odor that caused acute discomfort, including headache and nausea, even when handled in a well-ventilated fume hood. This experience led us to avoid repeating the synthesis. Infrared spectroscopy, nuclear magnetic resonance spectroscopy, and mass spectrometry univocally allowed the determination of the structures of the zero-valent metal isonitrile complexes **2–6** (Fig. 1 and Scheme 2). For two compounds, single crystal X-ray structure determination proves the connectivity of the metal atoms to be trigonal bipyramidal (**2**: Fe) and tetrahedral (**5**: Ni). However, crystals of **2** are heavily twinned despite numerous synthetic efforts and thus a further discussion of the data is omitted. It is noteworthy that only mononuclear  $\text{Fe}(0)$  isonitrile complexes were isolated in our case, whereas dinuclear species have also been reported in the literature.<sup>16</sup> The structure of **5** is discussed in detail later. The iron(0), cobalt(0), and nickel(0) isonitrile compounds exhibit well-resolved  $^1\text{H}$  NMR spectra, indicative of their diamagnetic behavior. Table 1 summarizes the NMR data and their corresponding assignments. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, the carbon atoms of the cyanide residues in the complexes are observed to shift to higher ppm values compared to the free ligands. For the cobalt complex **4**, two sets of the isonitrile ligands can be observed in the  $^1\text{H}$



**Fig. 1** Solid-state crystal structure of **5** (hydrogen atoms omitted for clarity). Selected bond lengths [ $\text{\AA}$ ] and angles [ $^{\circ}$ ]:  $\text{Ni1}-\text{C1}$  1.8530(17),  $\text{Ni1}-\text{C21}$  1.8536(17),  $\text{Ni1}-\text{C41}$  1.8374(19),  $\text{Ni1}-\text{C61}$  1.8362(19),  $\text{Ni2}-\text{C81}$  1.8278(18),  $\text{Ni2}-\text{C101}$  1.830(1),  $\text{Ni2}-\text{C121}$  1.8308(19),  $\text{Ni2}-\text{C141}$  1.8467(18),  $\text{N1}-\text{C1}$  1.172(2),  $\text{N2}-\text{C}(21)$  1.168(2),  $\text{N3}-\text{C41}$  1.177(2),  $\text{N4}-\text{C61}$  1.179(2).



**Scheme 2** Synthesis of cobalt and nickel complexes **4**, **5**, and **6**.

NMR spectrum. The signals for the protons of the bridged ligands are slightly shifted to a lower field compared to the proton signals of the terminal ones. A prominent IR peak

**Table 1** NMR chemical shifts for the free ligands and the homoleptic compounds **2**, **3**, **4**, **5** and **6**

	<sup>1</sup> H			<sup>13</sup> C{ <sup>1</sup> H}	<sup>19</sup> F
	(CH <sub>3</sub> )	CH	Aromatic	C≡N	F–C
DippNC	1.05	3.36	6.99 6.85	172.0	
<b>2</b>	1.21	3.42	7.22 7.16	194.9	
<b>5</b>	1.26	3.69	6.95	176.4	
<b>4</b>	1.20	3.70	7.05–6.87	176.5	
	1.26	3.58			
4-FPI			6.56 6.33	164.7	–109.3
<b>3</b>			7.30 6.98	183.5	–115.7
<b>6</b>			6.72 6.31	170.2	–113.0

**Table 2** IR and mass spectroscopic data for the free ligands and the homoleptic compounds **2**, **3**, **4**, **5** and **6**

	$\tilde{\nu}(\text{C}\equiv\text{N})$	$\tilde{\nu}(\text{C–F})$	MW	Ion observed
DippNC	2120			
4-FPI	2139	1300		
<b>2</b>	2093(a), 2052(e)		992.6	[M + H] <sup>+</sup>
<b>5</b>	2009, 1972		807.5	[M + H] <sup>+</sup>
<b>4</b>	2099(t), 1578(b)		1614.9	[C <sub>65</sub> H <sub>85</sub> CoN <sub>5</sub> ] <sup>+</sup>
<b>3</b>	2112(a), 1945(e)	1235	662.1	[M + H] <sup>+</sup>
<b>6</b>	2043, 2002	1232	543.1	[M + H] <sup>+</sup>

