Synthesis and Catalytic Properties of Rhodium(I) and Copper(I) Complexes Bearing Dipyrido-Annulated *N*-Heterocyclic Carbene Ligands

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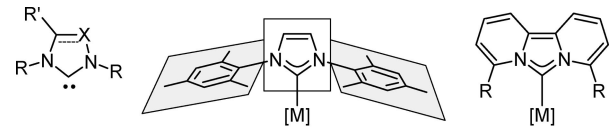
Starting from the in situ generated free carbenes dipyrido[1,2-*c*;2′,1′-*e*]imidazolin-6-ylidene (dipiy) and 2,10-di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazolin-6-ylidene (dipiy$^{t\mathrm{Bu}}$), the synthesis of the new carbene complexes [RhCl(COD)(dipiy)] and [RhCl(COD)(dipiy$^{t\mathrm{Bu}}$)] can be achieved. Upon chloride abstraction and coordination of phosphine, a very active precursor for the catalytic hydrosilylation of ketones is formed. The reaction was also followed by NMR spectroscopy. In addition the respective CuI(dipiy$^{t\mathrm{Bu}}$) complex was synthesized and fully characterized. X-ray structure analysis reveals this compound to be a trimer [CuI(dipiy$^{t\mathrm{Bu}}$)]$_3$ with two Cu−Cu bonds in the solid state. However, unlike the imidazolinylidene analogues, this complex and in situ prepared CuX(dipiy) complexes (X = I, Cl) were found to be inactive in the hydrosilylation of ketones.

Introduction

N-Heterocyclic carbenes[1,2] **A** were found to be valuable ligands for various catalyst systems. As ligands, they are compatible for main group as well as early and late transition metal complexes, and their modifiability has made them a class of ligands that on the long-term could even scope the importance of phosphine ligands, which can be substituted by NHCs. The latter are more σ-electron donating and show at the same time less π-acceptor character. However, substitution of phosphine ligands by NHCs not necessarily leads to an improvement of the catalytic activity, as the NHCs bind more tightly, thus blocking necessary coordination sites. As was demonstrated by the second generation Grubbs' catalyst,[3] interplay between phosphine and NHC ligands can lead to a very active catalyst system.

Modification of the electronic and/or steric character of the NHC ligands can be achieved by varying the substituents R, adding substituents R′, having saturated or unsaturated rings, or changing the ring size or the type or number of heteroatoms X (Chart 1, **A**). *N*-Heterocyclic carbenes take in a rather "fence"-like coordination space with the aryl substituents oriented orthogonal to the NHC plane (Chart 1, **B**). This is different with

Chart 1



pyrido-anellated NHCs which were first investigated by Weiss.[4] The anellated substituent lies in the NHC plane, thus any ortho substituents R would shield the side of a coordinated metal (Chart 1, **C**). By X-ray structure analysis we showed that the 14π electron system consists of alternating single and double bonds rather than of aromatic bonds, both in the free carbene and in the ligand.[5] The small NCN angle correlates with the very low ^{13}C NMR chemical shift of only 196 ppm in the free carbene. The free σ-orbital is less basic than in other carbenes, but at the same time, due to the conjugated 14π e$^-$ system the π-orbital is less acidic, which seems to balance out the overall donor ability of this ligand.[6] Though the pure donor character seems to be similar to that of other *N*-heterocyclic carbenes,[5] the properties of this ligand in a catalytic system have not been investigated so far although small steric and/or electronic change of a ligand can sometimes result in a dramatic effect on reactivity and/or selectivity of a catalyst.

Therefore we have prepared neutral rhodium(I) complexes with the dipyridoimidazolinylidene (dipiy) and the 2,10-di(*tert*-butyl)dipyridoimidazolinylidene (dipiy$^{t\mathrm{Bu}}$) ligand as well as a cationic mixed phosphine−dipiy Rh(I) complex to test them in

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(2) (a) Reviews: Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913–921. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91. (c) Herrmann, W. A. *Angew. Chem.* **2002**, *114*, 1342–1363;*Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (d) Hahn, F. E. *Angew. Chem.* **2006**, *118*, 1374–1378;*Angew. Chem., Int. Ed.* **2006**, *45*, 1348–1352. (e) N-Heterocyclic Carbenes in Transition Metal Catalysis. In *Topics in Organometallic Chemistry*; Glorius, F., Vol. Ed.; Springer: Heidelberg, Germany, 2006; Vol. 21. (f) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006.

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(4) (a) Weiss, R.; Reichel, S.; Handke, M.; Hampel, F. *Angew. Chem.* **1998**, *110*, 352–354;*Angew. Chem. Int. Ed.* **1998**, *37*, 344–346. (b) Weiss, R.; Reichel, S. *Eur. J. Inorg. Chem.* **2000**, 1935–1939.

(5) Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *Chem. Commun.* **2006**, 1378–1380.

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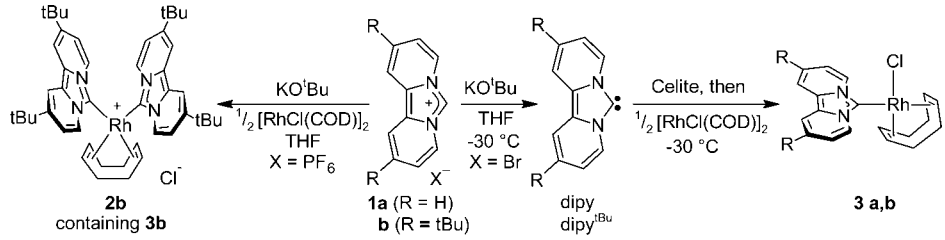
Scheme 1



the hydrosilylation of ketones.[7] In addition we synthesized a CuI(dipiy^{tBu}) complex for the same purpose, as recent results by Sadighi, Buchwald,[8] and Nolan[9] showed NHC−Cu(I) complexes to be highly active catalysts.

Results and Discussion

Preparation of the Complexes. Attempts to synthesize the carbene complexes of type **3** by a one-pot procedure with use of sodium *tert*-butanolate as base to generate the carbene in situ and then adding [RhCl(COD)]$_2$ resulted in a mixture containing a 1:3 ratio of the desired product **3b** and complex **2b**, which bears two NHC ligands coordinated to rhodium (Scheme 1). Attempts to separate the products by fractionate crystallization resulted in isolation of complex **2b** as determined by X-ray crystal structure analysis (Figure 1). To avoid formation of **2b** we kept the concentration of the free carbene low by adding dropwise a solution of the in situ generated and over Celite filtered carbene in tetrahydrofuran to a solution of [RhCl(COD)]$_2$ in toluene at −30 °C. Warming to room temperature led to formation of the product **3b** as a bright yellow precipitate.

