

Synthesis, Structural Diversity, and Ligand-Transfer Potential of (Carbene)copper(I) Complexes

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Copper(I) complexes comprising different N-heterocyclic carbene ligands were prepared *via in situ* deprotonation and metallation. Depending on the wingtip groups on the carbene ligand (alkyl vs. aryl, chelating or monodentate), a variety of different structural motifs were identified, such as a trigonal planar geometry (alkyl wingtips) and an unprecedented see-saw-type structure (pyridinyl wingtip groups). While aryl wingtip groups increase the stability of the complexes, alkyl substituents induce rapid demetallation in the presence of moisture. The reactivity of these complexes was used to establish a carbene-transfer protocol, which is illustrated by the formation of new cyclic thiourea compounds (transfer to sulfur) and new (carbene)ruthenium(II) complexes (transfer to ruthenium). This suggests that (carbene)copper(I) complexes could become valuable alternatives to (carbene)silver(I) complexes for synthesizing (carbene)metal systems *via* transmetallation.

Introduction. – Copper(I) complexes containing N-heterocyclic carbene (NHC) ligands have been demonstrated to be highly useful for catalysis [1]. While in some cases, defined complexes have been employed as catalyst precursors [2], often, the active species has been reported to be generated *in situ* by adding the 1*H*-imidazolium salt and a base along with a copper(I) source [3]. This latter method provides some potential pitfalls, *e.g.*, for catalyst optimization, as the assumed bonding mode and surmised coordination geometry may be incorrect¹). In addition, it is widely known that, in copper-catalyzed reactions in particular, subtle structural differences in the catalytically active species may induce considerably different activities [5]. Hence, insights into structural properties and selective reactivity patterns of [Cu^I(carbene)] complexes may be very instructive for further catalyst development.

Various methodologies have been developed for the preparation of [Cu^I(carbene)] complexes. Most frequently²), a route *via* free carbenes has been applied including either isolation of the free carbene before copper addition or utilization of an *in situ* procedure, avoiding manipulations with the potentially sensitive free carbene. The metal precursor, CuX, strongly influences the Cu/carbene stoichiometry in the formed complexes. Ionic homoleptic [Cu(carbene)₂]X systems are generally obtained with copper salts that comprise only weakly coordinating anions such as TfO⁻, BF₄⁻, or PF₆⁻

¹) For example, abnormal carbene bonding or formation of an ion-pair complex may occur [4].

²) Alternative routes have been used for the synthesis of [Cu^I(carbene)] complexes, including the *N*-alkylation of 1*H*-imidazolylcopper complexes, the use of Cu₂O for direct metallation, and transmetallation from [Ag^I(carbene)] complexes. For key examples, see [6].

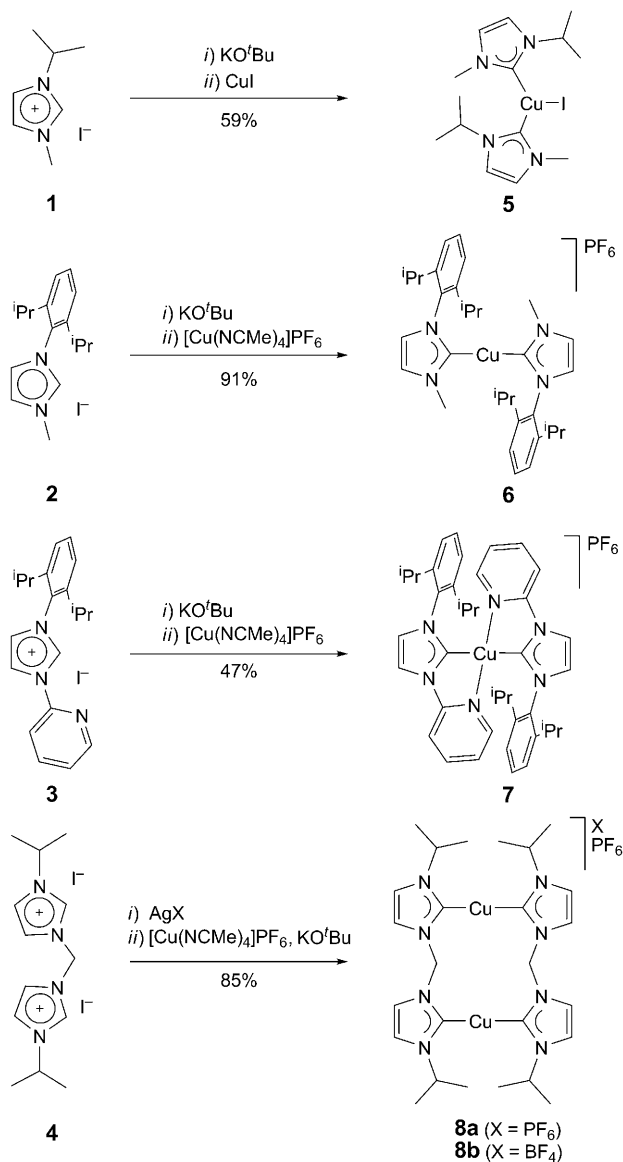
[7]. Homoleptic complexes are also obtained when a transmetallation protocol from $[\text{Ag}^{\text{I}}(\text{carbene})]$ complexes is used [6c][6d]. With coordinating anions ($\text{X} = \text{halide}, \text{AcO}^-$), monocarbene complexes of the type $[\text{CuX}(\text{carbene})]$ are usually formed [8]. While these considerations are valid in general, allowing for a rational synthesis of simple $[\text{Cu}(\text{carbene})]$ complexes (alkyl or aryl wingtip groups at the carbene), prediction of the product composition becomes increasingly difficult when the carbene-ligand wingtips comprise functional groups. For example, coordinating phosphine donors were found to stabilize a rare complex comprising a carbene bound to two different Cu^{I} -centers in what is probably best described as a 3-center-2-electron bond [9]. Meyer and co-workers produced, depending on the steric bulk at the carbene wingtips, T-shaped and tetrahedral $[\text{Cu}^{\text{I}}(\text{carbene})]$ complexes from a tripodal tris-carbene ligand comprising a central amine as additional donor site [10]. A similar perturbation of the typically linear Cu coordination into distorted tetrahedral and T-shaped geometries has been observed when hard alkoxide or softer pyridine donor groups are attached to the carbene [6b][11].

