

Synthesis and Characterization of [Cu(NHC)₂]X Complexes: Catalytic and Mechanistic Studies of Hydrosilylation Reactions

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Abstract: The preparation of two series of [Cu(NHC)₂]X complexes (NHC = N-heterocyclic carbene, X = PF₆ or BF₄) in high yields from readily available materials is reported. These complexes have been spectroscopically and structurally characterized. The activity of these cationic bis-NHC complexes in the hydrosilylation of ketones was examined, and both the ligand and the counterion showed a significant influence on the catalytic performance. Moreover, when compared with related

[Cu(NHC)]-based systems, these cationic complexes proved to be more efficient under similar reaction conditions. The activation step of [Cu(NHC)₂]X precatalysts towards hydrosilylation was investigated by means of ¹H NMR spectroscopy. Notably, it was shown that one of the *N,N'*-bis(2,6-di-

isopropylphenyl)imidazol-2-ylidene (IPr) ligands in [Cu(IPr)₂]BF₄ is displaced by *t*BuO⁻ in the presence of NaOtBu, producing the neutral [Cu(IPr)(OtBu)]. This copper alkoxide is known to be a direct precursor of an NHC-copper hydride, the actual active species in this transformation. Furthermore, reagent loading and counterion effects have been rationalized in light of the species formed during the reaction.

Keywords: copper • hydrosilylation • ketones • N-heterocyclic carbenes • reaction mechanisms

Introduction

The reduction of carbonyl and pseudocarbonyl functions is an essential transformation in organic synthesis.^[1] Main-group metal hydrides, in particular those of boron and aluminum, can accomplish this transformation, but they are required in stoichiometric amounts, which renders them unattractive from both practical and economic points of view.

Transition-metal catalysis has been successfully applied for the reduction of olefins, alkynes, and many carbonyl compounds by hydrogenation or hydrosilylation.^[2] Hydrogenation reactions often proceed in good yields, but only under high pressure or elevated temperature. In contrast, since the first report of a metal-catalyzed hydrosilylation of ketones in the presence of the Wilkinson's catalyst,^[3] smooth reaction conditions can be employed, and in consequence, over-reduced products are rarely detected. A sequence of hydrosilylation/hydrolysis reactions leads to the formation of alcohols and amines. Alternatively, the silyl group can also be retained as a protecting group, a process that is of great interest in organic synthesis. Moreover, this approach replaces the use of hazardous dihydrogen with easy-to-handle hydrosilanes.

Pioneering work by Stryker et al. showed that hexameric [CuH(Ph₃P)]₆ was an efficient reagent in the conjugate reduction of a number of carbonyl derivatives, with high regioselectivity.^[4] This stabilized form of copper hydride, which was first reported by Osborn et al.,^[5] put an end to the assumption that Cu-H was too unstable to have any potential applications in organic chemistry.^[6] The combination of the Stryker's catalyst and a hydrosilane as a hydride source allowed the regioselective conjugate reduction of carbonyl compounds under mild conditions.^[7] This methodology has

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been expanded to different hydrosilanes and ancillary ligands,^[8] and developed asymmetrically.^[9]

N-Heterocyclic carbenes (NHCs)^[10] are an interesting alternative to phosphines for the copper-catalyzed hydrosilylation of carbonyl groups. [CuCl(IPr)] (IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is an efficient catalyst for the hydrosilylation of unhindered ketones^[11] and for the conjugate reduction of tri- and tetra-substituted α,β -unsaturated ketones and esters.^[12] More challenging ketones can be hydrosilylated in the presence of [CuCl(ICy)] (ICy = *N,N'*-bis(cyclohexyl)imidazol-2-ylidene) or [CuCl(SIMes)] (SIMes = *N,N'*-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene).^[13] In addition, we recently reported the preparation and application of [Cu(IPr)₂]X complexes (**1a**: X = PF₆, **1b**: X = BF₄) in catalysis.^[14] Herein, we describe the preparation and characterization of two series of homoleptic bis-NHC complexes, and explore their catalytic activity in the hydrosilylation of ketones. The structures of the NHC ligands employed in this study are shown in Figure 1.

Results and Discussion

Synthesis of [Cu(NHC)₂]X complexes: Two series of [Cu(NHC)₂]X complexes (**2a–7a**, **2b–7b**) were synthesized in very good yields from the corresponding tetrakis(acetonitrile)copper(I) and azolium salts in the presence of a strong base (Table 1).^[14] An excess of base was generally used to ensure total conversion of the carbene precursor. However, these conditions were avoided in the case of complexes **5** and **7**, bearing ICy and *ItBu* ligands, because partial decomposition of the expected products was observed if an excess of base was used. The pure white complexes isolated are

Abstract in Spanish: *Se presenta la preparación de dos series de complejos [Cu(NHC)₂]X (NHC = carbeno N-heterocíclico, X = PF₆ o BF₄) en altos rendimientos a partir de materiales de fácil acceso. Estos complejos han sido caracterizados espectroscópicamente y estructuralmente. La actividad de estos complejos catiónicos bis-NHC en la hidrosililación de cetonas ha sido examinada y el ligando así como el contra-ión mostraron una influencia significativa en la eficacia catalítica. Además, al compararlos con otros sistemas [Cu(NHC)] relacionados, estos complejos catiónicos mostraron ser más eficientes bajo similares condiciones de reacción. La activación de los pre-catalizadores [Cu(NHC)₂]X hacia la hidrosililación ha sido investigada mediante ¹H RMN. En particular, se ha mostrado que uno de los ligandos IPr en [Cu(IPr)₂]BF₄ es desplazado por *t*BuO[−] en la presencia de NaOtBu, produciendo el complejo neutral [Cu(IPr)(OtBu)]. Este alcóxido de cobre es conocido como un precursor directo de un hidruro de NHC-cobre, la verdadera especie activa en esta transformación. Asimismo, la influencia de la carga de reactivos y del contra-ión han sido racionalizados según las especies formadas en la reacción catalítica.*

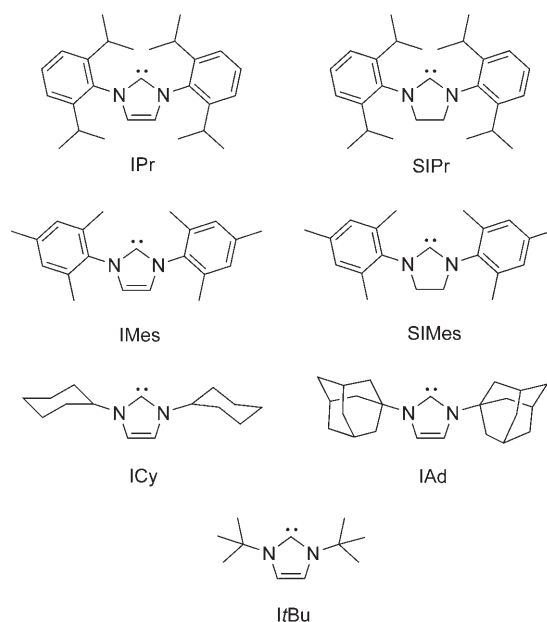


Figure 1. Structures of the NHC ligands studied.

Table 1. Preparation of [Cu(NHC)₂]X complexes.