Synthesis of the [RhCl(COD)(dipiy)] complex **3a** was achieved by the same procedure. As the unsubstituted carbene is not stable at room temperature, it is required to handle the carbene at −30 °C. In the ^{13}C NMR spectrum, formation of complex **3a** can easily be verified by the doublet of the carbene carbon at 162.9 ppm. The strong high field shift of the carbene signal compared to analogous carbene complexes in literature (δ 172–212[10]) can be explained by an already high field shifted signal of the free carbene itself.[4,5] The ^1J(Rh−C$_{carbene}$) coupling constant of 52.8 Hz lies within a typical range.[10]

By slow diffusion of pentane into a solution of **3a** in dichloromethane we were able to obtain single crystals suitable for X-ray structure analysis. The molecular structure (Figure 2) shows a square-planar coordination sphere around the Rh center with typical bond lengths for [RhCl(COD)(NHC)] complexes. The Rh−C$_{COD}$ distances trans to the carbene (2.21

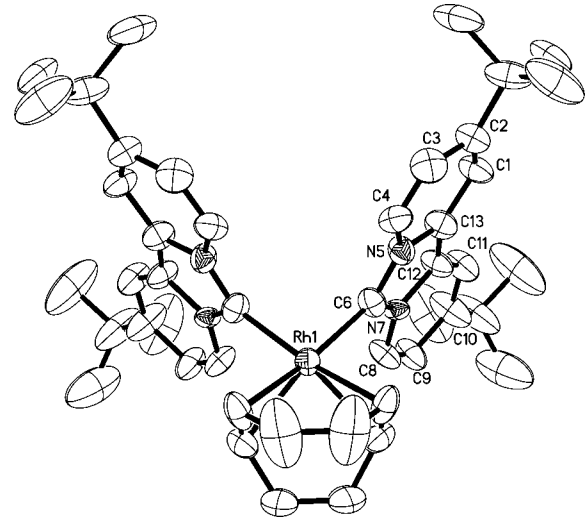


Figure 1. Molecular structure of compound **2b** bearing two NHC ligands. Hydrogen atoms and the counterion have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Because of the limited quality a detailed discussion of the geometry cannot be made.

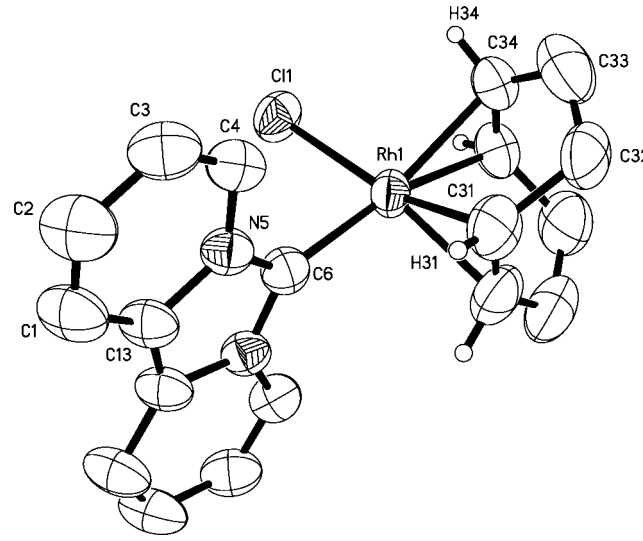


Figure 2. Molecular structure of complex **3a**. Calculated hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−Cl1 = 2.369(1), Rh1−C31 = 2.105(3), Rh1−C34 = 2.214(3), Rh1−C6 = 2.007(4), N5−C6 = 1.366(3), N5−C13 = 1.403(3), C13−C13′ = 1.377(6); N5−C6−N5′ = 102.5(3).

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(8) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417–2420.

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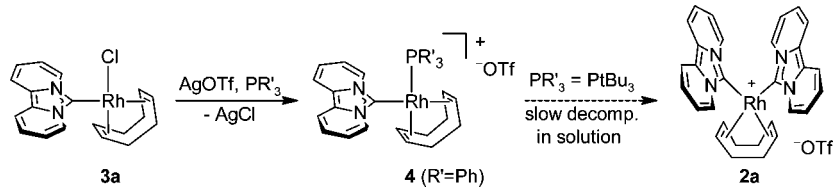
(10) (a) Typical examples of RhCl(COD) complexes of imidazolidinylidenes (212 ppm, 48 Hz): Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219–224. (b) Imidazolinylidenes (185 ppm, 53 Hz): Yu, X.-Y.; Patrick, B. O.; James, B. R. *Organometallics* **2006**, *25*, 2359–2363. (c) Imidazopyridinylidenes (172 ppm, 51 Hz): Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290–3291.

Scheme 2



Å) are longer than those trans to the chloride (2.11 Å) due to the stronger trans influence of the carbene. The Rh−$C_{carbene}$ distance of 2.007(4) Å is rather short, which can be interpreted by a lack of steric hindrance of the carbene ligand upon coordination to the metal. The NCN angle of only 102.5(3)° is one of the most acute angles found in [RhCl(COD)(NHC)] complexes.[11] Compared with the free carbene, the angle is opened up by 2.3°—a trend that is also found for the angles of other imidazol-derived carbenes and their complexes.[11]

Reactivity of RhCl(COD)(dipiy). Cationic complexes are often more reactive catalysts compared to their neutral counterparts. Recently, Crabtree, Gade, and Bellemin-Lapponnaz used cationic Rh(I) complexes as catalysts for the hydrosilylation of ketones[7d,f] and enones.[7e] Testing the influence of our dipiy ligands we tried to generate the cationic catalyst precursor **4** by chloride abstraction from complex **3a** and addition of a phosphine ligand (Scheme 2). Though mixed NHC−phosphine complexes were obtained by Crabtree upon reaction with AgOTf followed by addition of PPh_3,[7a] we found the reaction to be cleaner for our case by first dissolving the rhodium complex **3a** and PPh_3 in dichloromethane and then adding AgOTf to the reaction mixture. The $^{31}P\{^1H\}$ NMR spectrum indicates formation of the cationic complex by a characteristic doublet at 25.5 ppm with a ^1J(Rh−P) coupling constant of 154.5 Hz. These values fit well with those reported in literature.[7a]