In the framework of our research program directed towards the development of new types of NHC complexes [4b][12], we report here on the coordination ability of a small but diverse set of NHC ligands comprising variable degrees of steric bulk and donor functionality at the wingtip groups. Metallation of these 1*H*-imidazolium salts gave rise to a variety of known as well as unprecedented structural motifs in $[\text{Cu}^{\text{I}}(\text{carbene})]$ chemistry. Some of these complexes proved to be useful carbene-transfer agents. Hence, $[\text{Cu}^{\text{I}}(\text{carbenes})]$ may become valuable precursors as alternative to the more frequently used silver route for carbene transfer, for example when hygroscopic substrates are involved.

Results and Discussion. – *Synthesis of the Complexes.* Deprotonation of the 1*H*-imidazolium precursors **1–4** with stoichiometric quantities of KO^tBu and *in situ* metallation afforded the $[\text{Cu}^{\text{I}}(\text{carbene})]$ complexes **5–8** in moderate to excellent yields (*Scheme 1*)³. The carbene complexes **6** and **7** are stable in air for several weeks, while gradual decomposition was observed for complexes **5** and **8** comprising only alkyl wingtip groups. In the absence of an inert atmosphere, the decomposition was accelerated in solution ($t_{1/2}$ ca. 24 h) as compared to solid-state degradation (several days). According to NMR spectroscopy, the corresponding 1*H*-imidazolium salt was the major product from this decomposition, suggesting hydrolysis as the predominant reaction pathway. Hence, moisture seems of bigger concern than O₂ when storing such $[\text{Cu}^{\text{I}}(\text{carbene})]$ complexes.

The complexes **5–8** were characterized in solution and in the solid state. In solution, NHC metallation is indicated by the low-field resonance of the metal-bound carbene ligand ($\delta(\text{C})$ 176–180), characteristic of Cu complexes with N-heterocyclic carbenes [7][8]. Notably, the bulky Ar* wingtip groups in complexes **6** and **7** prevent rotation about the Cu–C(carbene) bond, as evidenced by the presence of two nonequivalent isopropyl Me resonances in the ¹³C-NMR spectra of these complexes (Ar* = 2,6-ⁱPr₂C₆H₃). In complex **8**, the methylene protons appear as an *AB d* located at $\delta(\text{H})$ 6.34 and 5.83 (²*J* = 13.5 Hz), which is a direct consequence of the restricted flexibility of the

³) All our attempts to install the copper center by direct metallation with Cu₂O failed, see [11].

Scheme 1. Synthesis of the [Cu^I(Carbene)] Complexes 5–8

Cu–C(carbene) bonds in the 12-membered dimetallacycle. Due to the rigid carbene coordination, one methylene proton is oriented towards the metal center, while the other one points outwards.

Solid-State Structures. All complexes **5**–**8** were analyzed by single-crystal X-ray diffraction. The molecular structures illustrate the high structural diversity in [Cu^I(carbene)] chemistry.

The coordination geometry in complex **5** is distorted trigonal, a coordination mode that is only rarely observed in [Cu^I(carbene)] complexes (*Fig. 1*) [11]. While, typically, linear structures X–Cu–carbene were found, we assume that the trigonal coordination in complex **5** is facilitated by the relatively small wingtip groups as compared to mesityl (=2,4,6-trimethylphenyl) and Ar* groups (see **6**, *Fig. 2*). The Cu-center and the I-ligand are located on a crystallographic axis of rotation. The sum of the angles around the Cu-center is, therefore, exactly 360.0°. Notably, the Cu–I bond (Cu(1)–I(1) 2.7623(7) Å) is rather long, perhaps due to the steric bulk imposed by the ⁱPr wingtip groups of the carbene ligands. The two carbene heterocycles are twisted out of the trigonal coordination plane by approximately 57°, which results in a propeller-like structure where one blade is represented by the I-ligand.

