N-Heterocyclic Carbenes

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Direct Synthesis of Iron, Cobalt, Nickel, and Copper Complexes of N-Heterocyclic Carbenes by Using Commercially Available Metal Powders**

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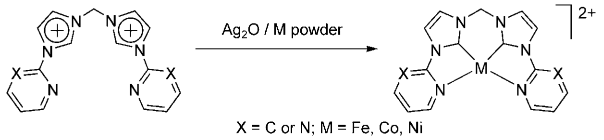
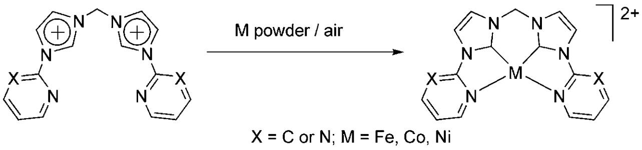
The development of transition-metal-catalyzed organic transformations based on the first-row transition metals such as Fe, Co, Ni, and Cu is of importance because of their relatively low cost and toxicity relative to precious metals.[1] The strongly σ-donating N-heterocyclic carbenes (NHCs) offer a good opportunity to tune the reactivity and selectivity of transition-metal catalysts.[2] A large number of NHC complexes of precious metals have recently been prepared and characterized, and their catalytic applications in various organic transformations have been widely studied. In contrast, catalytic processes based on NHC complexes of non-noble metals such as manganese, iron, and cobalt have not been well studied.[3,4] One of the reasons is that NHC complexes of the first-row metals have to be prepared from free carbenes[5,6] or through reactions of basic metal acetates, alkoxides, or amides with imidazolium salts.[7] The generation of free carbenes often requires special bases, and handling unstable free carbenes requires harsh conditions. The second route is also restricted because metal acetates, alkoxides, and amides are not always available, and such metal salts are moisture-sensitive. The most popular approach to noble-metal–NHC complexes is the transmetalation of NHCs from silver complexes that can be synthesized by treating Ag_2O with the imidazolium salts.[2] However, the carbene-transfer reactions of silver–NHC complexes with light metal salts such as Mn, Fe, and Co are not simple. Thus, the development of practical and convenient synthetic approaches to NHC complexes of non-noble metals is highly desired.

As a continuation of our research on the nickel and palladium chemistry of NHCs,[8] we herein report practical and convenient synthetic procedures of divalent iron, cobalt, nickel, and copper complexes by direct reactions of metal powders with imidazolium salts or silver–NHC complexes.

Treatment of $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3$[8f] (L1 = bis(pyridylimidazolylidene)methane) in situ generated from bis(pyridylimidazoliumyl)methane dihexafluorophosphate $[H_2L1(PF_6)_2]$ and Ag_2O with an excess of commercially available iron, cobalt, and nickel powders allowed the isolation of $[M(L1)_2](PF_6)_2$ [M = Fe (**1**); Co (**2**); Ni (**3**)] in 51.7–94.1% yields (Scheme 1). Complexes **1**–**3** could also be obtained in similar yields by simply mixing $H_2L1(PF_6)_2$, Ag_2O, and metallic powders in acetonitrile. The procedure is simple, and the unreacted metal powders and silver can be easily removed by filtration. Further studies revealed that compounds **1**–**3** could be prepared by directly treating $H_2L1(PF_6)_2$ with the corresponding metal powders in air (Scheme 2). The acidity of imidazolium salts is too weak for the reactions of imidazolium salts with metals (M = Fe, Co, Ni, and Cu) to release H_2 to be dynamically preferred. However, the reactions took place smoothly upon exposure to an O_2 atmosphere with the formation of water.



Scheme 1. Synthesis of complexes **1**–**3**, **5**, and **6** via Ag–NHC complexes and metal powders.



Scheme 2. Synthesis of complexes **1**–**3**, **5**, and **6** via imidazolium salts and metal powders.