By slow diffusion of pentane into a solution of **4** in dichloromethane, we were able to obtain two modifications of single crystals both suitable for X-ray structure analysis. One is triclinic (space group $P\bar{1}$, **4t**), the other monoclinic (space group $C2/c$, **4m**). This is the first example of a structurally characterized cationic carbene−phosphine rhodium complex with a nonchelating carbene ligand. The molecular structures (cation) of both modifications are fitted in Figure 3 and show only small deviations. The coordination geometry around Rh is square planar with the NHC ring and the COD double bonds perpendicular to the coordination plane. Within the range of error the Rh−C_{COD} as well as the C=C bonds are equal for structures **4t** and **4m**. One phenyl group is almost parallel to the NHC plane. The shortest distance of a phenyl carbon (C31) to the dipiy plane is 3.03 Å (**4t**). This is much closer than the $\pi-\pi$ distance found in graphite and therefore the interaction is probably repulsive. However the phenyl group is bent toward the dipiy plane by 4° indicating an attractive interaction for the more distant carbon atoms (largest distance: C34−dipiy = 3.69 Å).

The attempt to prepare the cationic tri(*tert*-butyl)phosphine complex did not result in formation of the desired complex, possibly due to steric congestion. After leaving a 1.0×10^{-2} M solution of the reaction mixture in dichloromethane at −35 °C under nitrogen for two weeks, colorless crystals have formed. The X-ray structure analysis reveals the cationic complex **2a** with two dipyridocarbene ligands at the metal (Figure 4).

Synthesis of Cu(I)−Dipyridocarbene Complexes. We were motivated to prepare Cu complexes with a dipyridocarbene ligand as recent reports describe the high catalytic activity of CuCl(NHC) complexes in the hydrosilylation of ketones.[8,9] In a one-pot procedure the imidazolium salt **1b**, Cu(I)−iodide, and a slight excess of potassium *tert*-butoxide are reacted in tetrahydrofuran for 24 h. Filtration over Celite and crystallization from a dichloromethane−pentane mixture gave the yellow Cu complex **5** in 63% yield (Scheme 3). To our knowledge this is the first reported synthesis of a Cu−iodide complex with a monodentate NHC ligand. The $^{13}C\{^1H\}$ NMR spectrum exhibits the characteristic carbene signal at 157.6 ppm. The chemical shifts of the other signals are similar to those of the rhodium complex **3b**.

Single crystals suitable for X-ray structure analysis were obtained by slow diffusion of pentane into a solution of **5** in dichloromethane. The molecular structure is depicted in Figure 5 showing a trimeric complex. Two L^{tBu}−Cu−I moieties are bridged over the iodide atoms with unsymmetric bond lengths and a Cu(1)−Cu(2) distance of 2.67 Å. The third L^{tBu}−Cu−I moiety is coordinated by Cu(3)−Cu(2) and I(3)−Cu(1) interactions. The Cu−$C_{carbene}$ bond lengths are in the range between 1.913(6) and 1.940(5) Å and the NCN angles are in a range between 101.9(4) and 102.4(5)°—an angle the same size as observed in complex **3b**.

Hydrosilylation of Ketones and α,β-Unsaturated Ketones. We first investigated the performance of the neutral and cationic rhodium catalyst precursors **3a**, **3b**, and **4** in the hydrosilylation of acetophenone with diphenylsilane. The reactions were carried out at room temperature with subsequent hydrolysis of the silyl ether under the conditions reported.[7f,k,12] However, to get

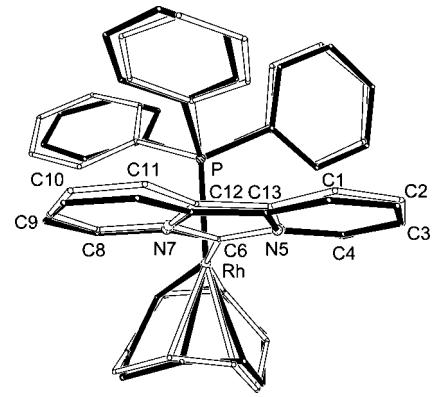


Figure 3. Fit of the two molecular structures of compound **4** (at the atoms Rh1, P1, and C6) in the tetrahedral (black) and monoclinic (white) modification. The differences in geometries are due to packing effects. Selected bond distances (Å) and angles (deg): **4t**, Rh1−C6 = 2.028(3), Rh1−P1 = 2.3268(8), N5−C6 1.371(4), N5−C13 1.406(4), C6−N7 1.368(4), N7−C12 1.410(4), C12−C13 1.376(4); C6−Rh1−P1 = 88.31(8), N5−C6−N7 = 102.6(2); **4m**, Rh1−C6 = 2.023(3), Rh1−P1 = 2.2983(7), N5−C6 = 1.361(3), N5−C13 = 1.408(3), C6−N7 1.365(3), N7−C12 = 1.409, C12−C13 = 1.382(4); C6−Rh1−P1 = 88.66(7), N5−C6−N7 = 103.2(2).

(11) Cambridge Structural Database Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.

(12) Comte, V.; Balan, C.; Le Gendre, P.; Moïse, C. *Chem. Commun.* **2007**, 713–715.