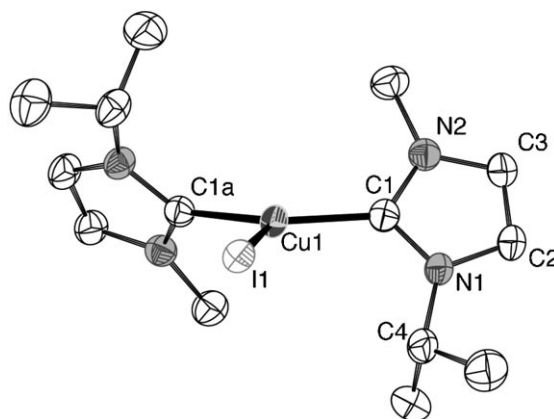


Fig. 1. *Thermal-ellipsoid plot of complex 5* (50% probability, H-atoms omitted). Selected bond lengths [Å]: Cu(1)–C(1) 1.930(3), Cu(1)–I(1) 2.7623(7), and C(2)–C(3) 1.350(5); selected bond angles [°]: C(1)–Cu(1)–C(1a) 141.80(17), C(1)–Cu(1)–I(1) 109.10(8), and N(1)–C(1)–N(2) 103.7(2); N(1)–C(1)–Cu(1)–I(1) 59.3(3) and N(2)–C(1)–Cu(1)–I(1) –124.8(2).

Complex **6**, comprising a sterically more demanding Ar* wingtip as opposed to the ⁱPr group in **5**, displays the linear geometry as expected for homoleptic [Cu(carbene)₂] complexes that were synthesized from [Cu(NCMe)₄]PF₆ precursors (*Fig. 2*) [7]. The Cu-center resides on a crystallographic inversion center. As a consequence, the two carbene heterocycles are crystallographically related. They adopt a virtually coplanar orientation, as illustrated by the torsion angle between the N(1)–C(1) bond and the C(1a)–N(2a) bond of 1.2(5)°. The two Ar* wingtip groups appear to efficiently shield the Cu-coordination sphere in **6**, thus preventing coordination of iodide as in **5**.

Substitution of the Me wingtip in **6** by a potentially chelating pyridinyl substituent as in **7** has a marked influence on the coordination geometry (*Fig. 3,a*). While the carbene ligands remain in a *pseudo-trans* arrangement (C–Cu–C 168.52(19)°), the short Cu–N_{py} distances, 2.310(4) and 2.439(4) Å, suggest that the pyridinyl N-atoms weakly coordinate to the Cu-center. Pyridinyl bonding results in a distorted see-saw-

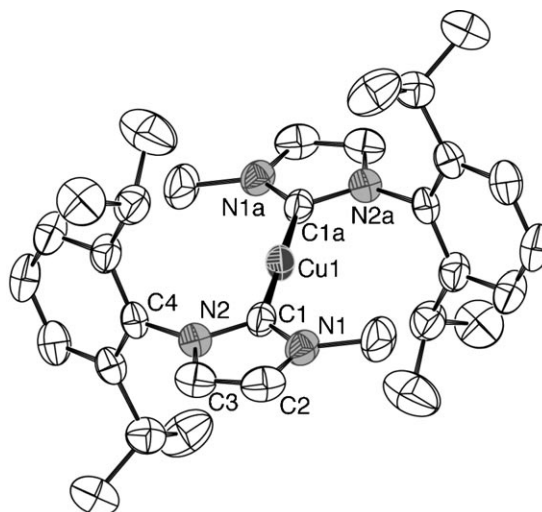


Fig. 2. Thermal-ellipsoid plot of the cationic portion of complex **6** (50% probability, H-atoms omitted, disorder in one of the ⁱPr groups not shown). Selected bond lengths [Å]: Cu(1)–C(1) 1.877(4), and C(2)–C(3) 1.336(6); selected bond angles [°]: C(1)–Cu(1)–C(1a) 180.0(4) and N(1)–C(1)–N(2) 103.3(3); N(1)–C(1)⋯C(1a)–N(2a) 1.2(5).

type structure (disphenoidal geometry). To the best of our knowledge, this structural motif is unprecedented in (carbene)copper chemistry⁴⁾. The distortion originates from a strong deviation of the N-atoms from an ideal 90° angle with respect to the C–Cu–C axis. For example, the C(2)–Cu(1)–N(1) angle is 77.67(17)°, while C(22)–Cu(1)–N(1) is significantly larger, 110.42(15)°. No H-atoms were found that could be in a location suitable for completing a possible trigonal bipyramidal or even an octahedral geometry, either *via* agostic or conventional H-bonding to the Cu-center. Notably, the two heterocycles of each ligand are virtually coplanar (N_{py}–C_{py}–N_{NHC}–C_{NHC} 0.8° and 4.3° for the two ligands, resp.). Such an arrangement may favor Cu–C_{NHC} π bonding [14]. However, the mutual torsion of the two carbene heterocycles is 61° (*cf.* angle φ in Fig. 3, *b*), while π-bond interactions of the carbene with metal d orbitals would be largest for 0° or 90° torsion angles. Hence, only a small π contribution is assumed for the Cu–C_{NHC} bonds in complex **7**.

The structure of complex **8b** reveals again a quasi linear Cu-coordination geometry (C–Cu–C 171.5(3)°; Fig. 4). Since the dicarbene ligand is too constrained for *trans* chelation to a metal center, a dimeric structure is formed in which both carbene units of a ligand bind to different Cu-centers. This macrocyclic structural motif is reminiscent of that observed for related silver(I) complexes comprising this type of dicarbene ligand [15]. In the crystal structure of **8b**, the Cu-centers and the two dicarbene ligands are symmetry-related. Presumably as a consequence of the bridging character of the dicarbene ligand, the Cu–C bond length is considerably stretched (average 2.09 Å) and

⁴⁾ A related strongly distorted bis(pyridinyl-carbene)-type structure was reported for a palladium complex [13].