The three complexes are isostructural with each other, and their ^{1}H and ^{13}C NMR spectra show almost the same resonance signals due to pyridine and imidazolylidene moieties. The imidazolylidene backbone protons appear as two doublets at $\delta = 8.62$ and 8.13 ppm. ^{13}C NMR spectra show singlets at $\delta = 159.1$, 159.1, and 158.9 ppm for **1**–**3**, respectively, which is characteristic of metal–carbenic carbon atom resonances. ESIMS spectra of **1**–**3** exhibit peaks for $[M(L1)(PF_6)]^+$ and $[M(L1)]^{2+}$ moieties.

The structures of **1**–**3** were further characterized by X-ray diffraction analysis. Nickel complex **3** is the same as that prepared from $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3$ and $[Ni(PPh_3)_2Cl_2]$, and its structure has been described previously.[8f] The structure of **1** is shown in Figure 1, and that of complex **2** is given as Figure S1 in the Supporting Information. The

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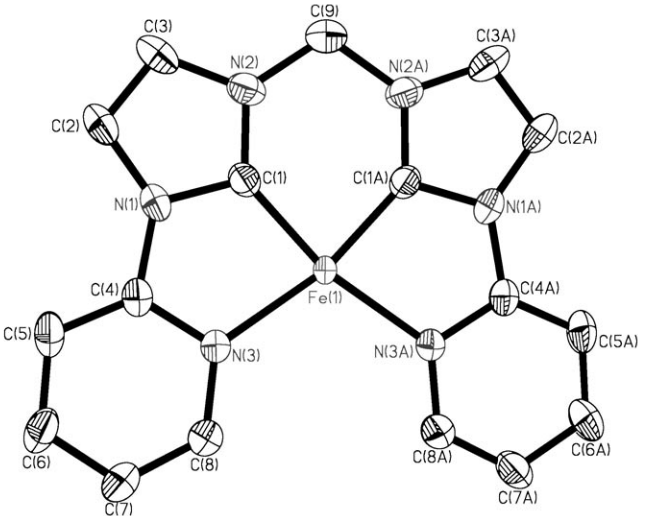
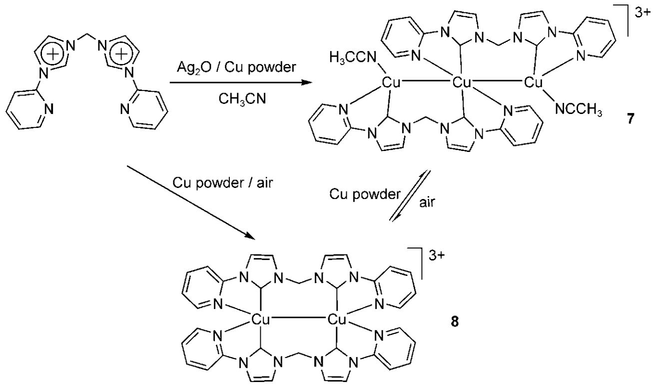


Figure 1. Molecular structure of $[Fe(L1)]^{2+}$ (**1**) with ellipsoids drawn at 30% probability. Selected bond lengths [Å] and angles [°]: Fe(1)–C(1) 1.801(6), Fe(1)–N(3) 1.983(5), C(1A)-Fe(1)-C(1) 84.9(4), C(1)-Fe(1)-N(3) 82.2(2), C(1)-Fe(1)-N(3A) 166.9(2), N(3)-Fe(1)-N(3A) 110.8(3). Symmetry code: #A $-x+2$, y, $-z+1/2$.



Scheme 3. Synthesis of **7** and **8**.