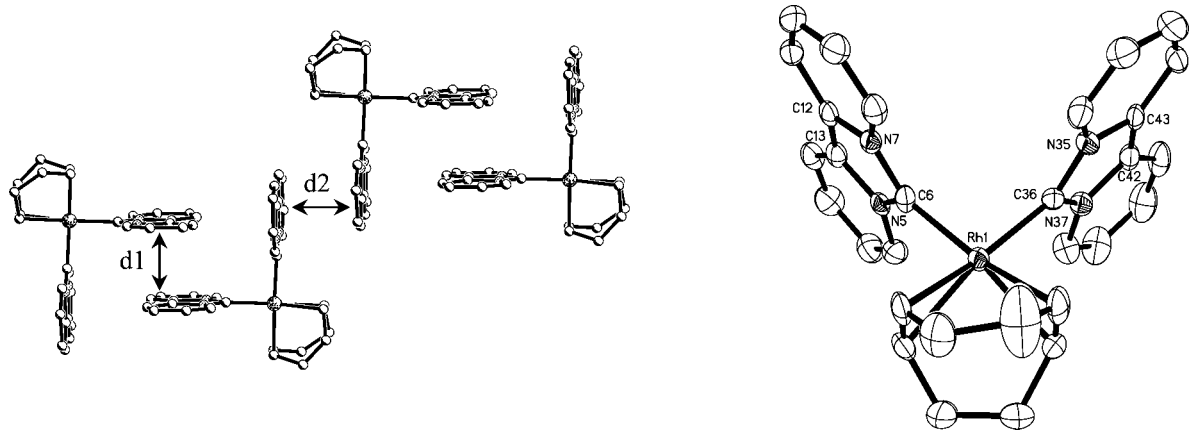
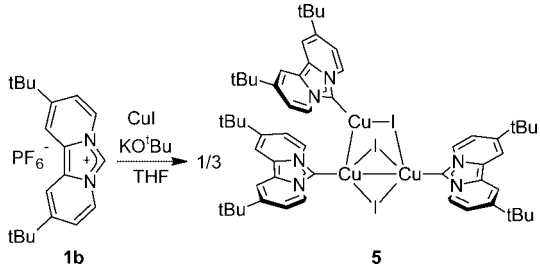


Figure 4. View of the arrangement of the molecules of compound **2a** in the crystal along the *b* axis (left) and molecular structure of **2a** (right). Thermal ellipsoids are drawn at 50% probability and the hydrogen atoms are omitted for clarity. The intermolecular distances between the symmetry related NHC planes are only d1 = 3.37 and d2 = 3.45 Å. Selected bond distances (Å) and angles (deg): Ru1−C6 = 2.035(5), Rh1−C36 = 2.033(5), Ru1−C21 = 2.201(5), Ru1−C22 = 2.198(5), N5−C6 = 1.376(6), N5−C13 = 1.404(6), C6−N7 = 1.377(6), N7−C12 = 1.410(6), C12−C13 = 1.383(7), N35−C36 = 1.380(6), N35−C43 = 1.417(6), C36−N37 = 1.370(6), N37−C42 = 1.406(6), C42−C43 = 1.377(7); N5−C6−N7 = 102.1(4), N35−C36−N37 = 102.0(4), C36−Rh1−C6 = 91.38(18).

Scheme 3



complete quenching of the reaction with catalysts **3a** and **3b** (Table 1, entries 2 and 4), it was necessary to first generate a cationic species upon addition of a solution of silver(I) triflate in diethyl ether and subsequent hydrolysis with a methanolic solution of potassium carbonate. At room temperature the reaction with the neutral complexes is quite slow and attempts to enhance the reactivity by applying a hydrogen atmosphere as reported by Comte et al.[12] was not successful for our systems. However, the cationic precatalyst **4** turned out to be very active, after 10 min almost full conversion was obtained. Monitoring this reaction by NMR at 0 °C showed that after an induction period of 10 min the reaction is completed within 2 h.

We then tested other ketones as substrates in the hydrosilylation with catalyst **4**. After 5 min only *p*-bromoacetophenone and 2-decanone gave almost complete conversion (Table 2, entries 2 and 6). 1-Acetonaphthone and benzylacetone gave only medium conversion and diphenylacetone (entry 4) showed no reaction after 5 min. After 5 h conversion of all substrates was almost complete and the alcohols were isolated in very good yields with one exception—in the case of *p*-bromoacetophenone only 70% of the desired product along with 28% of 1-phenylethylalcohol stemming from debromination were isolated.

Hydrosilylation of α,β-unsaturated ketones gave a mixture of 1,2- and 1,4-addition products in variable amounts depending on the substrate and catalyst. With cyclohexenone the 1,4-addition is a side reaction whereas with benzylideneacetone 1,4-addition becomes the dominant reaction (Table 3).

Hydrosilylation experiments with copper complex **5** with use of diphenylsilane turned out to give no conversion of the ketone at all. Therefore we applied the same conditions reported by Nolan.[9] However, also in situ generation of the dipiy complex with CuI or CuCl from the imidazolium salt with a 5-fold excess of sodium *tert*-butoxide and the use of triethylsilane as a reactant again yielded no product.

The results show that the dipyrido-anellated NHCs are suitable ligands for Rh catalysts in the hydrosilylation of ketones. The neutral complexes **3a** and **3b** are less active catalysts than the cationic complex **4** bearing both a phosphine and a carbene ligand. Catalyst **4** turned out to be active in the hydrosilylation of various dialkyl- and alkylarylketones. In contrast to the results reported in the literature,[8,9] our copper complex **5** bearing the dipiy ligand turned out to be inactive as a hydrosilylation catalyst. So far we do not know the reason for this unexpected result and further studies have to prove if this dramatic effect is based on steric and/or subtle electronic differences.

Conclusion

We were able to synthesize and fully characterize Rh and Cu complexes with the dipyrido-anellated NHC ligand dipiy. The analytical and structural data of the neutral Rh carbene complexes **3a** and **3b** reveal characteristic data for the dipiy ligand with respect to ^{13}C NMR chemical shift and the NCN angle. By chloride abstraction and addition of phosphine we synthesized and structurally characterized the cationic mixed phosphine−carbene Rh complex **4**. Reaction of CuI with the in situ generated carbene from **1b** yielded copper complex **5** in good yield. X-ray structure analysis showed a trimeric complex with two Cu−Cu bonds. The cationic Rh complex **4** turned out to be an effective catalyst in the hydrosilylation of various ketones including diphenylketone. For still unknown reasons neither the Cu complex **5** nor the in situ prepared Cu dipiy complexes were active catalysts in the hydrosilylation of acetophenone. The results show that the dipyrido carbene is an interesting ligand with similar but not identical properties as imidazolinylidenes. Modifications to take advantage of the special planar shape of this interesting carbene type with respect to sterics and chiral information are the current subject of our research.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under an atmosphere of dry argon with standard Schlenk