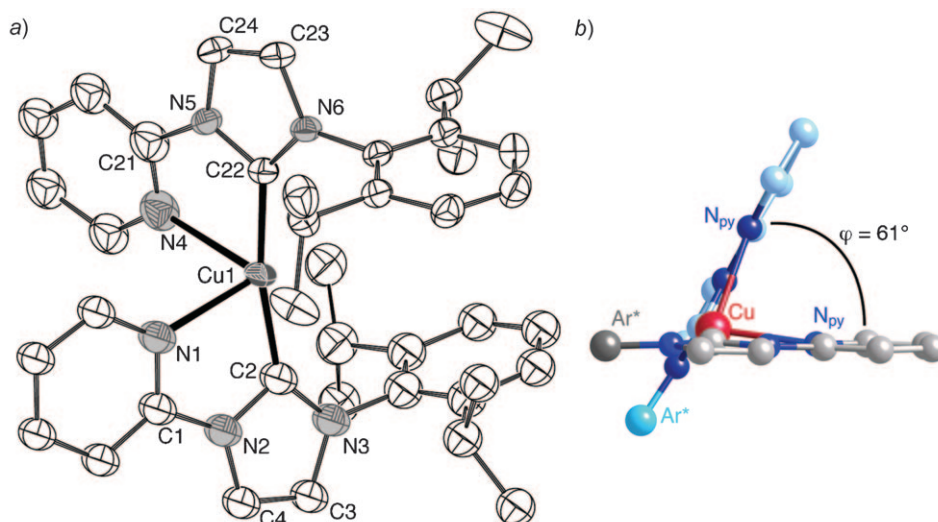


Fig. 3. a) ORTEP Plot of the cationic portion of complex **7** (50% probability; noncoordinating PF₆ anion, co-crystallized Et₂O, and H-atoms omitted). Selected bond lengths [Å]: Cu(1)–C(2) 1.903(5), Cu(1)–C(22) 1.889(4), Cu(1)–N(1) 2.310(4), Cu(1)–N(4) 2.439(4), C(3)–C(4) 1.337(7), and C(23)–C(24) 1.337(6); selected bond angles [°]: C(2)–Cu(1)–C(22) 168.52(19), C(2)–Cu(1)–N(1) 77.67(17), C(2)–Cu(1)–N(4) 114.7(2), C(22)–Cu(1)–N(1) 110.42(15), C(22)–Cu(1)–N(4) 75.19(15), and N(1)–Cu(1)–N(4) 82.67(16); N(2)–C(2)⋯C(22)–N(6) 114.4(5). b) View of the molecular structure of **7**. The perspective along the C(2)–Cu(1)–C(22) vector illustrates the coplanar arrangement of the pyridinyl and the N-heterocyclic carbene heterocycles for each ligand residue (only C_{ipso} of the Ar* wingtip groups are shown).

constitutes the longest Cu–C_{NHC} bond observed thus far. Unlike in monodentate complexes such as **6**, in which the two carbene residues are mutually coplanar, the two heterocycles in **8b** are significantly twisted with a 44.9° torsion angle for the N(1)–C(1)⋯C(7a)–N(3a) system. Since a 45° angle minimizes any π -bond overlap [14], the long Cu–C_{NHC} distances (2.076(9) and 2.112(8) Å, resp., cf. 1.88–1.93 Å in complexes **5–7**) possibly reflect σ -only bonds, which are preserved due to the conformational rigidity of the metallamacrocycle. The separation of the two Cu-centers (Cu 3.2268(7) Å) does not suggest significant metal–metal interactions in **8**.

Carbene-Transfer Ability. Carbene-ligand transfer from a metal to an acceptor site has wide synthetic utility. We initially probed the ability to transfer the carbene ligand from the Cu-center in complexes **5–8** to elemental sulfur. When starting from complex **5**, substitution of the Cu-center by sulfur and formation of the cyclic thiourea species **9** occurred within 4 h at room temperature (*Scheme 2*). The carbene transfer was highly selective and afforded compound **9** in essentially quantitative yields. Product characterization was facilitated by comparison with an authentic sample prepared from the free carbene and sulfur [16]. Notably, tetrasubstituted thioureas are known to be useful precursors for free carbenes [17]. Products identical to **9** were observed when a disulfide such as MeSSMe was used as acceptor in the presence of **5**; however, the reaction proceeded less selectively, and significant amounts of impurities were formed.

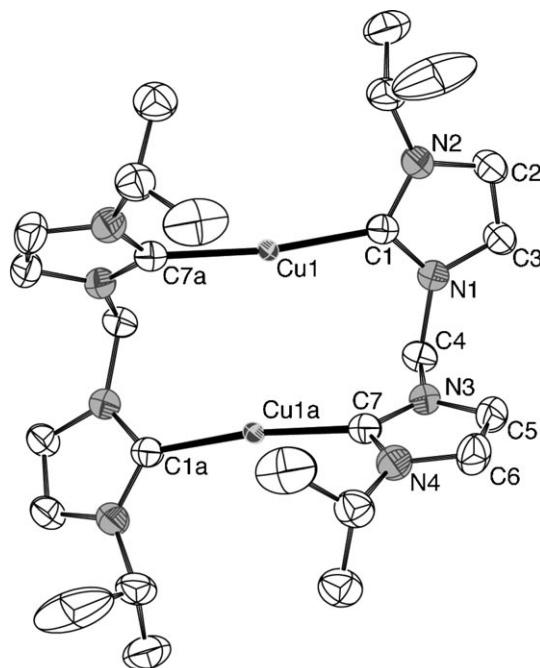
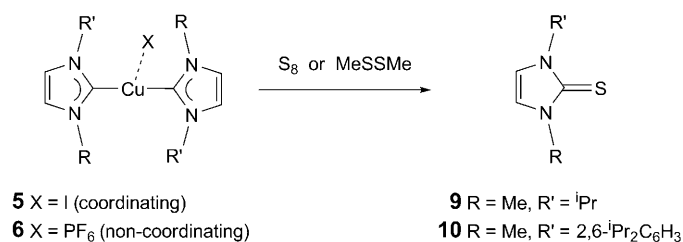