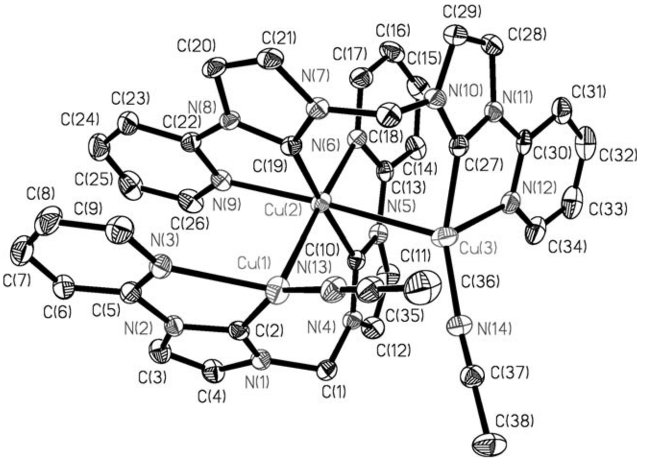


Figure 2. Molecular structure of $[Cu_3(L1)_2(CH_3CN)_2]^{3+}$ (**7**) with ellipsoids drawn at 30% probability. Selected bond lengths [Å] and angles [°]: Cu(1)–Cu(2) 2.8518(10), Cu(2)–Cu(3) 2.7210(10), Cu(1)–C(2) 1.902(5), Cu(2)–C(10) 1.928(4), Cu(2)–C(19) 1.935(4), Cu(3)–C(27) 1.909(5), Cu(1)–N(13) 1.882(5), Cu(1)–N(3) 2.338(4), Cu(2)–N(9) 2.257(4), Cu(2)–N(6) 2.265(4), Cu(3)–N(14) 1.889(5), Cu(3)–N(12) 2.383(4), N(13)-Cu(1)-C(2) 153.9(2), N(13)-Cu(1)-N(3) 116.81(17), C(2)-Cu(1)-N(3) 76.68(18), C(10)-Cu(2)-C(19) 171.7(2), C(10)-Cu(2)-N(9) 109.19(17), C(19)-Cu(2)-N(9) 78.11(17), C(10)-Cu(2)-N(6) 78.41(18), C(19)-Cu(2)-N(6) 106.00(17), N(9)-Cu(2)-N(6) 90.28(14), N(14)-Cu(3)-C(27) 146.5(2), N(14)-Cu(3)-N(12) 113.99(18), C(27)-Cu(3)-N(12) 76.45(19), Cu(3)-Cu(2)-Cu(1) 86.12(3).

central M^{II} ions (M = Fe, Co, and Ni) are all tetracoordinated by two pyridine and two NHC carbon atoms in square-planar geometry. The non-hydrogen atoms of the cation are almost perfectly coplanar, as indicated by the small dihedral angles (1.5–3.8°) between the coordination planes defined by MC_2N_2 and the imidazolylidene and pyridine rings. The M–C and M–N bond lengths of the three complexes are very similar to each other. To the best of our knowledge, complexes **1** and **2** are the first square-planar 14-electron iron and 15-electron cobalt complexes possessing imidazolylidene ligands. So far, only a few Fe^{II} complexes with 14-electron configuration displaying tetrahedral geometry have been reported,[5a,9] and structurally characterized 15-electron cobalt–NHC complexes are also scarce.[5d,10] Unlike these tetrahedral iron complexes, the present Fe^{II} and Co^{II} complexes are stable towards air and moisture. Their corresponding M–C bond lengths are significantly shorter than the known 16–18-electron iron(II)[6a–e,11] and cobalt(II) NHC complexes.[6f–j,10,11b]

The reaction of bis(pyrimidylimidazoliumyl)methane dihexafluorophosphate ($H_2L2(PF_6)_2$) with Ag_2O yielded dinuclear $[Ag_2(L2)_2](PF_6)_2$ (**4**, Figure S2 in the Supporting Information). Treatment of **4** with an excess of cobalt or nickel powders afforded $[M(L2)](PF_6)_2$ [M = Co (**5**); Ni (**6**)] in good yields. The same complexes could also be prepared from reactions of $H_2L2(PF_6)_2$ and the corresponding metal powders. Complexes **5** and **6** have essentially the same square-planar structures as **1**–**3**, and their structures are shown in Figures S2–4 in the Supporting Information.