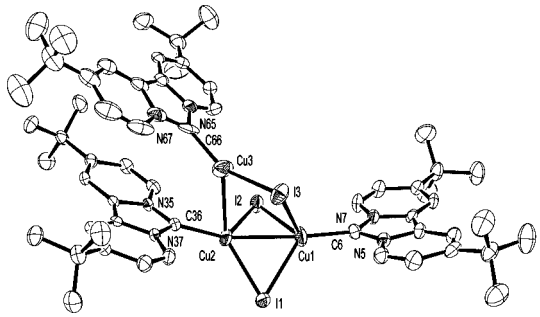
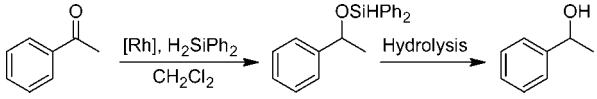


Figure 5. ORTEP diagram of the $[CuI(L'^{Bu})]_3$ trimer **5** with 50% ellipsoids and bond lengths (Å) in the $[Cu-I]_3$ core. Selected bond distances (Å) and angles (deg): Cu1−Cu2 = 2.6736(9), Cu1−I1 = 2.6438(8), Cu1−I2 = 2.8036(8), Cu1−I3 = 2.8236(9), Cu2−I1 = 2.5929(8), Cu2−I2 = 2.6363(8), Cu2−Cu3 = 2.6530(11), Cu3−I3 = 2.4481(8), Cu1−C6 = 1.940(5), Cu2−Cu36 = 1.934(5), Cu3−C66 = 1.913(6); N7−C6−N5 = 101.9(4), N35−C36−N37 = 102.0(4), N65−C66−N67 = 102.4(5).

Table 1. Catalytic Hydrosilylation of Acetophenone[a] by Diphenylsilane



entry	catalyst	cond	time	yield (%)
1		rt	20 h	0
2	**3a**	rt	20 h	64
3[b]	**3a**	rt	20 h	65
4	**3b**	rt	20 h	75
5	**4**	rt	20 h	98
6	**4**	rt	5 min	94
7	**4**	rt	10 min	98
8[c]	**4**	0 °C	2 h	98

[a] 1.0 mmol of acetophenone, 1.2 mmol of diphenylsilane, 1% Rh, 1.0 mL of CH_2Cl_2, yield determined by GC. [b] Under 8 atm of H_2. [c] NMR experiment: 0.35 mmol of acetophenone, 0.42 mmol of diphenylsilane, 1% Rh, 0.35 mL of CD_2Cl_2.

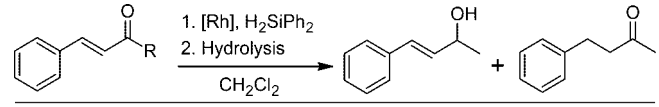
Table 2. Catalytic Hydrosilylation of Ketones[a] by Diphenylsilane with the Cationic Catalyst 4 at Room Temperature

entry	substrate	turnover (5 min, %)[b]	turnover (5 h, %)[b]	isolated (%)
1	acetophenone	94	98[c]	n.i.
2	*p*-bromoacetophenone	92	97	70[d]
3	1-acetonaphthone	59	92	92
4	diphenylacetone	0	90	89
5	benzylacetone	35	99	98
6	2-decanone	86	97	96

[a] 1.0 mmol of ketone, 1.2 mmol of diphenylsilane, 1% Rh, 1.0 mL of CH_2Cl_2. [b] Determined by GC. [c] After 10 min. [d] Along with 28% of 2-phenylethanol. n.i. = not isolated.

techniques or were performed in a nitrogen-filled glovebox. All solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purification. Dipyrido[1,2-*c*;2′,1′-*e*]imidazoliumbromide (**1a**) and 2,10-di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazoliumbromide (**1b**) were synthesized as reported.[5] ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX 250, DRX 300, or DRX 500 spectrometer. $^1H/^{13}C$ chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (2.49/39.5 ppm, DMSO-d_6; 5.32/53.8 ppm, CD_2Cl_2). Assignments of ^{13}C NMR spectra were made with the aid of 2D correlation spectra. Except where otherwise noted NMR spectra were acquired at room temperature. Mass spectra were recorded on a JEOL JMS-700 or a Bruker ApexQe hybrid 9.4 T FT-ICR instrument. Melting points were determined with a Büchi B 540 melting point apparatus. Elemental analyses were performed by the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

Table 3. Hydrosilylation of α,β-Unsaturated Ketones[a] by Diphenylsilane



entry	catalyst	substrate	recovered substrate (%)	enol 1,2-addition (%)	ketone 1,4-addition (%)
1	**3a**	cyclohexenone	0	50	8
2	**3b**	cyclohexenone	0	29	5
3	**3a**	benzylideneacetone	12	24	28
4	**3b**	benzylideneacetone	2	10	53
5	**4**	benzylideneacetone	0	27	66[b]

[a] 1.0 mmol of ketone, 1.2 mmol of diphenylsilane, 1% Rh, 20 h, 1 mL of CH_2Cl_2, rt. Yields determined by GC. [b] 5% of 4-phenyl-2-butanol is detected.

Dipyrido[1,2-*c*;2′,1′-*e*]imidazoliumhexafluorophosphate (1a). Dipyrido[1,2-*c*;2′,1′-*e*]imidazoliumbromide (200 mg, 0.800 mmol) is dissolved in 2 mL of water and 148 mg (0.800 mmol) of potassiumhexafluorophosphate are dissolved in 5 mL of water. The solutions are combined and the product is precipitated at 4 °C, washed with 2 mL of cold water, and dried in vacuo to give the product as yellow crystals in 70% yield (177 mg). ^1H NMR (DMSO-d_6): δ 6.88–8.02 (m, 4H, 3-H and 9-H, 2-H and 10-H), 8.66 (d, 2H, 1-H and 11-H, $^3J_{HH}$ = 9.1 Hz), 9.00 (d, 2H, 4-H and 8-H, $^3J_{HH}$ = 7.0 Hz), 10.26 (s, 1H, 6-H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 116.1 (C6), 118.7 (C1, C11), 120.4 (C3, C9), 121.8 (C11a, C11b), 122.7 (C2, C10), 123.4 (C4, C8). Mp: 212 °C dec. MS (ESI, *m*/*z*) 169.4 $[M]^+$. Anal. Calcd for $C_{11}H_9F_6N_2P$: C, 42.05; H, 2.89; N, 8.92. Found: C, 42.14; H, 3.02; N, 8.86.