corresponding to the stretching mode of the C≡N bond is notably sensitive to metal coordination (Table 2). In comparison with the stretching frequencies  $\nu$  C≡N of the isonitrile ligands (DippNC: 2120 cm<sup>−1</sup> and 4-FPI: 2139 cm<sup>−1</sup>), there is a considerable shift towards a lower frequency after metal coordination. The C≡N vibrations of the axial ligands for **2** and **3** are located at higher wavenumbers (2093 cm<sup>−1</sup> for **2**, 2112 cm<sup>−1</sup> for **3**) compared to the free ligands, while the C≡N vibrations of the equatorial ligands appear at lower wavenumbers (2052 cm<sup>−1</sup> for **2**, 1945 cm<sup>−1</sup> for **3**). **4** exhibits two characteristic  $\nu$  C≡N stretching modes, indicating the presence of both terminal (2099 cm<sup>−1</sup>) and bridging (1578 cm<sup>−1</sup>) isocyanide ligands at the cobalt center. The observed lower frequency absorptions compared to the free isonitrile ligands suggest substantial d → π\* backbonding to these ligands. This phenomenon is consistent with the presence of electron-rich metal (0) centers. In compounds **5** and **6**, a splitting of the  $\nu$  C≡N band is observed. This has been caused by the angulation of the Ni–C≡N–R coordination and is attributed to a reduction in symmetry lower than the usual T<sub>d</sub>.<sup>17,18</sup> The molecular structure of the tetrahedrally coordinated nickel(0) isonitrile complex (**5**) shows a structural distortion which is reflected in the C–Ni–C bond angles, which range from 102.71° to 113.21° deviating significantly from the ideal value of 109.5° due to the steric constraints of the bulky diisopropyl groups (Fig. 1). The Ni–C bond lengths in **5** range from 1.8278

(**18**) to 1.8536(17) Å, with only minor variations in agreement with those observed in other homoleptic nickel(0) isonitrile complexes.<sup>12</sup> Four distinct C≡N–C angles were observed, ranging from 164.25° to 170.44°. This variation in bond angles suggests a deviation from perfect linearity, which is likely driven by steric interactions and crystal packing effects. Notably, these values are consistent with a number of other homoleptic nickel(0) isonitrile complexes, indicating that such distortions are a common structural feature within this class of compounds.<sup>12</sup> Despite these obvious structural similarities, the C≡N stretching vibration appears at a significantly lower wavenumber ( $\Delta\nu$  = 20 cm<sup>−1</sup>) compared to that of the tetrakis(phenylisocyanide)nickel(0) complexes [Ni(CNR)<sub>4</sub>](R = C<sub>6</sub>H<sub>5</sub>; R = C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>; R = C<sub>6</sub>H<sub>4</sub>-2-NO<sub>2</sub>). However, the C≡N triple bond remains unchanged compared to these complexes.<sup>12</sup> Therefore, it is unlikely that the observed shift of the  $\nu_{\text{CN}}$  stretching frequency can be solely attributed to changes in the Ni–C or C≡N bond lengths. Instead, it is likely that enhanced π-back bonding from the nickel center to the isonitrile ligands increases electron density in the antibonding orbitals of the C≡N bond, weakening it significantly electronically rather than structurally.

## Experimental

### General

The metal-atom reactions took place in a 5 L custom-made, all-glass reactor, following the design outlined by Klabunde.<sup>14</sup> The metal was evaporated using tungsten crucibles coated with aluminum oxide cement and calcined prior to use at temperatures above 600 °C under vacuum. During metal-vapor reactions, approximately 20% of the metal is typically lost due to the deposition of metal vapor outside the reaction zone where direct metal atom and toluene co-condensation occurs. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques in combination with a high-vacuum line or in a glovebox filled with dry argon. Before using the solvents, they were dried, freshly distilled, and stored under argon. Elemental analyses were performed by Mikrolab-Kolbe, Oberhausen/Ruhr, or in the microanalytical laboratory of the Chemistry Department at TU Darmstadt (for CHN). A JASCO FT/IR-550 spectrometer and Impact 2 were applied to record Fourier transform infrared and mass spectra. NMR spectra were recorded on a Bruker Avance Neo 500 instrument (500.15 and 125.77 MHz and 470.56 for <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F, respectively) at room temperature. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR-chemical shifts ( $\delta$  values) are given in ppm relative to the solvent signal. 2,6-Diisopropylaniline, 4-fluorophenylamine, phosphorus oxychloride (POCl<sub>3</sub>), formic acid, iron, cobalt, and nickel were purchased from Sigma-Aldrich. They were used without any further purification. Aluminum oxide and Celite® were dried at 150 °C in a dynamic vacuum for 18 h and stored under an argon atmosphere. 2,6-Diisopropylphenylisonitrile (DippNC)<sup>19</sup> and 4-fluorophenylisonitrile (4-FPI)<sup>20</sup> were synthesized according to the reported procedures. Caution: 4-FPI



is a highly malodorous and volatile isonitrile compound that causes acute discomfort (e.g., headache, nausea) even at low concentrations. All manipulations must be carried out in a specifically well-ventilated hood while using personal protective equipment.