Commercially available copper powder also reacts with $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3$ in acetonitrile at 50 °C to give a red solution and metallic silver, and complex **7** was isolated as red crystals (Scheme 3). The ^{13}C NMR spectrum of **6** shows a singlet at $\delta = 181.6$ ppm, which is indicative of Cu–NHC complex formation. Complex **7** (Figure 2) is a trinuclear copper(I) complex consisting of three independent copper(I) atoms surrounded by two L1 ligands. Each L1 interacts with two Cu^I ions. In the triangular Cu_3 core, Cu(2) is tetracoordinated by two carbenic carbon atoms and two nitrogen atoms of pyridine groups from two different L1 ligands. Two NHC carbon atoms are linearly bound to Cu(2) with a C-Cu-C angle of 171.7(2)°. The two imidazolylidene rings coordinated to Cu(2) bisect each other with dihedral angle of 88.62°. The other two copper ions are each coordinated by a carbenic carbon atom and a pyridine ring of the same ligand as well as an acetonitrile molecule, displaying triangular geometry. The lengths of the four Cu–C bonds fall in the range 1.902(5)–1.935(4) Å, which is consistent with the reported values of known copper(I)–NHC complexes.[12,13] The $Cu-N_{acetonitrile}$ bonds are of normal length, whereas the $Cu-N_{pyridine}$ bonds are unusually long. Weak Cu–Cu interactions are observed for the Cu_3 angle, as indicated by the short Cu–Cu contacts of around 2.85 and 2.72 Å for Cu(1)–Cu(2) and Cu(2)–Cu(3), respectively. Short Cu–Cu separations have been found in several copper clusters as a result of cuprophilicity.[13,14]

Unexpectedly, reaction of $H_2L1(PF_6)_2$ with one equivalent of copper powder in acetonitrile did not afford **7**. Instead, an unusual dinuclear Cu(1.5)–Cu(1.5) complex {$[Cu_2(L1)_2](PF_6)_3$ (**8**)} was obtained as dark green crystals. Oxidation of **7** in air also yielded **8**. The red solution of **7** in acetonitrile gradually changed color to dark green in air upon standing and **8** was isolated from the solution. Interestingly, addition of copper powder to the green solution of **8** reversely turned the solution red, and **7** could be recovered after workup. The paramagnetic nature of **8** results in broad resonance signals in the ^1H NMR spectrum, and no ^{13}C NMR spectrum could be obtained.

The solid-state structure of **8** revealed by X-ray diffraction analysis is shown in Figure 3. The mixed-valence Cu_2^{3+} complex contains two crystallographically equivalent Cu centers, which are doubly bridged by two L1 ligands. The virtual equality of two Cu ions illustrates that the lone electron is fully delocalized. The short Cu–Cu distance of 2.587 Å reflects the formation of a covalent Cu(1.5)–Cu(1.5) bond (the sum of covalent radii of two copper atoms is 2.64 Å). The copper ions are each tetracoordinated by two carbenic carbon atoms and two nitrogen atoms of pyridine rings from two different L1 ligands. The C-Cu-C angle of 179.0(3)° shows that the two NHC rings are linearly arranged. The two copper centers display severely distorted tetrahedral geometry as a consequence of Cu(1.5)–Cu(1.5) bond. The Cu–C bond lengths are 1.920(8) and 1.932(9) Å, which are similar to those of other reported Cu^I carbene complexes.[13] The two imidazolylidene rings coordinated to the same copper ion are bisected with an dihedral angle of 79.64°. So far, only a few mixed valence Cu(1.5)–Cu(1.5) complexes have been reported with short Cu–Cu bonds (2.39–2.73 Å).[15] To our knowledge, this is the first example of a fully delocalized mixed Cu(1.5)–Cu(1.5) complex supported by NHC ligands.