2,10-Di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazoliumhexafluorophosphate (1b). 2,10-Di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazoliumbromide (149 mg, 0.410 mmol) and potassiumhexafluorophosphate (76.0 mg, 0.410 mmol) are solved in 40 mL of water each. The two solutions are combined and the precipitated product collected by filtration and washed with 40 mL of water. After drying in vacuo the yellow product is obtained in quantitative yield (174 mg, 99%). ^1H NMR (DMSO-d_6): δ 1.40 (s, 18H, $C(CH_3)_3$), 7.72 (dd, 2H, 3-H and 9-H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.1 Hz), 8.61 (s, 2H, 1-H and 11-H), 8.91 (d, 2H, 4-H and 8-H, $^3J_{HH}$ = 6.9 Hz), 10.06 (s, 1H, 6-H). Mp: 213.0 °C dec. MS (ESI, *m*/*z*): 281.2 $[M]^+$. Anal. Calcd for $C_{19}H_{25}F_6N_2P$: C, 53.52; H, 5.91; N, 6.57. Found: C, 53.34; H, 5.89; N 6.62.

Synthesis of [RhCl(dipiy)(COD)] (3a). In a Schlenk tube, 348 mg (1.40 mmol) of dipiy·HBr and 157 mg (1.40 mmol) of potassium *tert*-butoxide are stirred in 15 mL of tetrahydrofuran at −30 °C for 30 min. The resulting light green solution is filtered over Celite and added to a solution of 300 mg (0.610 mmol) of $[\{RhCl(COD)\}_2]$ in 15 mL of toluene at −30 °C. The reaction mixture is stirred and warmed to room temperature during a period

Table 4. Crystal Data and Structure Refinement Details for 3a, 4t, and 4m

	3a	4t	4m
empirical formula	$C_{19}H_{20}ClN_2Rh$	$C_{39}H_{37}Cl_2F_3N_2O_3PRhS$	$C_{39}H_{37}F_3N_2O_3PRhS$
formula weight	414.73	875.55	875.55
temp (K)	293(2)	200(2)	200(2)
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pnma*	$P\bar{1}$	*C*2/*c*
Z	4	2	8
unit cell			
a (Å)	15.7757(13)	10.7542(2)	34.2822(5)
b (Å)	14.1046(12)	11.5377(1)	11.4527(2)
c (Å)	7.8106(7)	17.6280(3)	19.4145(3)
α (deg)	90.0	100.869(1)	90.0
β (deg)	90.0	99.333(1)	90.741(1)
γ (deg)	90.0	114.976(1)	90.0
V (Å^3)	1737.9(3)	1873.95(5)	7622.0(2)
calcd density (g/cm^3)	1.59	1.55	1.53
abs coeff (mm^{-1})	1.14	0.75	0.74
crystal color	yellow	yellow	yellow
crystal shape	polyhedron	polyhedron	polyhedron
θ range (deg)	2.6 to 27.9	1.2 to 27.5	1.3 to 27.5
index ranges	$-20 \le h \le 20$	$-13 \le h \le 13$	$-44 \le h \le 44$
	$-18 \le k \le 18$	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-10 \le l \le 10$	$-22 \le l \le 22$	$-25 \le l \le 25$
no. of rflns collected	16742	18208	38442
no. of indep rflns (*R*(int))	2164 (0.0387)	8434 (0.0541)	8728 (0.062)
no. of obsd rflns ($I > 2\sigma(I)$)	1826	6810	6807
max, min transmission	0.95, 0.78	0.90, 0.84	0.67, 0.86
no. of data/restraints/params	2164/19/126	8434/10/482	8728/142/570
goodness-of-fit on F^2	1.12	1.03	1.07
final *R* indices ($I > 2\sigma(I)$)			
R1	0.034	0.041	0.036
*w*R2	0.072	0.096	0.098
largest diff peak, hole (e/Å^3)	0.67, −0.31	0.74, −0.70	1.05, −0.80

of 60 min. The resulting bright yellow precipitate is collected by filtration, then washed twice with a mixture of 2 mL of tetrahydrofuran and 2 mL of toluene and three times with 2 mL of pentane. The powder is dried in vacuo to give the rhodium complex in 252 mg (50%) yield. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of **3a** in dichloromethane. ^{1}H NMR (CD_2Cl_2): δ 1.95–2.09 (m, 4H, $H_{COD}(CH_2)$), 2.48–2.57 (m, 4H, $H_{COD}(CH_2)$), 3.33–3.37 (m, 2H, $H_{COD}(C{=}CH)$), 5.11–5.16 (m, 2H, $H_{COD}(C{=}CH)$), 6.94–6.98 (m, 2H, 2-H and 10-H), 7.01 (td, 2H, 3-H and 9-H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz), 7.79 (dt, 2H, 1-H and 11-H, $^3J_{HH} = 9.2$ Hz, $^{4/5}J_{HH} = 1.2$ Hz), 9.21 (dt, 2H, 4-H and 8-H, $^3J_{HH} = 7.2$ Hz, $^{4/5}J_{HH} = 1.2$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 29.6 ($C_{COD}(CH_2)$), 33.7 ($C_{COD}(CH_2)$), 69.2 (d, $C_{COD}(C{=}C)$, $^1J_{RhC} = 13.2$ Hz), 100.0 (d, $C_{COD}(C{=}C)$, $^1J_{RhC} = 5.7$ Hz), 116.5 (C3, C9), 118.1 (C1, C11), 119.5 (C2, C10), 123.8 (C11a, C11b), 127.5 (C4, C8), 162.9 (d, C6, $^1J_{RhC} = 52.8$ Hz). Mp: 312 °C dec. MS (FD+; LIFDI in CH_2Cl_2, *m*/*z*): 414.0 [M]$^+$. Anal. Calcd for $C_{19}H_{20}ClN_2Rh$: C, 55.02; H, 4.86; N, 6.75. Found: C, 54.65; H, 4.82; N, 6.86.