[Cu(NCCH ₃) ₄]X + 2 NHC·HBF ₄		NaOtBu		[Cu(NHC) ₂]X	
		THF, RT, t			
NHC	X	Complex	Base [equiv]	t [h]	Yield [%]
SIPr	PF ₆	2a	1.3	15	68
SIPr	BF ₄	2b	1.3	6	63
IMes	PF ₆	3a	1.0	15	91
IMes	BF ₄	3b	1.3	15	74
SIMes	PF ₆	4a	1.3	15	86
SIMes	BF ₄	4b	1.3	15	86
ICy	PF ₆	5a	1.0	15	80
ICy	BF ₄	5b	1.1	15	93
IAd	PF ₆	6a	1.3	15	84
IAd	BF ₄	6b	1.3	15	95
<i>ItBu</i>	PF ₆	7a	1.1	6	99
<i>ItBu</i>	BF ₄	7b	1.1	6	100

highly stable to air and moisture with the exceptions of **7a** and **7b**.^[15] These *ItBu*-containing complexes decomposed slowly over several weeks, but this could be avoided by simply flushing the storage vial with an inert atmosphere, for example, argon.

The ¹H NMR spectra of complexes **3a**, **3b**, **5–7a**, and **5–7b**, which contain unsaturated NHC ligands, are characterized by a single resonance signal for the two imidazole protons at low field ($\delta = 7.34–7.64$ ppm), as well as signals that are characteristic of their corresponding side chains. The ¹³C NMR spectra give rise to characteristic low-field resonance signals for the carbenic carbon at around $\delta = 175$ ppm. Saturated complexes **2a**, **2b**, **4a**, and **4b** result in ¹H NMR spectra with resonances at around $\delta = 4.00$ ppm for the protons in the imidazole ring, and the expected signals for the mesityl and isopropylphenyl side chains. For these complexes, the ¹³C NMR spectroscopy data show one signal

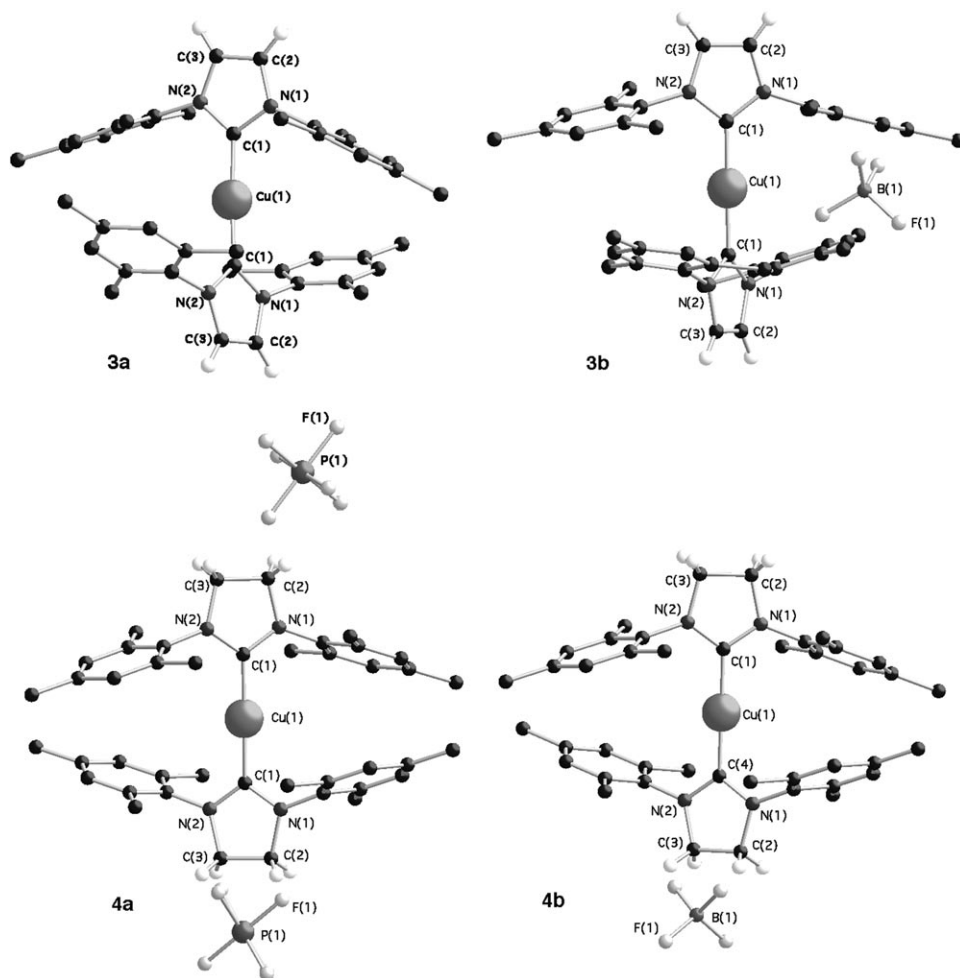


Figure 2. Ball and stick representations of $[\text{Cu}(\text{IMes})_2]\text{PF}_6$ (**3a**), $[\text{Cu}(\text{IMes})_2]\text{BF}_4$ (**3b**), $[\text{Cu}(\text{SIMes})_2]\text{PF}_6$ (**4a**), and $[\text{Cu}(\text{SIMes})_2]\text{BF}_4$ (**4b**). Most hydrogen atoms have been omitted for clarity.

for the carbenic carbon atoms at significantly lower field ($\delta = 200$ ppm) when compared with that of their unsaturated analogues. No influence of the counterion in the NMR spectroscopic data was observed.

Crystallographic studies were carried out to unambiguously confirm the structures of these complexes. Crystals suitable for X-ray diffraction were grown for complexes **2a**, **3a**, **3b**, **4a**, **4b**, **6a**, **6b**, and **7b**. Repeated attempts to crystallize the other complexes were unsuccessful and generally led to the formation of decomposition products and the corresponding azolium salt. Ball and stick representations of the complexes are given in Figure 2 (**3a**, **3b**, **4a**, and **4b**) and Figure 3 (**6a**, **6b**, **2a**, and **7b**). A comparison of selected bond lengths and angles is provided in Tables 2 and 3 and relevant crystallographic data for these complexes are summarized in Table 4. All of the complexes have a two-coordinate copper(I) atom in a near-linear environment with a C–Cu–C angle very close to or equal to 180° . As seen for other crystallographically characterized complexes that contain NHC ligands with *N*-aryl substituents, the aryl groups are twisted almost perpendicularly with respect to the imidazole plane, which results in a favorable steric arrangement with

the metal center. For all compounds, the Cu–C bond lengths lie in the range of 1.87 to 2.00 \AA , comparable to the reported Cu–C bond lengths in bis-NHC complexes.^[16] An increase in the Cu–C distances as a function of steric hindrance of the *N*-aryl substituent was observed. The bulkiness brought by such substituents could also be correlated to the torsion angle between the ligands. Complexes with the bulkiest ligands (IAd and IrBu; **6a**, **6b**, and **7b**) have the longest Cu–C bond lengths and a torsion angle between the ligands of close to 90° (Table 3, last entry). Complexes **4** and **5**, which have the less hindering ligands IMes and SIMes, have shorter Cu–C bond lengths and smaller torsion angles. Complex **2a** (Table 2), which has two bulky SIPr ligands, has a long Cu–C bond length, but the ligands are only slightly twisted. In this particular case, the presence of two sp^3 carbon atoms in the heterocyclic ring allowed the formation of torsion angles of 15.7 and 8.7° in the saturated backbones of the SIPr ligands. Interestingly, SIMes complexes **4a** and **4b** do not show such a feature and the imidazoline rings are planar. We assume that in the case of **2a**, the steric congestion around the metal center owing to the isopropyl groups is preferentially released by the torsion of the imidazoline rings rather than by ligand twisting.