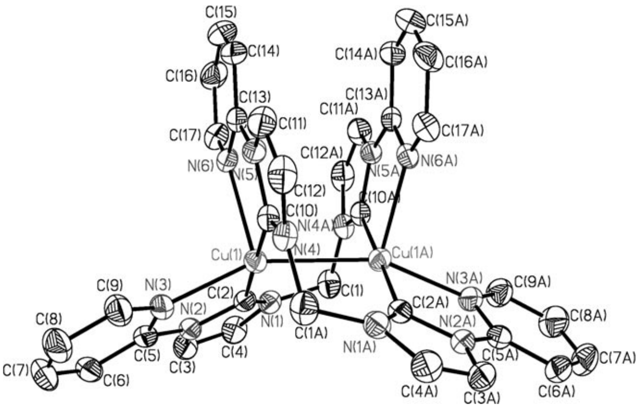


Figure 3. Molecular structure of the cation $[Cu_2(L1)_2]^{3+}$ (**8**) with ellipsoids drawn at 30% probability. Selected bond distances [Å] and angles [°]: Cu(1)–Cu(1A) 2.587(2), Cu(1)–C(10) 1.920(8), Cu(1)–C(2) 1.932(9), Cu(1)–N(3) 2.160(7), Cu(1)–N(6) 2.261(7), C(10)-Cu(1)-C(2) 179.0(3), C(10)-Cu(1)-N(3) 100.6(3), C(2)-Cu(1)-N(3) 79.9(3), C(10)-Cu(1)-N(6) 78.0(3), C(2)-Cu(1)-N(6) 102.8(3), N(3)-Cu(1)-N(6) 101.8(3), Symmetry code: #A −x, y, −z+1/2.

Quite different from $H_2L1(PF_6)_2$, reactions of **4** or $H_2L2(PF_6)_2$ with copper powder gave $[Cu_2(L2)_2](PF_6)_2$ (**9**) as the sole product. $[Cu_2(L2)_2]^{2+}$ has a similar framework to that of **8**. The Cu^I–Cu^I distance is 3.370 Å, which excludes an important metal–metal interaction. The Cu–C bond lengths are comparable to those of **7**, but Cu–N distances are remarkably longer (Figure S5 in the Supporting Information). Attempts to oxidize **9** to $[Cu_2(L2)_2]^{3+}$ through the loss of one electron were unsuccessful.

In summary, we have demonstrated that metal–NHC complexes of Fe, Co, Ni, and Cu can be easily prepared in good yields from Ag–NHC complexes or imidazolium salts with commercially available metal powders. These approaches open up a practical and convenient rotue to the preparation of metal–NHC complexes, especially of first-row non-noble metals. By using such simple procedures, we have prepared rare examples of Fe^{II}, Co^{II}, and Cu^I complexes. All of these compounds are air-stable. The potential application of these non-noble-metal complexes as catalysts in organic synthesis and their redox properties will be studied further.

Experimental Section

General procedure for the preparation of **1**–**3**, **5**–**7**, and **9** via Ag–NHC complexes: A solution of $H_2L1(PF_6)_2$ (240 mg, 0.4 mmol) in CH_3CN (10 mL) was treated with Ag_2O (116 mg, 0.5 mmol) and excess metal powder. The mixture was allowed to react at the required temperature. The solution was filtered through celite to remove a small amount of unreacted Ag_2O and excess metal powder. The solution was concentrated to approximately 2 mL. Addition of Et_2O (10 mL) to the filtrate yielded the product. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into their CH_3CN solutions at room temperature.

General procedure for the preparation of **1**–**3**, **5**, **6**, **8**, and **9** via imidazolium salts and metal powders: A solution of $H_2L(PF_6)_2$ (240 mg, 0.4 mmol) in CH_3CN (20 mL) was treated with excess metallic powder. The mixture was allowed to react at 80 °C in air for several days. The solution was filtered through celite to remove excess metal powder. The filtrate was concentrated to approximately 2 mL, and addition of Et_2O (10 mL) led to isolation of the product.