Synthesis of [RhCl(dipiy$^{t\mathrm{Bu}}$)(COD)] (3b). In a Schlenk tube, 360 mg (1.00 mmol) of dipiy$^{t\mathrm{Bu}}$·HBr and 106 mg (0.940 mmol) of potassium *tert*-butoxide are stirred in 10 mL of tetrahydrofuran at −30 °C for 30 min. The resulting reddish solution is filtered over Celite and added to a solution of 200 mg (0.410 mmol) of [{RhCl(COD)}$_2$] in 15 mL of toluene at ambient temperature and then stirred for 12 h. The resulting bright yellow precipitate is collected by filtration, then washed with a mixture of 2 mL of tetrahydrofuran and 2 mL of toluene and three times with 2 mL of pentane. The powder is dried in vacuo to give 142 mg (33%) of the rhodium complex. ^{1}H NMR (CD_2Cl_2): δ 1.36 (s, 18H, $C(CH_3)_3$), 1.94–2.06 (m, 4H, $H_{COD}(CH_2)$), 2.45–2.55 (m, 4H, $H_{COD}(CH_2)$), 3.31–3.36 (m, 2H, $H_{COD}(C{=}CH)$), 5.07–5.10 (m, 2H, $H_{COD}(C{=}CH)$), 7.03 (dd, 2H, 3-H and 9-H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 2.3$ Hz), 7.59 (d, 2H, 1-H and 11-H, $^4J_{HH} = 2.3$ Hz), 9.06 (d, 2H, 4-H and 8-H, $^3J_{HH} = 7.5$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 29.7 ($C_{COD}(CH_2)$), 30.6 ($C(CH_3)_3$), 33.7 ($C_{COD}(CH_2)$), 35.2 ($C(CH_3)_3$), 69.0 ($C_{COD}(C{=}C)$, $^1J_{RhC} = 14.3$ Hz), 99.7 ($C_{COD}(C{=}C)$, $^1J_{RhC} = 7.1$ Hz), 111.8 (C1, C11), 116.1 (C3, C9), 123.4 (C11a, C11b), 127.0 (C4, C8), 142.5 (C2, C10), signal C6 is not observed. Mp: 321–323 °C dec. MS (FD+, LIFDI in CH_2Cl_2, *m*/*z*): 526.2 [M]$^+$. MS (HR-FAB in NBA, *m*/*z*): 526.1655 [M(35Cl)]$^+$ (calcd 526.1622), 528.1641 [M(37Cl)]$^+$ (calcd 528.1626).

Generation of [Rh(dipiy)(COD)(PPh$_3$)][OTf] (4). For preparation of the catalyst solution 10.4 mg (25.0 mmol) of [RhCl(dipiy)(COD)] (**3a**) and 7.9 mg (30 mmol) of triphenylphosphine are dissolved in 2 mL of dichloromethane and the solution is stirred for 5 min. Then, under exclusion of light, 6.9 mg (25 μmol) of silver(I) triflate is added and the solution is stirred for another 5 min. The mixture is filtered and the filter residue is washed with approximately 0.5 mL of dichloromethane. The organic layers are combined and filled up to exactly 2.5 mL. For NMR studies, CD_2Cl_2 was used as a solvent. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into the solution. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.5 (d, $^1J_{RhP} = 154.5$ Hz). MS (HR-ESI in CH_2Cl_2): 641.15882 [M]$^+$ (calcd 641.15929).

Synthesis of [{CuI(dipiy$^{t\mathrm{Bu}}$)}$_3$] (5). In a sealed Schlenk tube 120 mg (0.280 mmol) of dipiy$^{t\mathrm{Bu}}$·HPF$_6$ (**1b**), 52.0 mg (0.270 mmol) of copper(I) iodide, and 29.0 mg (0.300 mmol) of potassium *tert*-butoxide are stirred in 7 mL of tetrahydrofuran for 24 h at room temperature. The resulting red solution is filtered over Celite, evaporated to dryness, and dissolved in 2.5 mL of dichloromethane. By slow diffusion of pentane into the solution the product is crystallized out and collected by filtration. After evaporation of residual solvent in vacuo the product can be obtained as yellow crystals in 63% yield (83.0 mg). ^{1}H NMR (CD_2Cl_2): δ 1.34 (s, 18H, $C(CH_3)_3$), 6.77 (dd, 2H, 3-H and 9-H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz), 7.53 (s, 2H, 1-H and 11-H), 8.83 (d, 2H, 4-H and 8-H, $^3J_{HH} = 7.5$ Hz). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 30.6 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 111.4 (C1, C11), 115.8 (C3, C9), 122.3 (C11a,11b), 127.6 (C4, C8), 143.2 (*C*2), 157.6 (C6). Mp: 296 °C dec. MS (FAB in NBA, *m*/*z*): 343.2.1 [M − I]$^+$. Anal. Calcd for $C_{19}H_{24}N_2CuI$: C, 48.47; H, 5.14; N, 5.95. Found: C, 48.38; H, 5.23; N, 5.79.

Table 5. Crystal Data and Structure Refinement Details for 2a, 2b, and 5

	2a	2b	5
empirical formula	$C_{32}H_{30}Cl_2F_3N_4RhS$	$C_{46}H_{60}F_6N_4PRh$	$C_{62}H_{84}Cu_3I_3N_6$
formula weight	781.47	916.86	1484.67
Temperature (K)	200(2)	200(2)	200(2)
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$Fmm2$	$P\bar{1}$
Z	4	20	2
unit cell			
a (Å)	14.1443(1)	37.0267(3)	13.5316(2)
b (Å)	13.4668(3)	37.1976(3)	14.4058(1)
c (Å)	16.7571(2)	23.6545(3)	18.1071(3)
α (deg)	90.0	90.0	98.348(1)
β (deg)	90.184(1)	90.0	99.734(1)
γ (deg)	90.0	90.0	113.699(1)
V (Å^3)	3173.29(8)	32579.4(6)	3095.38(7)
calcd density (g/cm^3)	1.64	0.94	1.59
abs coeff (mm^{-1})	0.83	0.33	2.56
crystal color	colorless	yellow	yellow
crystal shape	polyhedron	polyhedron	polyhedron
θ range (deg)	1.9 to 27.5	1.6 to 25.4	1.2 to 25.5
index ranges	$-18 \le h \le 18$	$-44 \le h \le 44$	$-16 \le h \le 16$
	$-13 \le k \le 17$	$-44 \le k \le 44$	$-17 \le k \le 17$
	$-20 \le l \le 21$	$-38 \le l \le 28$	$-21 \le l \le 21$
no. of rflns collected	18816	72890	2673
no. of indep rflns (R(int))	7083 (0.0888)	15451 (0.1150)	11266 (0.0542)
no. of obsd rflns ($I > 2\sigma(I)$)	3727	12273	7532
max, min transmissn	0.98, 0.75	0.95, 0.87	0.82, 0.49
no. of data/restraints/params	7083/91/488	15451/820/755	11266/0/666
goodness-of-fit on F^2	0.98	1.18	1.00
final R indices ($I > 2\sigma(I)$)			
R1	0.056	0.087	0.040
wR2	0.100	0.221	0.091
largest diff peak, hole (e/Å^3)	1.01, −0.85	1.64, −0.94	2.24, −1.70