Fig. 4. ORTEP Plot of the cationic portion of complex **8b** (30% probability; noncoordinating anions, co-crystallized solvent molecule, and H-atoms omitted). Selected bond lengths [Å]: Cu(1)–C(1) 2.076(9), Cu(1)–C(7a) 2.112(8), C(2)–C(3) 1.332(12), and C(5)–C(6) 1.321(13); selected bond angles [°]: C(1)–Cu(1)–C(7a) 171.5(3), N(1)–C(1)–N(2) 104.1(7), and N(3)–C(7)–N(4) 107.6(7); N(1)–C(1)⋯C(7a)–N(3a) –44.9(11) and C(1)–Cu(1)⋯Cu(1a)–C(7) 33.5(4).

Scheme 2. Carbene Transfer to Sulfur

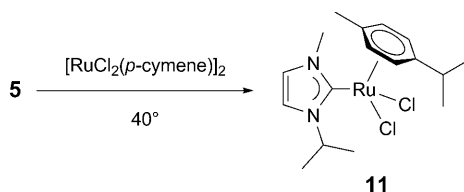


While the carbene transfer was efficiently accomplished with complex **5** comprising alkylated NHC N-atoms, demetallation was slightly slower with the monoarylated carbene **6** (giving **10**, see *Scheme 2*), and it essentially failed with the chelate-stabilized complex **7**. Even upon prolonged heating in 1,2-dichloroethane, no substitution of the Cu-center by sulfur was noted. Apparently, strong chelation increases the stability not only with respect to hydrolysis but also for ligand-transfer reactions. Interestingly, the dinuclear complex **8** did not undergo a clean carbene transfer, and mixtures of products were obtained according to IR and NMR analyses. Mass spectrometry of a purified

sample showed isotope patterns that are diagnostic for Cu-complexes. This result suggests that the formed product still contains Cu-ions, perhaps due to the presence of two, potentially chelating thiourea residues in the anticipated product.

A related transfer of the carbene ligand was also accomplished by using a metal center as acceptor. Upon exposure of complex **5** to $[\text{RuCl}_2(p\text{-cymene})]_2$ ($p\text{-cymene}$ = 1-methyl-4-(1-methylethyl)benzene), the new $[\text{Ru}^{\text{II}}(\text{carbene})]$ complex **11** was formed in excellent yields under mild reaction conditions (40° , 4 h; *Scheme 3*). The spectral properties of this complex are similar to those of closely related (carbene)ruthenium complexes [18] and feature a carbene resonance at $\delta(\text{C})$ 172.

Scheme 3. Carbene Transfer to Ruthenium(II)



The successful use of $[\text{Cu}^{\text{I}}(\text{carbene})]$ complexes for transmetalation may become particularly attractive in cases in which the frequently used procedure *via* $[\text{Ag}^{\text{I}}(\text{carbenes})]$ [19] is impractical. A general applicability of this transmetalation protocol will strongly depend on the accessibility of a wide range of $[\text{Cu}(\text{carbene})]$ precursors and on the versatility of carbene transfer to a variety of (transition) metals.

Conclusions. – Structural analysis of a number of new copper(I) complexes with NHC ligands revealed a rich coordination chemistry and provided structural motifs that have been rare or even unprecedented thus far. Such a structural diversity due to (weak) chelation of wingtip groups may play an important role in the activity and selectivity of Cu^{I} -mediated catalytic transformations. Our results further indicated that low steric shielding of the metal by wingtip substituents increases the reactivity of the carbene–copper bond. Based on these findings, a transmetalation method was established as an alternative to the more popular (carbene)silver(I) route. Selective carbene-ligand transfer may find application in synthesis as well as perhaps in analytics.

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Experimental Part

General. All reactions involving copper(I) salts were carried out under Ar with *Schlenk* techniques. THF and CH_2Cl_2 were dried by passage through solvent-purification columns. The 1*H*-imidazolium salts **1–4** [20] and $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ were prepared according to literature procedures [21], all other chemicals are commercially available and were used as received. IR Spectra: *Mattson-5000-FT-IR* instrument; MeCN solns.; $\tilde{\nu}$ in cm^{-1} . ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectra: *Bruker* spectrometer at 360 and 90 MHz, resp., unless specified otherwise; chemical shifts δ in ppm rel. to residual solvent ^1H or ^{13}C resonances, coupling constants J in Hz; assignments based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift-correlation spectroscopy.

ESI-MS: Bruker-4.7-T-Bio-APEX-II instrument; in MeCN; in *m/z*. Elemental analysis were performed by the Microanalytical Laboratory of the ETH Zürich, Switzerland.