In **3b**, the unit cell contains two independent half-molecules of the $[\text{Cu}(\text{IMes})_2]^+$ cation and the BF_4^- anion. The geometries of each pair of cations and anions are constrained by a crystallographic two-fold rotation axis passing through the copper and boron atoms, respectively. In **4a**, the PF_6^- anion was disordered and the positions of the six independent fluorine atoms were assigned fixed site occupancy factors of 0.25 and refined by restraining the twelve F...F distances along the edges of the octahedral array of fluorine atoms to $(2.24 \pm 0.02) \text{ \AA}$. On the other hand, both Cu(1) and P(1) lie at the intersection of three orthogonal two-fold rotation axes and the carbenic carbon, labeled C(1), lies on one of the crystallographic C_2 axes that passes through Cu(1). Similarly, unusually large thermal ellipsoids were observed for the independent fluorine atom of the tetrafluoroborate anion in **7b**, which reflects significant vibrational motion normal to the B–F bonds within this anion. Finally,

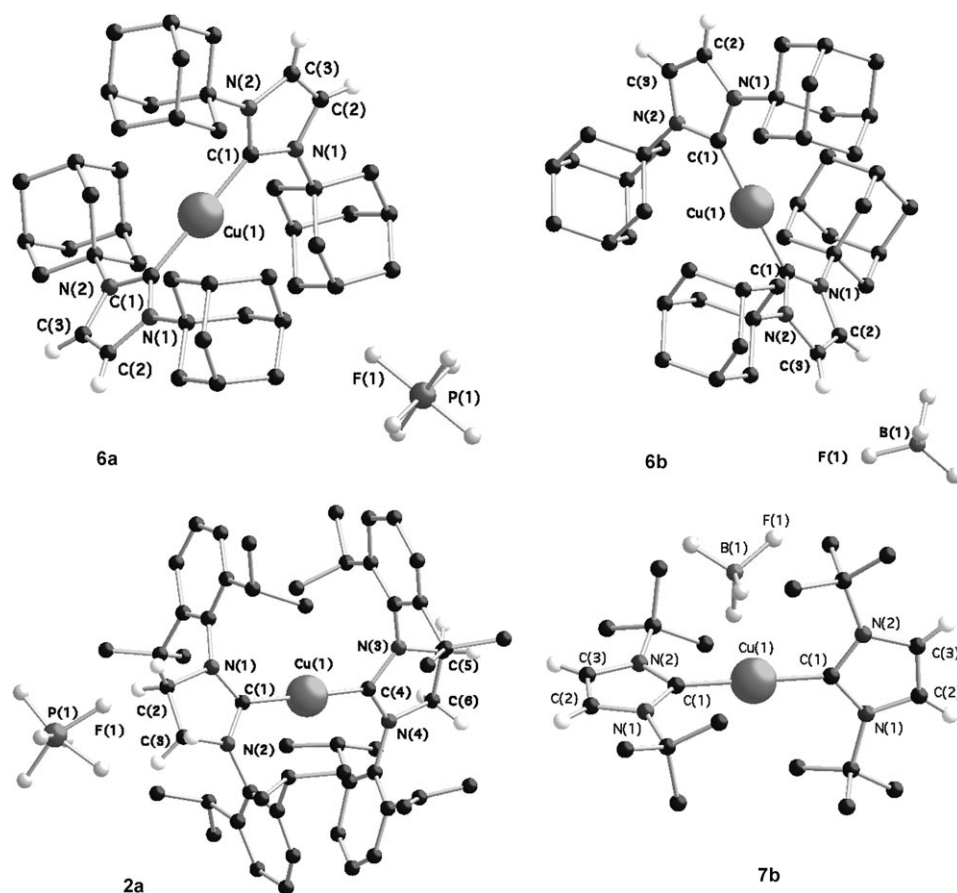


Figure 3. Ball and stick representations of [Cu(IAd)₂]*PF*₆ (**6a**), [Cu(IAd)₂]*BF*₄ (**6b**), [Cu(SIPr)₂]*PF*₆ (**2a**), and [Cu(IrBu)₂]*BF*₄ (**7b**). Most hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complex **2a**.

Cu(1)–C(1)	2.000(15)	C(1)–Cu(1)–C(4)	179.0(7)
Cu(1)–C(4)	1.910(15)	N(1)–C(1)–N(2)	109.2(12)
N(1)–C(1)	1.297(16)	N(3)–C(4)–N(4)	104.9(11)
N(3)–C(4)	1.390(16)	C(3)–C(2)–N(1)	101.7(11)
N(2)–C(1)	1.306(17)	C(6)–C(5)–N(3)	101.7(10)
N(4)–C(4)	1.366(16)	N(1)–C(1)–C(4)–N(3)	28.24
N(1)–C(2)	1.485(17)		
N(3)–C(5)	1.488(16)		
N(2)–C(3)	1.450(18)		
N(4)–C(6)	1.519(18)		
C(2)–C(3)	1.52(2)		
C(5)–C(6)	1.50(2)		
Cu(1)···P(1)	8.338		

Table 3. Selected bond lengths [Å] and angles [°] for complexes **3a**, **3b**, **4a**, **4b**, **6a**, **6b**, and **7b**.

	3a	3b ^[a]	4a	4b	6a	6b	7b
Cu(1)–C(1)	1.871(3)	1.884(2)	1.899(3)	1.896(4)	1.938(5)	1.933(5)	1.909(2)
N(1)–C(1)	1.353(3)	1.349(2)	1.328(2)	1.331(3)	1.367(4)	1.357(6)	1.360(2)
N(2)–C(1)	1.357(3)	1.349(2)	1.328(2)	1.331(3)	1.367(4)	1.368(6)	1.360(2)
N(1)–C(2)	1.382(4)	1.382(2)	1.483(3)	1.487(4)	1.394(5)	1.370(6)	1.376(2)
N(2)–C(3)	1.386(4)	1.383(2)	1.483(3)	1.487(4)	1.394(5)	1.388(6)	1.376(2)
C(2)–C(3)	1.337(4)	1.336(3)	1.531(5)	1.531(6)	1.335(7)	1.334(6)	1.337(4)
Cu(1)···P(1) or B(1)	7.961	7.586	7.332	7.151	7.092	7.746	7.475
C(1)–Cu(1)–C(1)'	175.15(11)	179.88(9)	180.0	180.0	180.0	177.97(19)	180.0
N(1)–C(1)–N(2)	104.2(2)	104.33(15)	109.1(3)	109.2(4)	104.2(4)	104.2(4)	104.95(15)
C(3)–C(2)–N(1)	106.7(3)	106.34(17)	102.3(1)	102.36(16)	107.1(2)	107.9(4)	107.31(9)
N(1)–C(1)–C(1)–N(1)'	67.05	54.00	27.74	30.05	80.55	85.76	82.10

[a] Two molecular units are present.

short distances in space were observed in several examples between hydrogen atoms in the NHC backbone and the fluorine atoms in the counterion. H···F distances of around 3 Å are present in **2a**, **3a**, **4a**, **6a**, and **6b** and the closest contacts are 2.468, 2.695, or 2.314 Å in **3a**, **6a**, and **6b**, respectively. These values are close to or smaller than the sum of the van der Waals radii of hydrogen and fluorine (2.55 Å), and therefore, these data could imply that there is some interaction. However, the distances do not fall into the usual range for hydrogen bonds.

Catalytic studies on the hydrosilylation of ketones: We investigated the catalytic activity of complexes **2–7** in the hydrosilylation of carbonyl compounds. Cyclohexanone was used as a model substrate under the reaction conditions we previously reported for complexes **1a** and **2b**.^[14] The results are presented in Table 5. Low conversions to the silyl ether were obtained with IMes-, SIMes-, and *Ir*Bu-

containing complexes; ICy-containing complexes **5a** and **5b** and SIPr-containing complexes **2a** and **2b** led to good conversion after relatively short reaction times. As often observed, these screening results cannot be rationalized by purely steric or electronic effects.^[10f] The less bulky ligands, IMes and SIMES, were not efficient in this transformation, nor was the very bulky *Ir*Bu ligand. Furthermore, we observed a significant counterion effect and the BF₄[–] compounds were systematically superior to their PF₆[–] analogues. The most important difference was observed with the bis-IAd complexes: whereas reduction of cyclohexanone was

Table 4. Crystallographic data for **2a**, **3a**, **3b**, **4a**, **4b**, **6a**, **6b**, and **7b**.