Single crystals of these complexes were recrystallized from acetonitrile, mounted in inert oil, and transferred to the diffractometer. The structures were solved using direct methods and refined by full-matrix least-squares methods on F^2.[16]

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[16] Crystal data for **1**: $C_{17}H_{14}F_{12}FeN_6P_2$, monoclinic, $C2/c$, $a = 16.579(2)$, $b = 11.5559(12)$, $c = 14.0775(19)$ Å, $\beta = 124.855(2)°$, $V = 2213.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.945$ Mg m^{-3}, 5672 reflections collected, 1947 reflections independent [$R_{int} = 0.0390$], GOF on F^2 1.031, R [$I > 2\sigma I$]: 0.0688, 0.1765; **2**: $C_{17}H_{14}CoF_{12}N_6P_2$, monoclinic, $C2/c$, $a = 16.5720(19)$, $b = 11.5538(11)$, $c = 14.0741(13)$ Å, $\beta = 124.829(2)°$, $V = 2212.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.959$ Mg m^{-3}, 5612 reflections collected, 1946 reflections independent [$R_{int} = 0.0237$], GOF on F^2 1.066, R [$I > 2\sigma I$]: 0.0379, 0.0983; **4**: $C_{68}H_{60}Ag_4F_{24}N_{35}P_4$, triclinic, $P\bar{1}$, $a = 12.4750(13)$, $b = 14.1259(17)$, $c = 14.4619(18)$ Å, $\alpha = 118.345(2)$, $\beta = 96.6770(10)$, $\gamma = 95.8930(10)°$, $V = 2191.1(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.803$ Mg m^{-3}, 11256 reflections collected, 7579 reflections independent [$R_{int} = 0.0466$], GOF on F^2 1.098, R [$I > 2\sigma I$]: 0.0637, 0.1521; **5**: $C_{15}H_{12}CoF_{12}N_8P_2$, monoclinic, $C2/c$, $a = 16.468(3)$, $b = 11.4179(11)$, $c = 13.8343(18)$ Å, $\beta = 124.332(2)°$, $V = 2148.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.020$ Mg m^{-3}, 5287 reflections collected, 1893 reflections independent [$R_{int} = 0.0328$], GOF on F^2 1.071, R [$I > 2\sigma I$]: 0.0353, 0.0881; **6**: $C_{15}H_{12}F_{12}N_8NiP_2$, monoclinic, $C2/c$, $a = 16.509(2)$, $b = 11.4442(10)$, $c = 13.8689(12)$ Å, $\beta = 124.342(2)°$, $V = 2163.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.005$ Mg m^{-3}, 5103 reflections collected, 1909 reflections independent [$R_{int} = 0.0407$], GOF on F^2 0.919, R [$I > 2\sigma I$]: 0.0383, 0.0860; **7**: $C_{40}H_{37}Cu_3F_{18}N_{15}P_3$, monoclinic, $P2_1/n$, $a = 11.7891(10)$, $b = 21.331(3)$, $c = 20.873(3)$ Å, $\beta = 95.099(2)°$, $V = 5228.2(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.719$ Mg m^{-3}, 24807 reflections collected, 9203 reflections independent [$R_{int} = 0.0384$], GOF on F^2 1.015, R [$I > 2\sigma I$]: 0.0486, 0.1070; **8**: $C_{38}H_{34}Cu_2F_{18}N_{14}P_3$, monoclinic, $C2/c$, $a = 21.723(2)$, $b = 13.0755(13)$, $c = 17.2147(15)$ Å, $\beta = 98.088(2)°$, $V = 4841.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.713$ Mg m^{-3}, 12422 reflections collected, 4261 reflections independent [$R_{int} = 0.0583$], GOF on F^2 1.030, R [$I > 2\sigma I$]: 0.0574, 0.1437; **9**: $C_{32}H_{27}Cu_2F_{12}N_{17}P_2$, triclinic, $P\bar{1}$, $a = 12.5710(10)$, $b = 14.1550(13)$, $c = 14.3100(16)$ Å, $\alpha = 119.314(2)$, $\beta = 97.6350(10)$, $\gamma = 96.2780(10)°$, $V = 2155.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.644$ Mg m^{-3}, 10799 reflections collected, 7421 reflections independent [$R_{int} = 0.0228$], GOF on F^2 1.067, R [$I > 2\sigma I$]: 0.0588, 0.1595. CCDC 726608–726615 (**1**, **2**, **4**–**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.uk/data request/cif.