Bis[1,3-dihydro-1-methyl-3-(1-methylethyl)-2H-imidazol-2-ylidene]iodocopper (**5**). A mixture of 1H-imidazolium salt **1** (504 mg, 2.0 mmol), KO^tBu (224 mg, 2.0 mmol), and CuI (194 mg, 1.0 mmol) in dry THF (40 ml) was stirred at r.t. for 12 h. The suspension was filtered through a plug of *Celite*, and the solvent was evaporated. The crude product was redissolved in THF (2 ml) and precipitated by addition of Et₂O (20 ml). This precipitation procedure was repeated twice: **5** (257 mg, 59%). Off-white solid. Crystals suitable for X-ray crystal-structure determination were obtained by slow diffusion of pentane into a THF soln. of **5**. ¹H-NMR (CD₂Cl₂, 360 MHz): 6.95 (s, 2 H_{im}); 6.92 (s, 2 H_{im}); 4.90 (sept., ³J = 6.8, 2 Me₂CH); 3.85 (s, 2 MeN); 1.48 (d, ³J = 6.8, 2 Me₂CH). ¹³C-NMR (CD₂Cl₂, 90 MHz): 182.3 (C–Cu); 121.6 (C_{im}); 116.6 (C_{im}); 53.8 (Me₂CH); 38.2 (MeN); 23.8 (Me₂CH). ESI-MS: 311.2 ([M – I]⁺). Anal. calc. for C₁₄H₂₄CuIN₄ (438.82): C 38.32, H 5.51, N 12.77; found: C 37.99, H 5.31, N 12.15.

Bis[1-[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-3-methyl-2H-imidazol-2-ylidene]copper(I+) Hexafluorophosphate(I–) (1:1) **6**. To a soln. of 1H-imidazolium salt **2** (250 mg, 0.67 mmol) in THF (40 ml) was added KO^tBu (75 mg, 0.67 mmol) and [Cu(MeCN)₄]PF₆ (125 mg, 0.335 mmol). The mixture was stirred at r.t. for 12 h and subsequently filtered through a plug of *Celite*. The solvent was evaporated and the residue washed with Et₂O (2 × 25 ml) and then precipitated from THF (2 ml) by addition of Et₂O (20 ml): **6** (210 mg, 91%). White solid. Crystals suitable for X-ray crystal-structure determination were obtained by slow diffusion of Et₂O into a CH₂Cl₂ soln. of **6**. ¹H-NMR (CDCl₃): 7.41 (t, ³J = 7.7, 2 arom. H); 7.21 (s, 2 H_{im}); 7.20 (d, ³J = 7.7, 4 arom. H); 6.83 (s, 2 H_{im}); 3.30 (s, 2 MeN); 2.27 (sept., ³J = 6.8, 4 Me₂CH); 1.03 (d, ³J = 6.8, 4 Me₂CH). ¹³C-NMR (CDCl₃): 178.5 (C–Cu); 146.1, 134.6, 130.3, 124.0 (4 arom. C); 123.2 (C_{im}); 122.7 (C_{im}); 37.3 (MeN); 28.1 (Me₂CH); 24.5 (Me₂CH); 24.2 (Me₂CH). ESI-MS: 547.3 ([M – PF₆]⁺). Anal. calc. for C₃₂H₄₄CuF₆N₄P (693.24): C 55.44, H 6.40, N 8.08; found: C 55.17, H 6.35, N 7.91.

Bis[1-[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-3-(pyridin-2-yl-κN¹)-2H-imidazol-2-ylidene]-copper(I+) Hexafluorophosphate(I–) (1:1) **7**. To a soln. of 1H-imidazolium salt **3** (200 mg, 0.52 mmol) in THF (40 ml), solid KO^tBu (58 mg, 0.52 mmol) and [Cu(MeCN)₄]PF₆ (97 mg, 0.26 mmol) were added, and the mixture was stirred at r.t. for 6 h. The mixture was then filtered through a plug of *Celite*, and the solvent was evaporated. The crude product was dissolved in a minimum amount of CH₂Cl₂ and precipitated by addition of Et₂O: **7** (100 mg, 47%). Yellow solid. Crystals suitable for a single-crystal structure determination were obtained by slow diffusion of Et₂O into a CH₂Cl₂ soln. of **7**. ¹H-NMR (CDCl₃): 7.99 (d, ³J = 1.8, 2 H_{im}); 7.92–7.83 (m, 6 H_{py}); 7.32 (t, ³J = 7.7, 2 arom. H); 7.19–7.16 (m, 2 H_{py}); 7.09 (d, ³J = 7.7, 4 arom. H); 7.05 (d, ³J = 1.8, 2 H_{im}); 2.39 (sept., ³J = 6.8, 4 Me₂CH); 1.05 (d, ³J = 6.8, 12 H, Me₂CH); 0.62 (d, ³J = 6.8, 12 H, Me₂CH). ¹³C-NMR (CDCl₃): 183.2 (C–Cu); 150.0 (C_{py}–N); 147.2 (C_{py}); 145.2 (2 C_o (Ar)); 140.2 (C_{py}); 135.3 (C_{ipso} (Ar)); 130.0 (C (Ar)); 125.2 (C_{im}); 123.7 (C(Ar)); 123.3 (C_{py}); 117.3 (C_{im}); 112.9 (C_{py}); 28.1 (Me₂CH); 24.1 (Me₂CH); 23.5 (Me₂CH). ESI-MS: 673.3 ([M – PF₆]⁺). Anal. calc. for C₄₀H₄₆CuF₆N₆P (818.27) · 0.25 CH₂Cl₂: C 57.51, H 5.58, N 10.00; found: C 57.82, H 6.03, N 9.96.