	2a	3a	3b	4a	4b	6a	6b	7b
formula	C ₃₄ H ₇₆ CuF ₆ N ₄ P	C ₄₂ H ₄₈ CuF ₆ N ₄ P	C ₄₂ H ₄₈ BCuF ₄ N ₄	C ₄₂ H ₅₂ CuF ₆ N ₄ P	C ₄₂ H ₅₂ BCuF ₄ N ₄	C ₄₆ H ₆₄ CuF ₆ N ₄ P	C ₄₉ H ₇₀ BCuF ₄ N ₄	C ₂₂ H ₄₀ BCuF ₄ N ₄
<i>M</i> [g mol ⁻¹]	989.70	817.35	759.19	821.39	763.23	881.52	881.44	510.93
<i>T</i> [K]	150(2)	150(2)	295(2)	223(2)	150(2)	150(2)	150(2)	295(2)
crystalline system	monoclinic	triclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	tetragonal
space group	Cc	<i>P</i> $\bar{1}$	<i>Pnna</i>	<i>Pnnn</i>	<i>Pnnn</i>	<i>I</i> 222	<i>Pna</i> 2 ₁	<i>P</i> 4 ₁ / <i>nbc</i>
<i>a</i> [Å]	17.6928(8)	10.9435(5)	16.155(1)	8.2343(6)	8.1289(6)	11.4622(5)	40.1657(18)	12.0350(5)
<i>b</i> [Å]	17.7186(8)	12.1449(6)	31.477(2)	12.1349(9)	11.7680(8)	12.3125(5)	19.3869(9)	12.0350(5)
<i>c</i> [Å]	16.7094(7)	15.7673(7)	16.007(1)	20.6916(15)	20.4815(14)	14.1833(6)	11.3387(5)	17.7379(10)
α [°]	90.00	91.1810(10)	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	99.4310(10)	94.2690(10)	90.00	90.00	90.00	90.00	90.00	90.00
γ [°]	90.00	92.4800(10)	90.00	90.00	90.00	90.00	90.00	90.00
<i>V</i> [Å ³]	5167.5(4)	2087.23(17)	8139.6(10)	2067.6(3)	1959.3(2)	2001.67(15)	8829.3(7)	2569.2(2)
<i>Z</i>	4	2	8	2	2	2	8	4
ρ_{calcd} [g cm ⁻³]	1.272	1.301	1.239	1.319	1.294	1.463	1.326	1.321
μ [mm ⁻¹]	0.514	0.622	5.88	6.28	0.611	0.654	0.554	8.95
<i>F</i> (000)	2104	852	3184	860	804	932	3760	1080
crystal size [mm]	0.60 × 0.25 × 0.15	0.50 × 0.30 × 0.20	0.32 × 0.40 × 0.50	0.12 × 0.28 × 0.38	0.60 × 0.30 × 0.15	0.70 × 0.50 × 0.30	0.80 × 0.40 × 0.20	0.15 × 0.30 × 0.40
θ [°]	1.64–20.00	2.10–20.00	1.29–27.52	2.66–27.50	2.70–20.00	2.19–20.00	1.01–20.00	2.30–27.50
index range								
<i>h</i>	±16	±10	–21 to 20	–10 to 9	±7	±11	±38	–14 to 15
<i>k</i>	±17	±11	±40	±15	±11	±11	±18	±15
<i>l</i>	±16	±15	–20 to 19	±26	±19	±13	±10	–23 to 22
no. of data	4788	3887	9309	2374	920	921	8215	1480
no. of restraints	689	488	0	12	110	146	1203	1
parameters	612	500	483	168	124	134	1086	79
Gof on <i>F</i> ²	1.080	1.058	1.047	1.081	1.115	1.118	1.086	1.053
R values (all data)	<i>R</i> ₁ = 0.0664 <i>wR</i> ₂ = 0.1652	<i>R</i> ₁ = 0.0311 <i>wR</i> ₂ = 0.0689	<i>R</i> ₁ = 0.0848 <i>wR</i> ₂ = 0.1573	<i>R</i> ₁ = 0.0570 <i>wR</i> ₂ = 0.1271	<i>R</i> ₁ = 0.0348 <i>wR</i> ₂ = 0.0839	<i>R</i> ₁ = 0.0272 <i>wR</i> ₂ = 0.0721	<i>R</i> ₁ = 0.0373 <i>wR</i> ₂ = 0.0885	<i>R</i> ₁ = 0.0606 <i>wR</i> ₂ = 0.1506

Table 5. Catalyst screening for the hydrosilylation of cyclohexanone.

Complex	Conversion ^[a] [%] <i>t</i> = 0.5 h	Conversion ^[a] [%] <i>t</i> = 2 h	Conversion ^[a] [%] <i>t</i> = 24 h
1a ^[b]	30	99	–
1b ^[b]	99	–	–
2a	22	89	97 (2.5 h)
2b	64	97 (1 h)	–
3a	<5	<5	<5
3b	<5	<5	<5
4a	<5	<5	11
4b	6	17	52
5a	7	30	97 (8 h)
5b	9	41	94 (4 h)
6a	<5	5	12
6b	17	52	98 (4 h)
7a	<5	<5	24
7b	<5	12	49

[a] Determined by GC. [b] Values from reference [14].

completed in 4 h in the presence of **6b**, only 12% of the expected silyl ether was formed with **6a** after 24 h.

We were also interested in the possible influence of the NHC ligand and/or counterion on the diastereoselectivity of the reaction. Cationic catalysts capable of reaching comple-

tion in the reaction with the model substrate were then screened for the hydrosilylation of 2-methylcyclohexanone. As shown in Table 6, no significant differences were observed, which indicates that NHC ligands are moderately diastereo-directing for this particular reaction. The reactivity trend depending on the counterion was also confirmed here, although there was no influence on the diastereoselectivity. For the sake of comparison, the reaction was also carried

Table 6. Influence of copper catalyst on the diastereoselectivity of the reaction.

Complex	<i>t</i> [h]	Yield ^[a] [%]	<i>cis/trans</i> ^[b]
[CuCl(IPr)]	1	95	20:80
1a ^[c]	6	92	10:90
1b ^[c]	3	90	15:85
2a	24	50 ^[d]	10:90
2b	24	60 ^[d]	10:90
5a	10	98	15:85
5b	6	99	20:80
6b	24	95	25:75

[a] Isolated yields are the average of two runs. [b] Determined by ¹H NMR spectroscopy. [c] Values from reference [14]. [d] Conversion determined by ¹H NMR spectroscopy.

out with [CuCl(IPr)] as the catalyst,^[13] again with no effect on the diastereoisomeric ratio.

Another trend can be observed from the results presented in Table 6. The methyl group in the α position to the carbonyl group considerably prolonged the required reaction times. This effect was especially significant for SIPr-containing complex **2b**: whereas cyclohexanone was reduced in 1 h, only 60% conversion was obtained for 2-methylcyclohexanone after 24 h. However, ICy-based complexes showed the smallest influence of the steric hindrance around the carbonyl group. These observations are consistent with our previous results concerning hydrosilylation reactions in the presence of [CuCl(NHC)] complexes.^[13]

To verify this trend, the more hindered ketone, dicyclohexyl, was used as a model substrate for comparing our different catalytic systems (Table 7). When comparing the ac-

Table 7. Comparison of catalysts.