### Synthesis and characterization of pentakis(2,6-diisopropylphenylisonitrile)iron (2)

Iron vapor (3.00 g, 53.7 mmol) was co-deposited with toluene (150 mL) at  $-196^{\circ}\text{C}$  and  $10^{-2}$  Pa over a period of 90 min. After warming up to  $-78^{\circ}\text{C}$ , the suspension was stirred for 15 min. Unreacted metal was filtered with a pad of aluminum oxide at  $-78^{\circ}\text{C}$ . A solution of 2,6-diisopropylphenylisonitrile (3.00 g, 15.9 mmol) in toluene (20 mL) was added at  $-78^{\circ}\text{C}$ , and the resulting solution was stirred for 18 h at  $-40^{\circ}\text{C}$ . Toluene was removed under vacuum, and the remaining red solid was dissolved in diethyl ether. The resulting deep red solution was filtered, concentrated, and cooled to  $-30^{\circ}\text{C}$  to afford 2 as red crystals (2.33 g, 2.35 mmol, 74%, based on added isonitrile).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 7.22 (t, 5 H, *m*-H), 7.16 (d, 10 H, *o*-H), 3.42 (sept, 10 H, CH), 1.21 (d, 60 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 194.9 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 143.1 (s,  $\text{C}-\text{N}\equiv\text{C}$ ), 125.5 (s, aromatic), 122.7 (s, aromatic), 29.6 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 22.3 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ). IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 2951(s), 2868(m), 2093(s), 2052(s), 1983(m), 1581(m), 1459(s), 1360(m), 1328(m), 1258(s), 1058(w), 796(m), 745(w), 670(w), 562(w). MS (EI, *m/z*): required for  $[\text{C}_{65}\text{H}_{85}\text{N}_5\text{Fe} + \text{H}]^+$ : 992.62; found: 992.62  $[\text{M} + \text{H}]^+$ . EA: calcd for  $\text{C}_{65}\text{H}_{85}\text{FeN}_5$ : C 78.68, H 8.63, N 7.06; found: C 78.74, H 8.66, N 7.01.

### Synthesis and characterization of pentakis(4-fluorophenylisonitrile)iron (3)

Compound 3 was synthesized following the same procedure as that for compound 2. Starting from 3.0 g of iron (53.7 mmol) and 2.0 g (16.4 mmol) of 4-fluorophenylisonitrile, 1.75 g (2.65 mmol, 81%) of 3 was obtained as a red crystalline solid.  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  = 7.30 (q, 10 H, aromatic), 6.98 (t, 10 H, aromatic).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  = 183.5 (s,  $\text{C}_6\text{FH}_4\text{NC}$ ), 162.8 (t, C-F), 160.8 (s,  $\text{C}-\text{N}\equiv\text{C}$ ), 127.9 (s, aromatic), 115.8 (s, aromatic).  $^{19}\text{F}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  =  $-115.7$  (s). IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 3062(w), 2112(s), 1945(w), 1596(w), 1499(s), 1235(s), 1152(m), 1093(m), 834(s), 556(s), 512(s), 482(s). MS (EI, *m/z*): required for  $[\text{C}_{35}\text{H}_{20}\text{F}_5\text{N}_5\text{Fe} + \text{H}]^+$ : 662.10; found: 662.11  $[\text{M} + \text{H}]^+$ . EA: calcd for  $\text{C}_{35}\text{H}_{20}\text{F}_5\text{N}_5\text{Fe}$ : C 63.56, H 3.05, F 14.36, N 10.59; found: C 63.25, H 2.99, F 14.22, N 10.54.

### Synthesis and characterization of $[\text{Co}(\text{CNDipp})_4]_2$ (4)

A mixture of 2,6-diisopropylphenylisonitrile (3.0 g, 15.9 mmol) and toluene (20 mL) was placed at the bottom of the reactor. Cobalt (2.22 g, 37.7 mmol) was evaporated and co-deposited with toluene (150 mL) at  $-196^{\circ}\text{C}$  and  $10^{-2}$  Pa over a period of 90 min. The mixture was stirred for 2 h at  $-78^{\circ}\text{C}$ . Unreacted metal was filtered using a pad of alumina at  $-78^{\circ}\text{C}$ . Toluene was removed under vacuum, and the remaining dark brown