Bis{μ-[1,1'-methylenebis[1,3-dihydro-3-(1-methylethyl)-2H-imidazol-2-ylidene]]dicopper(I+) Hexafluorophosphate(I–) (1:2) (**8a**). A soln. of NH₄PF₆ (0.41 g, 2.5 mmol) in H₂O (5 ml) was added to bis[1H-imidazolium] salt **4** (0.20 g, 0.41 mmol) dissolved in H₂O (5 ml). Immediately a precipitate formed, which was separated by filtration, washed with H₂O (2 × 2 ml) and Et₂O (2 × 5 ml), and extracted into MeCN (6 ml). All volatiles were evaporated, thus affording the corresponding bis[1H-imidazolium] bis(hexafluorophosphate) as a white solid (0.22 g, quant.). This salt was suspended in dry MeCN (5 ml), and [Cu(MeCN)₄]PF₆ (150 mg, 0.40 mmol) was added, followed by KO^tBu (148 mg, 1.3 mmol). The mixture was stirred for 16 h and then filtered. Addition of Et₂O (20 ml) to the filtrate induced precipitation. The solid was collected, washed with Et₂O, and dried *in vacuo*: **8a** (201 mg, 56%). White powder. ¹H-NMR (CD₃CN, 360 MHz): 7.43 (s, 4 H_{im}); 7.19 (s, 4 H_{im}); 6.34 (A (d) of AB, ²J = 13.5, 2 H, NCH₂N); 5.83 (B (d) of AB, ²J = 13.5, 2 H, NCH₂N); 4.33 (sept., ³J = 6.7, 4 Me₂CH); 1.33 (d, ³J = 6.7, 12 H, Me₂CH); 1.04 (d, ³J = 6.7, 12 H, Me₂CH). ¹³C-NMR (CD₃CN, 100 MHz): 176.7 (C–Cu); 122.5 (C_{im}); 120.0 (C_{im}); 64.6 (NCH₂N); 55.1 (Me₂CH); 23.8 (Me₂CH).

Bis{μ-[1,1'-methylenebis[1,3-dihydro-3-(1-methylethyl)-2H-imidazol-2-ylidene]]dicopper(I+) Hexafluorophosphate(I–) Tetrafluoroborate(I–) (1:1:1) (**8b**). As described for **8a**, with **4** (0.96 g,

2.0 mmol), AgBF₄ (0.78 g, 4.0 mmol) instead of NH₄PF₆, KO^tBu (0.58 g, 5.2 mmol), and [Cu(MeCN)₄]PF₆ (0.74 g, 2.0 mmol): **8b** (1.32 g, 85%). Gray solid. Spectroscopic data: identical to those of **8a**.

General Procedure for Carbene Transfer to Sulfur. To a soln. of (carbene)copper(I) in CHCl₃ (20 mm) was added elemental sulfur (5 mol-equiv.), and the suspension was stirred at r.t. for 16 h. The mixture was filtered through *Celite* and the filtrate was concentrated to give the cyclic thiourea product as an off-white solid in essentially quant. yield.

1,3-Dihydro-1-methyl-3-(1-methylethyl)-2H-imidazol-2-thione (9): IR (MeCN): 1224 (ν (C=S)). ¹H-NMR (CDCl₃): 6.72 (s, 1 H_{im}); 6.70 (s, 1 H_{im}); 5.08 (sept., ³J = 6.8, 1 Me₂CH); 3.61 (s, MeN); 1.35 (d, ³J = 6.8, Me₂CH). ¹³C-NMR (CDCl₃): 161.1 (C=S); 117.9 (C_{im}); 112.6 (C_{im}); 48.8 (Me₂CH); 34.7 (MeN); 21.8 (Me₂CH). Anal. calc. for C₇H₁₂N₂S (156.25): C 53.81, H 7.74, N 17.93; found: C 53.91, H 7.58, N 17.80.

1,3-Dihydro-1-[2,6-bis(1-methylethyl)phenyl]-3-methyl-2H-imidazol-2-thione (10): IR: 1226 (ν (C=S)). ¹H-NMR (CD₂Cl₂, 500 MHz): 7.50 (t, ³J = 7.8, 1 arom. H); 7.30 (d, ³J = 7.8, 2 arom. H); 6.98 (d, ³J = 2.3, 1 H_{im}); 6.76 (d, ³J = 2.3, 1 H_{im}); 3.77 (s, MeN); 2.45 (sept., ³J = 6.9, 2 Me₂CH); 1.25 (d, ³J = 6.9, Me₂CH); 1.08 (d, ³J = 6.9, Me₂CH). ¹³C-NMR (CD₂Cl₂, 125 MHz): 146.75, 133.32, 130.91, 124.91 (4 arom. C); 120.03 (C_{im}); 119.74 (C_{im}); 36.58 (MeN); 28.88 (Me₂CH); 24.62, 23.68 (2 Me₂CH); C=S not observed. ESI-HR-MS (pos.): 297.13990 ([M + Na]⁺, C₁₆H₂₂N₂NaS⁺; calc. 297.13959).