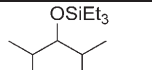
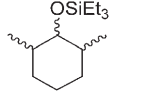
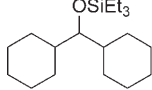
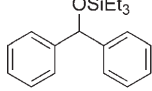
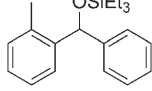
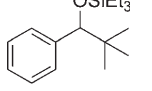
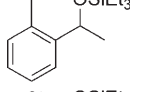
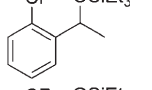
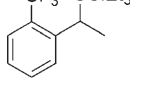
Entry	Complex	Et ₃ SiH [equiv]	Solvent	T [°C]	t [h]	Yield ^[a] [%]
1	5b	2	THF	55	1.5	98
2	1b	2	THF	55	9.0	40 ^[b]
3	1b	3	THF	55	3.0	98
4	[CuCl(ICy)]	3	toluene	80	0.5	99
5	[CuCl(ICy)]	3	toluene	55	1.5	98
6	[CuCl(ICy)]	2	toluene	55	1.5	50

[a] Isolated yields are the average of two runs. [b] Determined by GC.

tivity of **5b** with **1b**, half the reaction time was required for reaching comparable yields in the presence of the ICy-based catalyst (Table 7, entries 1 and 3). Furthermore, for this particular case, three equivalents of silane were required with **1b** to ensure good conversion. However, two equivalents were generally enough for other substrates.^[14] On the other hand, an even faster conversion was obtained with [CuCl(ICy)], but under more forcing conditions (Table 7, entry 4). However, when comparable reaction conditions were used ($T=55^\circ\text{C}$, 2 equiv of hydride source), **5b** was the optimal catalyst (Table 7, entries 5 and 6). We then further explored the activity of [Cu(ICy)₂]BF₄ **5b** with a number of ketones with varying steric congestion around the carbonyl bond under our hydrosilylation conditions. Under optimized conditions ([Cu] (3 mol %), base (12 mol %), silane (2 equiv) in THF at 55 °C), the expected silyl ethers were formed in excellent yields after short reaction times (Table 8). Acyclic, cyclic, and aromatic ketones were screened with comparable good results and the presence of functional groups, such as halogen or CF₃, were also compatible with our catalytic system (Table 8, entries 8 and 9).

It is important to note that for all of the substrates tested, ICy-containing complex **5b** was more efficient (i.e., shorter reaction times) than its IPr analogue **1b**, the greatest difference in reaction time being observed for aromatic ketones.

Table 8. [Cu(ICy)₂]BF₄-catalyzed hydrosilylation of hindered ketones.

Entry	Product	t [h]	Yield ^[a] [%]
1		0.25	99
2		5.0	96 ^[b]
3		1.5	98
4		0.5	95
5		1.0	97
6		2.5	94
7		0.25	95
8		2.5	92
9		4.0	82

[a] Isolated yields are the average of two runs. [b] *meso trans-cis/cis-trans/meso cis-cis* = 39:9:52.

Mechanistic studies: In our previous report, some insights into the mechanism of this hydrosilylation reaction were provided. Study of the hydrosilylation of cyclohexanone in the presence of [Cu(CH₃CN)₄]BF₄ (3 mol %) and IPr under different conditions indicated that a monocarbene copper compound rather than a bis-carbene complex would be the actual active species.^[14] When complexes **1b**, **5b**, or **6a** were heated in THF at reflux, no NHC decoordination or decomposition was observed after 24 h. Furthermore, displacement of an IPr moiety in [Cu(IPr)₂]BF₄ (**1b**) by a phosphine ligand was unsuccessful.^[17] Treatment of **1b** with PPh₃ or PCy₃ at temperatures ranging from 70 to 110 °C only led to the recovery of the starting complex.^[18] No reaction was observed after heating at reflux in [D₅]pyridine ether. All of the above results seem to indicate a fairly strong NHC–copper bond.

Next, we carried out several experiments, monitored by ¹H NMR spectroscopy, to clarify the nature of the postulated active monocarbene species. Complex **1b** was treated

with NaOtBu in $[D_8]THF$ under our catalytic conditions (base (4 equiv), $[Cu]$ (0.06 M), RT). The appearance of two new septuplet resonances (due to $-CH(CH_3)_2$ groups in the newly formed species) was observed. These signals could either imply the formation of two new compounds or the formation of one species in which both IPr ligands on the copper center are inequivalent.^[19] Integration of the 1H NMR spectrum showed that both of the new resonance signals had an equimolar proportion and that around 10% of the starting complex **1b** still remained. Interestingly, these proportions remained unchanged after longer reaction times (from 10 min to 19 h), higher reaction temperature (60 °C instead of RT), higher base loading (6 equiv of base instead of 4), or higher concentration (up to 0.9 M). However, a minimum of four equivalents of base were required to ensure optimal conversion of the starting complex.

We attempted to isolate the newly formed species by carrying out the same reaction on a larger scale. After stirring for two hours, the reaction mixture was filtered inside a glove box over a plug of Celite and the resulting solution was mixed with pentane. The white powder that formed was filtered and identified as a mixture of **1b** with some unidentified byproducts (around 15% of the mass balance). The filtrate was concentrated under vacuum and showed the signals previously discussed (Figures 4 and 5). By comparison with known samples, we could assign the signals in the 1H and ^{13}C NMR spectra to an equimolar mixture of IPr ligand and $[Cu(IPr)(OtBu)]$.^[20] All of the signals in the 1H and ^{13}C NMR spectra could be assigned in $[D_8]THF$ and C_6D_6 .^[19]

Formation of a copper hydride from $[Cu(NHC)(OtBu)]$ upon treatment with a hydrosilane has previously been evoked for the hydrosilylation of ketones and confirmed by

the isolation and characterization of such species.^[20] Relying on this report and on our own observations presented above, we propose a mechanism for this copper-catalyzed hydrosilylation of ketones, which is depicted in Scheme 1. First, formation of $[Cu(NHC)(OtBu)]$ from $[Cu(NHC)_2]BF_4$ and NaOtBu occurs. Then, the active catalyst, an NHC-copper hydride species, would be formed by σ -bond metathesis between $[Cu(NHC)(OtBu)]$ and the hydrosilane. Addition of hydride to the carbonyl carbon would result in a copper alkoxide that would undergo another σ -bond metathesis with the hydrosilane to form the expected silyl ether and regenerate the active catalyst.^[21] This proposed mechanism is also in agreement with the experimental evidence for the phosphine-copper catalyst systems.^[22]

Moreover, in our previous catalytic system based on $[CuCl(NHC)]$ complexes, we proposed that the excess base generally required would interact with the hydrosilane and facilitate the second σ -bond metathesis. With the present system, such excess is required for the efficient formation of $[Cu(NHC)(OtBu)]$. However, the presence of IPr (3 mol %), released from the initial bis-NHC complex, could also play such a role.^[23] As the hydrosilane loading is lower in this case (2 instead of 3 equiv), IPr would activate the hydride source more efficiently towards σ -bond metathesis. Hence, the better catalytic activity in the hydrosilylation of carbonyls of the cationic compounds $[Cu(NHC)_2]X$ when compared to that of $[CuCl(NHC)]$ can be tentatively rationalized. We therefore postulate that the favorable displacement of a neutral NHC instead of an anionic chloride from the copper center by a *tert*-butoxide adds up to the activating effect of the free NHC towards the hydrosilane in increasing the reaction rate.