solid was dissolved in diethyl ether. The resulting brown solution was filtered, concentrated, and cooled to  $-30^{\circ}\text{C}$  to afford 4 (2.29 g, 1.42 mmol, 71%, based on added isonitrile).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 7.05–6.87 (m, 24 H, aromatic), 3.70 (sept, 12 H,  $\text{CH}_{\text{terminal}}$ ), 3.58 (sept, 4 H,  $\text{CH}_{\text{bridged}}$ ), 1.26 (d, 72 H,  $\text{CH}_3$ ), 1.20 (d, 24 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 176.5 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 144.2 (s,  $\text{C}-\text{N}\equiv\text{C}$ ), 126.9 (s, aromatic), 123.3 (s, aromatic), 29.8 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 22.3 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ). IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 2956(s), 2868(m), 2170(s), 2099(m), 1624(s), 1578(s), 1459(s), 1361(s), 1321(s), 1259(s), 1069(m), 1051(m), 797(s), 746(m). MS (EI, *m/z*): required for  $[\text{C}_{104}\text{H}_{136}\text{Co}_2\text{N}_8 + \text{H}]^+$ : 1614.96; found: 994.61  $[\text{C}_{65}\text{H}_{85}\text{CoN}_5]^+$ . EA: calcd for  $\text{C}_{104}\text{H}_{136}\text{Co}_2\text{N}_8$ : C 77.29, H 8.48, N 6.93; found: C 77.17, H 8.53, N 6.91.

### Synthesis and characterization of tetrakis(2,6-diisopropylphenylisonitrile)nickel (5)

Compound 5 was synthesized following the same procedure as that for compound 4. Starting from 2.0 g of nickel (34.1 mmol) and 3.0 g (15.9 mmol) of 2,6-diisopropylphenylisonitrile, 2.77 g (3.43 mmol, 86%, based on added isonitrile) of 5 was obtained as yellow crystalline needles.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 6.95 (m, 12 H, aromatic), 3.69 (s, 8 H, CH), 1.26 (d, 48 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 297 K):  $\delta$  = 176.4 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 143.8 (s,  $\text{C}-\text{N}\equiv\text{C}$ ), 126.5 (s, aromatic), 123.1 (s, aromatic), 29.9 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ), 22.5 (s,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3\text{NC}$ ). IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 2960(s), 2869(m), 2009(s), 1972(s), 1584(m), 1460(m), 1434(m), 1330(w), 1256(w), 1103(w), 795(m), 746(m), 520(m). MS (EI, *m/z*): required for  $[\text{C}_{52}\text{H}_{68}\text{N}_4\text{Ni} + \text{H}]^+$ : 807.48; found: 807.48  $[\text{M} + \text{H}]^+$ . EA: calcd for  $\text{C}_{52}\text{H}_{68}\text{N}_4\text{Ni}$ : C 77.31, H 8.48, N 6.94; found: C 77.46, H 8.48, N 6.72.

### Synthesis and characterization of tetrakis(4-fluorophenylisonitrile)nickel (6)

Compound 6 was synthesized following the same procedure as that for compound 4. Starting from 2.0 g of nickel (34.1 mmol) and 2.0 g (16.4 mmol) of 4-fluorophenylisonitrile, 1.53 g (2.82 mmol, 69%, based on added isonitrile) of 6 was obtained as bright yellow needles.  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  = 6.72 (q, 8 H, aromatic), 6.31 (t, 8 H, aromatic).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  = 170.2 (s,  $\text{C}_6\text{FH}_4\text{NC}$ ), 162.8 (t, C-F), 160.8 (s,  $\text{C}-\text{N}\equiv\text{C}$ ), 128.0 (s, aromatic), 115.9 (s, aromatic).  $^{19}\text{F}$  NMR ( $\text{THF}-d_8$ , 500 MHz, 297 K):  $\delta$  =  $-113.0$  (s). IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 3071(w), 2043(s), 2002 (s), 1495(s), 1232(s), 1193(s), 1149(m), 1088(m), 830(s), 698(w), 510(s), 486(s), 463(s), 412(s). MS (EI, *m/z*): required for  $[\text{C}_{28}\text{H}_{16}\text{F}_4\text{N}_4\text{Ni} + \text{H}]^+$ : 542.07; found: 542.07  $[\text{M} + \text{H}]^+$ . EA: calcd for  $\text{C}_{28}\text{H}_{16}\text{F}_4\text{N}_4\text{Ni}$ : C 61.92, H 2.97, F 13.99, N 10.32; found: C 61.77, H 2.98, F 13.94, N 10.29.

## Conclusions

In conclusion, the metal vapor approach represents a versatile and direct method for synthesizing homoleptic Fe, Co, and Ni-isonitrile compounds. The high reactivity of isonitriles towards

solutions of these compounds is attributed to their significant donor capability and their ability to stabilize the highly reactive zerovalent metal atoms. Our study sheds new light on the metal atom synthesis technique, which still offers a versatile method for exploration and innovation in the field of coordination chemistry, having the potential to develop new materials and catalysts.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The NMR and IR spectra are provided in the ESI.† Crystallographic data for compound **5** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2441971.†

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