Dichloro-[1,3-dihydro-1-methyl-3-(1-methylethyl)-2H-imidazol-2-ylidene]-(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]ruthenium (11). A soln. of [RuCl₂(*p*-cymene)]₂ (122 mg, 0.2 mmol) in CH₂Cl₂ (10 ml) was added to a soln. of **5** (88 mg, 0.2 mmol) in CH₂Cl₂ (5 ml) (→ white precipitate). The mixture was stirred at 40° for 4 h and subsequently filtered through *Celite*. All volatiles were evaporated, and the residue was washed with Et₂O (3 × 5 ml): **11** (84 mg, 96%). Dark orange solid. ¹H-NMR (CDCl₃): 7.06 (s, 1 H_{im}); 7.00 (s, 1 H_{im}); 5.4 (br. s, 2 arom. H); 5.30 (sept., ³J = 7.0, Me₂CHN); 5.1 (br. s, 2 arom. H); 3.99 (s, MeN); 2.94 (sept., ³J = 6.8, Me₂CHC); 2.08 (s, Me); 1.44 (d, ³J = 7.0, Me₂CHN); 1.26 (d, ³J = 6.8, Me₂CHC). ¹³C-NMR (CDCl₃): 172.1 (C–Ru); 124.2 (C_{im}); 118.6 (C_{im}); 107.9 (arom. C); 98.96 (arom. C); 52.3 (Me₂CHN); 39.5 (MeN); 30.7 (Me₂CHC); 24.9 (Me₂CHN); 22.9 (Me₂CHC); 18.6 (Me₂CHN); 2 arom. CH not resolved. ESI-MS: 395.5 ([M – Cl]⁺). Anal. calc. for C₁₇H₂₆Cl₂N₂Ru (430.05): C 47.44, H 6.09, N 6.51; found: C 47.45, H 6.01, N 6.46.

Crystal-Structure Determinations (Table). Suitable single crystals were mounted on a *Stoe-Mark-II-Imaging-Plate* diffractometer system (*Stoe & Cie*, 2002) equipped with a graphite monochromator. Data collection was performed at –100° by using MoK_α radiation (λ 0.71073 Å) with a nominal crystal-to-detector distance of 70 mm (for **6**), 100 mm (for **7** and **8b**), and 135 mm (for **5**), resp. All structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least squares on *F*² with SHELXL-97 [22]. The H-atoms were included in calc. positions and treated as riding atoms with SHELXL-97 default parameters. All non-H-atoms were refined anisotropically, except for partially occupied solvent atoms, which were refined isotropically. For structure **5** and **8b**, a semiempirical absorption correction was applied with MULscanABS as implemented in PLATON03 [23].

Crystals of complex **7** contained half a molecule Et₂O in the asymmetric unit, which showed pronounced disorder. Therefore, the SQUEEZE option in PLATON03 was used to calculate the potential solvent-accessible volume (190 Å³, containing ca. 29 electrons). One Et₂O molecule (42 electrons) per unit cell was hence included in all further calculations. A disordered region of electron density was also found in crystals of **8b** and was removed using the SQUEEZE routine (676 Å³, ca. 197 electrons). One molecule of Et₂O per complex molecule was therefore included. Due to this disorder problem, the anions (PF₆[–] and BF₄[–] each half occupied) and parts of the ligand were refined with the same thermal values. Further details on data collection and refinement parameters are collected in the *Table*. CCDC 707733-707736 contain the supplementary crystallographic data for **5–8**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table. Crystallographic Data and Structure Refinement of Complexes 5–8

	5	6	7	8b
Color, shape	colorless block	colorless rod	yellow block	colorless rod
Size [mm]	0.45 × 0.35 × 0.25	0.45 × 0.40 × 0.35	0.50 × 0.35 × 0.30	0.35 × 0.30 × 0.30
Empirical formula	C ₁₄ H ₂₄ CuIN ₄	C ₃₂ H ₄₄ CuF ₆ N ₄ P	C ₄₀ H ₄₆ CuF ₆ N ₆ P · 0.5 C ₄ H ₁₀ O	C ₂₆ H ₄₀ BCu ₂ F ₁₀ N ₈ P · C ₄ H ₁₀ O
<i>M_r</i>	438.81	693.22	856.40	897.64
<i>T</i> [K]	223(2)	223(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>a</i> [Å]	13.8629(17)	9.5806(8)	10.5582(7)	21.9106(14)
<i>b</i> [Å]	10.5896(9)	13.2996(17)	13.2927(10)	14.3407(9)
<i>c</i> [Å]	13.0641(17)	14.3559(11)	15.7373(12)	14.0843(10)
α [°]	90	90	102.112(6)	90
β [°]	108.029(10)	105.623(9)	96.793(6)	115.929(5)
γ [°]	90	90	96.490(6)	90
<i>V</i> [Å ³]	1823.7(4)	1761.6(3)	2122.6(3)	3980.0(5)
<i>Z</i>	4	2	2	4
<i>D</i> _{calc} [g cm ⁻³]	1.598	1.307	1.340	1.498
μ [mm ⁻¹] (MoK α)	2.887	0.724	0.617	1.192
Total reflections	10686	13730	27538	17488
Unique reflections	2453	3344	11389	3756
<i>R</i> _{int}	0.0679	0.0480	0.0469	0.0394
Transm. range	0.317–0.646	–	–	0.606–0.694
No. parameters	95	204	353	164
No. restraints	0	6	2	16
<i>R</i> ^a , <i>R</i> _w ^b)	0.0378, 0.0973	0.0585, 0.1515	0.0856, 0.2340	0.0926, 0.2792
G.o.f.	1.015	0.951	1.119	1.274
Largest peak, hole [e Å ⁻³]	–1.743, 1.113	–0.804, 0.838	–2.154, 1.572	–2.262, 1.886

^a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for all $I > 2\sigma(I)$. ^b) $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

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