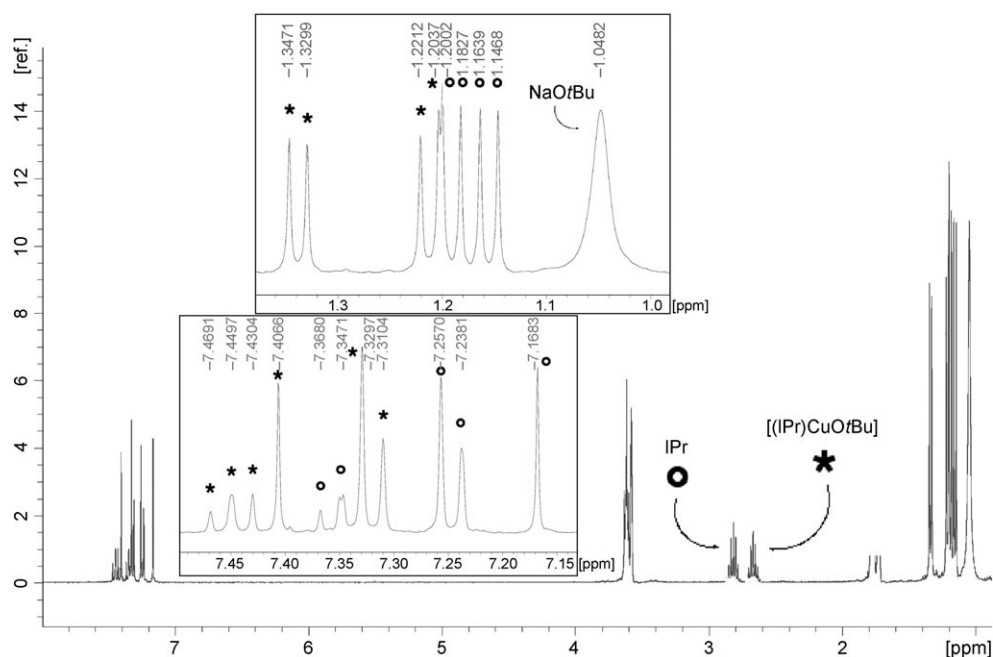
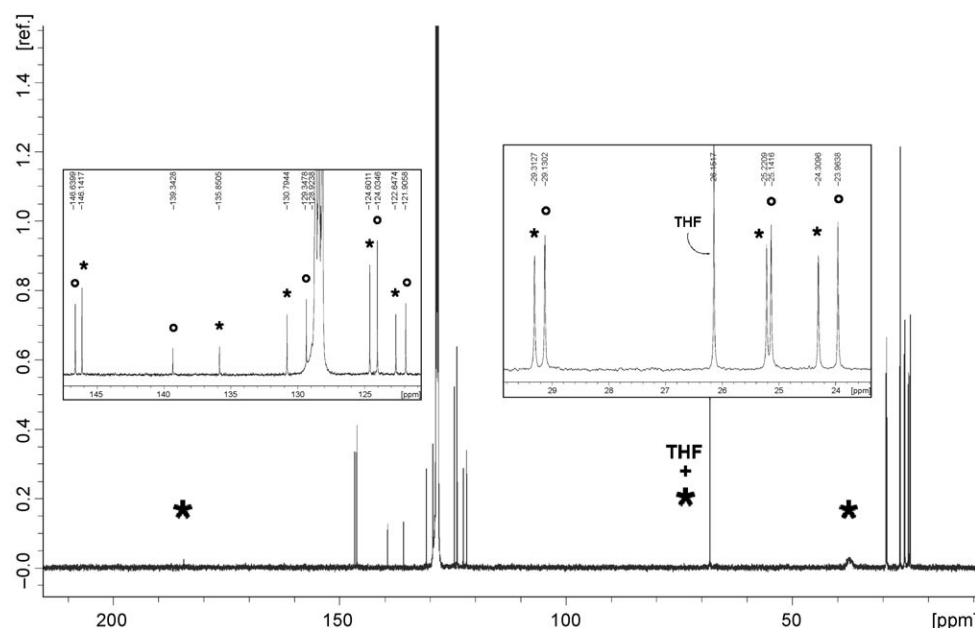
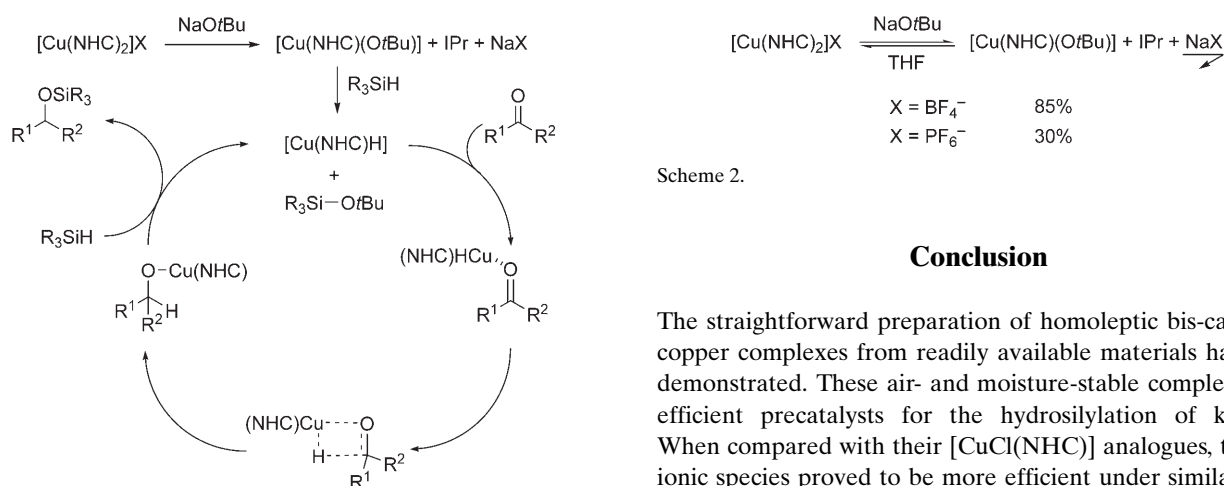
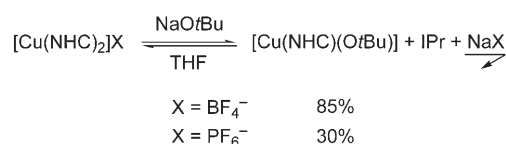


Figure 4. 1H NMR assignment of the isolated products in $[D_8]THF$.

Figure 5. ¹³C NMR assignment of the isolated products in C₆D₆.

Scheme 1. Proposed catalytic cycle.

Finally, to clarify the counterion effect observed during the catalytic studies, complex **1a** was treated with NaOtBu in [D₈]THF. Under the same conditions as those for **1b**, which yielded 85% of the alkoxide species (see above), only 30% of the complex was converted into [Cu(IPr)(OtBu)] and IPr, even after 24 h. This difference in reactivity could be rationalized by the different solubility of the inorganic salts formed in THF. Qualitative experiments showed that NaPF₆ is more soluble in THF than NaBF₄.^[24] The easier precipitation of NaBF₄ in the reaction mixture would act as a driving force in this transformation to shift the reaction equilibrium towards the formation of [Cu(NHC)(OtBu)] (Scheme 2).



Scheme 2.

Conclusion

The straightforward preparation of homoleptic bis-carbene-copper complexes from readily available materials has been demonstrated. These air- and moisture-stable complexes are efficient precatalysts for the hydrosilylation of ketones. When compared with their [CuCl(NHC)] analogues, the cationic species proved to be more efficient under similar reaction conditions. ¹H NMR spectroscopic studies clearly showed the activation of [Cu(NHC)₂]X complexes by NaOtBu to form [Cu(NHC)(OtBu)], which is the direct precursor of an NHC-copper hydride that is the actual active species in this transformation. Moreover, the observed counterion effect in the catalytic studies could be rationalized as a consequence of the difference in solubility of the inorganic salts formed. Applications to other carbonyl or pseudocarbonyl containing substrates and further activity studies are currently ongoing in our laboratories.

Experimental Section

General considerations: All ketones were used as received. Solid reagents were stored under argon in a glove box that contained less than 1 ppm of oxygen. Tetrakis(acetonitrile)copper(I) hexafluorophosphate and tetrafluoroborate,^[25] imidazolium, and imidazolium salts and IPr

were synthesized according to literature procedures.^[26] Solvents were distilled over appropriate drying agents. ¹H and ¹³C NMR spectra were recorded on a 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm with respect to tetramethylsilane as the internal standard. For ³¹P NMR spectroscopy, experiments were calibrated with H₃PO₄ as external standard. For ¹¹B NMR spectroscopy, experiments were calibrated with Et₂O·BF₃ as external standard. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ, USA). All reported yields are isolated yields and are the average of at least two runs.

Synthesis of [Cu(NHC)₂]X complexes

Bis[1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene]copper(I) hexafluorophosphate (2a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), SIPr-HBF₄ (0.478 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **2a** as a white solid (0.337 g, 68%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane from a saturated solution of **2a** in CH₂Cl₂. ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.42 (t, *J* = 7.5 Hz, 4H; H^{Ar}), 7.18 (d, *J* = 7.5 Hz, 8H; H^{Ar}), 3.96 (s, 4H; CH₂CH₂), 2.94 (septuplet, *J* = 6.8 Hz, CH(CH₃)₂), 1.16 (d, *J* = 6.8 Hz, 24H; CH₃), 0.92 ppm (d, *J* = 6.8 Hz, 24H; CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 199.8 (C, NCN), 146.1 (CH, C^{Ar}), 134.8 (C, C^{Ar}), 129.9 (CH, C^{Ar}), 125.0 (CH, C^{Ar}), 54.5 (CH₂, NCH₂), 28.6 (CH, CH(CH₃)₂), 25.1 (CH₃), 24.3 ppm (CH₃); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = -141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -72.8 ppm (d, *J*_{FP} = 706 Hz); elemental analysis calcd (%) for C₅₄H₇₆CuF₆N₄P: C 65.53, H 7.77, N 5.66; found: C 65.28, H 7.72, N 5.56.

Bis[1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene]copper(I) tetrafluoroborate (2b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), SIPr-HBF₄ (0.478 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 6 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **2b** as a white solid (0.295 g, 63%). ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.45 (t, *J* = 7.9 Hz, 4H; H^{Ar}), 7.26 (d, *J* = 7.9 Hz, 8H; H^{Ar}), 4.12 (s, 8H; CH₂CH₂), 3.08 (septuplet, *J* = 6.8 Hz, 8H; CH(CH₃)₂), 1.26 (d, *J* = 6.8 Hz, 24H; CH₃), 1.10 ppm (d, *J* = 6.8 Hz, 24H; CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 201.4 (C, NCN), 146.5 (CH, C^{Ar}), 134.3 (C, C^{Ar}), 129.7 (C, C^{Ar}), 124.4 (CH, C^{Ar}), 54.0 (CH₂, NCH₂CH₂N), 28.5 (CH, CH(CH₃)₂), 24.3 (CH₃), 23.6 ppm (CH₃); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = -0.97 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -153.7 ppm (s); elemental analysis calcd (%) for C₅₄H₇₆BCuF₄N₄: C 69.62, H 8.22, N 6.01; found: C 69.88, H 8.45, N 5.82.

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) hexafluorophosphate (3a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), IMes-HCl (0.340 g, 1 mmol), and NaOtBu (0.098 g, 1.0 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **3a** as a white solid (0.372 g, 91%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane from a saturated solution of **3a** in CH₂Cl₂. ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.46 (s, 4H; NCH), 7.05 (s, 8H; H^{Ar}), 2.45 (s, 12H; CH₃), 1.74 ppm (s, 24H; CH₃); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C, TMS): δ = 178.8 (C, NCN), 140.8 (C, C^{Ar}), 136.3 (C, C^{Ar}), 136.0 (C, C^{Ar}), 130.5 (CH, C^{Ar}), 124.5 (CH, NCH), 21.7 (CH₃), 17.7 ppm (CH₃); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = -141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -72.7 ppm (d, *J*_{FP} = 706 Hz); elemental analysis calcd (%) for C₄₂H₄₈CuF₆N₄P: C 61.72, H 5.92, N 6.85; found: C 61.45, H 5.64, N 6.52.

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) tetrafluoroborate (3b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), IMes-HCl (0.340 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **3b** as a white solid (0.280 g, 74%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane from a saturated solution of **3b** in CH₂Cl₂. ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.46 (s, 4H; NCH), 7.05 (s, 8H; H^{Ar}), 2.45 (s, 12H; CH₃), 1.75 ppm (s, 24H; CH₃); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C, TMS): δ = 178.8 (C, NCN), 140.7 (C, C^{Ar}), 136.3 (C, C^{Ar}), 135.9 (C, C^{Ar}), 130.5 (CH, C^{Ar}), 124.5 (CH, NCH), 21.6 (CH₃), 17.7 ppm (CH₃); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = -0.97 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -152.0 ppm (s); elemental analysis calcd (%) for C₄₂H₄₈BCuF₄N₄: C 66.44, H 6.37, N 7.38; found: C 66.25, H 6.50, N 7.28.

Bis[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]copper(I) hexafluorophosphate (4a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), SIMes-HBF₄ (0.393 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **4a** as a white solid (0.354 g, 86%). Crystals suitable for X-ray diffraction were grown by slow diffusion of methyl *tert*-butyl ether from a saturated solution of **4a** in CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 6.86 (s, 8H; H^{Ar}), 3.85 (s, 8H; CH₂CH₂), 2.39 (s, 12H; CH₃), 1.84 ppm (s, 24H; CH₃); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C, TMS): δ = 201.4 (C, NCN), 138.6 (C, C^{Ar}), 135.5 (CH, C^{Ar}), 134.7 (C, C^{Ar}), 129.4 (CH, C^{Ar}), 51.0 (CH₂, NCH₂CH₂N), 21.1 (CH₃), 17.2 ppm (CH₃); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = -141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -72.8 ppm (d, *J*_{FP} = 706 Hz); elemental analysis calcd (%) for C₄₂H₅₂CuF₆N₄P: C 61.41, H 6.38, N 6.82; found: C 61.53, H 6.33, N 6.71.

Bis[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]copper(I) tetrafluoroborate (4b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), SIMes-HBF₄ (0.393 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **4b** as a white solid (0.329 g, 86%). Crystals suitable for X-ray diffraction were grown by slow diffusion of methyl *tert*-butyl ether from a saturated solution of **4b** in CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 6.83 (s, 8H; H^{Ar}), 3.84 (s, 8H; CH₂CH₂), 2.37 (s, 12H; CH₃), 1.81 ppm (s, 24H; CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 201.3 (C, NCN), 138.7 (C, C^{Ar}), 135.8 (CH, C^{Ar}), 134.7 (C, C^{Ar}), 129.6 (CH, C^{Ar}), 51.2 (CH₂, NCH₂CH₂N), 21.3 (CH₃), 17.5 ppm (CH₃); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = -0.97 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = -152.1 ppm (s); elemental analysis calcd (%) for C₄₂H₅₂BCuF₄N₄: C 66.09, H 6.87, N 7.34; found: C 65.97, H 6.71, N 7.09.

Bis[1,3-bis(cyclohexyl)imidazol-2-ylidene]copper(I) hexafluorophosphate (5a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), ICy-HBF₄ (0.320 g, 1 mmol), and NaOtBu (0.096 g, 1.0 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (THF), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **5a** as a white solid (0.267 g, 80%). ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.51 (s, 4H; NCH imidazole), 4.54–4.32 (m, 4H; NCH cyclohexyl), 2.28–2.11 (m, 8H; CH₂), 2.09–1.84 (m, 16H; CH₂), 1.80–1.67 (m, 4H; CH₂), 1.57–1.39 (m, 8H; CH₂), 1.36–1.19 ppm (m, 4H; CH₂); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C): δ = 174.2 (C, NCN), 120.0 (CH, NCH imidazole), 62.7 (CH, NCH cyclohexyl), 36.1 (CH₂), 26.7 (CH₂), 26.2 ppm (CH₂); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = -141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ =

–72.7 ppm (d, $J_{\text{FP}}=706$ Hz); elemental analysis calcd (%) for C₃₀H₄₈CuF₆N₄P: C 53.52, H 7.19, N 8.32; found: C 53.58, H 7.18, N 8.25.

Bis[1,3-bis(cyclohexyl)imidazol-2-ylidene]copper(I) tetrafluoroborate (5b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), ICy·HBF₄ (0.320 g, 1 mmol) and NaOtBu (0.107 g, 1.1 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (THF), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **5b** (0.284 g, 93%). ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.51 (s, 4H; NCH imidazole), 4.55–4.33 (m, 4H; NCH cyclohexyl), 2.25–2.10 (m, 8H; CH₂), 2.01–1.85 (m, 16H; CH₂), 1.79–1.67 (m, 4H; CH₂), 1.57–1.39 (m, 8H; CH₂), 1.36–1.19 ppm (m, 4H; CH₂); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C): δ = 173.8 (C, NCN), 120.0 (CH, NCH imidazole), 62.4 (CH, NCH cyclohexyl), 35.8 (CH₂), 26.5 (CH₂), 25.9 ppm (CH₂); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = –0.97 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = –152.0 ppm (s); elemental analysis calcd (%) for C₃₀H₄₈BCuF₆N₄: C 58.58, H 7.87, N 9.11; found: C 58.44, H 7.81, N 9.00.

Bis[1,3-bis(adamantyl)imidazol-2-ylidene]copper(I) hexafluorophosphate (6a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), IAd·HBF₄ (0.424 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **6a** as a white solid (0.369 g, 84%). Crystals suitable for X-ray diffraction were grown by slow diffusion of methyl *tert*-butyl ether from a saturated solution of **6a** in CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.34 (s, 4H; NCH), 2.38 (s, 24H; CH), 2.23 (s, 12H; CH₂), 1.87–1.72 (m, 12H; CH), 1.72–1.50 ppm (m, 12H; CH); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 169.8 (C, NCN), 117.3 (CH, NCH), 58.0 (C, NCCH₂), 44.9 (CH), 35.7 (CH), 29.7 ppm (CH₂); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = –141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = –72.8 ppm (d, $J_{\text{FP}}=706$ Hz); elemental analysis calcd (%) for C₄₆H₆₄CuF₆N₄P: C 62.67, H 7.32, N 6.36; found: C 62.39, H 7.21, N 6.23.

Bis[1,3-bis(adamantyl)imidazol-2-ylidene]copper(I) tetrafluoroborate (6b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), IAd·HBF₄ (0.424 g, 1 mmol), and NaOtBu (0.127 g, 1.3 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 15 h. After filtering the reaction mixture through a plug of Celite (CH₂Cl₂), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **6b** as a white solid (0.389 g, 95%). Crystals suitable for X-ray diffraction were grown by slow cooling of a saturated solution of **6b** in acetone. One molecule of acetone crystallized with **6b**. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.36 (s, 4H; NCH), 2.39 (s, 24H; CH), 2.23 (s, 12H; CH₂), 1.85–1.72 (m, 12H; CH), 1.72–1.59 ppm (m, 12H; CH); ¹³C NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 169.9 (C, NCN), 117.3 (CH, NCH), 58.0 (C, NC), 44.9 (CH), 35.7 (CH), 29.8 ppm (CH₂); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = –0.90 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = –152.0 ppm (s); elemental analysis calcd (%) for C₄₆H₆₄BCuF₆N₄: C 67.10, H 7.83, N 6.80; found: C 67.23, H 7.82, N 6.99.

Bis[1,3-bis(tert-butyl)imidazol-2-ylidene]copper(I) hexafluorophosphate (7a): Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.186 g, 0.5 mmol), *t*Bu·HBF₄ (0.268 g, 1 mmol), and NaOtBu (0.107 g, 1.1 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 6 h. After filtering the reaction mixture through a plug of Celite (acetone), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **7a** (0.281 g, 99%). ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.64 (s, 4H; NCH), 1.84 ppm (s, 36H; CH₃); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C, TMS): δ = 171.7 (C, NCN), 119.9 (CH, NCH), 58.7 (C, C(CH₃)₃), 32.5 ppm (CH₃); ³¹P NMR (162 MHz, [D₆]acetone, 25 °C): δ = –141.1 ppm (m); ¹⁹F (376 MHz, [D₆]acetone,

25 °C): δ = –72.7 ppm (d, $J_{\text{FP}}=707$ Hz); elemental analysis calcd (%) for C₂₂H₄₀CuF₆N₄P: C 46.43, H 7.08, N 9.84; found: C 46.24, H 6.96, N 9.84.

Bis[1,3-bis(tert-butyl)imidazol-2-ylidene]copper(I) tetrafluoroborate (7b): Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.157 g, 0.5 mmol), *t*Bu·HBF₄ (0.268 g, 1 mmol), and NaOtBu (0.107 g, 1.1 mmol) were added to a vial fitted with a screw cap inside a glove box, and stirred in dry THF (12 mL) outside the glove box for 6 h. After filtering the reaction mixture through a plug of Celite (acetone), the filtrate was mixed with pentane to form a precipitate. A second filtration led to the isolation of **7b** (0.255 g, 100%). Crystals suitable for X-ray diffraction were grown by slow diffusion of methyl *tert*-butyl ether from a saturated solution of **7b** in THF. ¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 7.64 (s, 4H; NCH), 1.84 ppm (s, 36H; CH₃); ¹³C NMR (100 MHz, [D₆]acetone, 25 °C): δ = 171.2 (C, NCN), 119.8 (CH, NCH), 58.8 (C, C(CH₃)₃), 32.4 ppm (CH₃); ¹¹B NMR (128 MHz, [D₆]acetone, 25 °C): δ = –1.07 ppm (s); ¹⁹F (376 MHz, [D₆]acetone, 25 °C): δ = –153.7 ppm (s); elemental analysis calcd (%) for C₂₂H₄₀BCuF₆N₄: C 51.72, H 7.89, N 10.97; found: C 51.48, H 8.06, N 10.80.

General procedure for the hydrosilylation of ketones: Complex **5b** (18 mg, 0.03 mmol, 3 mol %) and sodium *tert*-butoxide (12 mg, 12 mol %) were added to a vial fitted with a septum screw cap inside a glove box, and stirred in dry THF (2 mL, 55 °C, 10 min) outside the glove box before adding triethylsilane (0.33 mL, 2 mmol, 2 equiv) through the septum by means of a syringe. After stirring for a further 10 min, the ketone (1 mmol) was added. When the starting material was a solid, it was added as a solution in THF. The reaction was monitored by GC. After consumption of the starting material or when no further conversion occurred, the reaction mixture was opened to air and filtered through a plug of active charcoal and Celite (ethyl acetate). The organic phase was concentrated in vacuo and the purity of the residue established by GC and ¹H NMR spectroscopy. Flash chromatography was then performed unless the crude product was estimated to be greater than 95 % pure.

X-ray crystallography: CCDC 652351, 652352, 652353, 652354, 652355, 652356, 652357, and 652358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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