X-ray Crystal Structure Determination. X-ray structures were obtained with a Bruker Smart diffractometer at 200 K (**2a**, **2b**, **4t**, **4m**, **5**) or a Bruker APEX diffractometer at 293 K (**3a**), both equipped with a Mo Kα radiation source ($\lambda = 0.71073$ Å) and a graphite monochromator. All intensities were corrected for Lorentz and polarization effects, and an absorption correction was applied in each case with use of SADABS[13] based on the laue symmetry of the reciprocal space. The structures were solved by direct methods or a Patterson method in the case of **4t**. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique against F^2 except for **2b**, where the poor data quality only allowed an isotropic refinement for parts of the structure. The hydrogen atom locations were calculated according to stereochemical aspects, except for the olefinic hydrogen atoms of the COD of **3a**, which were refined isotropically. We have observed and modeled some disorder in the anions (**2a**, **2b**, **4m**) or incorporated solvent molecules (**2b**, **4t**, **4m**, **5**), only in **3a** there is a slight disorder in the COD of the complex itself due to the special position of the molecule on a mirror plane (Tables 4 and 5). Structure solution and refinement were carried out with the SHELXTL (6.10) software package.[13] CCDC 668509 (**2a**), CCDC 668510 (**2b**), CCDC 668511 (**3a**), CCDC 668512 (**4t**), CCDC 668513 (**4m**), and CCDC 668514 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Hydrosilylation with the Neutral Rh Catalysts 3a and 3b. In a 3 mL Schlenk tube, 1.00 mmol of the corresponding ketone or α,β-unsaturated ketone is dissolved in 1 mL of a 10^{-2} M catalyst solution in dichloromethane. Diphenylsilane (220 mg, 1.20 mmol) is added dropwise within 2 min. A well-defined portion of *n*-dodecane (between 30 and 50 mg) as an internal standard is added. The tube is sealed and the reaction mixture is stirred for 20 h. Then, to 0.1 mL of the resulting mixture is added 0.5 mL of a 0.004 M solution of silver(I) triflate in diethyl ether to destroy the Rh catalyst. A saturated solution of potassium carbonate in methanol (1 mL) is added and the vigorously bubbling mixture is stirred for at least 1 h. Afterward, the yield is determined by GC.

Table 6. Attempts of the Hydrosilylation of Acetophenone with (dipiy)Cu Complexes

entry	catalyst	cond.	time (h)	yield (%)
1[a]	**5**	rt	20	0
2[a]	**5**	80 °C	1	0
3[a]	**5**, AgOTf	rt	2	0
4[b]	CuI, dipiy$^{t\mathrm{Bu}}$·HBr	rt	2	0
5[b]	CuI, dipiy·HBr	rt	2	0
6[b]	CuI, dipiy·HPF_6 (**1a**)	rt	2	0
7[b]	CuCl, dipiy·HPF_6 (**1a**)	rt	2	0

[a] 1.0 mmol of acetophenone, 1.2 mmol of diphenylsilane, 1% Cu, 1.0 mL of CH_2Cl_2. [b] 1.0 mmol of acetophenone, 5 mmol of triethylsilane, 3% Cu, 0.20 mmol of NaOtBu, 2 mL of toluene.

Hydrosilylation with a Neutral Rh Catalyst under Hydrogen Atmosphere in a Glass Autoclave. The reaction mixture is prepared as described above in a 10 mL glass autoclave. Then, the autoclave is pressurized with 8 atm of hydrogen and stirred for 20 h. After the pressure is removed, the yield is determined as described above.

General Procedure for Hydrosilylation with the Cationic Rh Catalyst 4. In a 3 mL Schlenk tube, 1 mL of a stock solution of [Rh(dipiy)(COD)(PR_3)][OTf] in dichloromethane is stirred with 1 mmol of the corresponding ketone for a few minutes. Then, over a period of 2 min, 220 mg (1.20 mmol) of diphenylsilane and a well-defined portion of *n*-dodecane (between 30 and 50 mg) are added and the reaction mixture is stirred for the given time. The reaction was monitored by taking small samples. In general, workup occurs by stirring the reaction mixture with 2 mL of a saturated potassium carbonate solution for at least 1 h. Yields are determined by either GC or after column chromatography (Silica, 2 × 20 cm, Pentan:Et_2O 4:1).

(13) Sheldrick, G. M. *SHELXTL*; Bruker Analytical X-ray Division: Madison, WI, 2001.

Hydrosilylation of Acetophenone with [CuI(dipiy$^{t\mathrm{Bu}}$)]$_3$ (5). A 3 mL Schlenk tube with 1 mL of a 10^{-2} M stock solution of the copper complex in CH_2Cl_2 is charged with a defined amount of *n*-dodecane as an internal standard (between 30 and 50 mg) and 220 mg (1.20 mmol) of diphenylsilane. The mixture is stirred for 8 min and then 120 mg (1.00 mmol) of acetophenone is added. The sample is then stirred for the given time at either room temperature or 80 °C. Workup and determination of the yield are performed as described above. No activity can be observed in any case.

Hydrosilylation of Acetophenone with an in Situ Generated Cu Catalyst. In a septum vial, 19.0 mg (0.20 mmol) of sodium *tert*-butoxide, 0.03 mmol of the copper salt (CuI, CuCl), and the same amount of the imidazolium salt (bipiy·HBr, bipiy$^{t\mathrm{Bu}}$·HBr or **1a**) are suspended in 2 mL of toluene. Then, 580 mg (5.00 mmol) of triethylsilane is added within 2 min and the reaction mixture is stirred for 8 min. Acetophenone (120 mg, 1.00 mmol) and a defined amount of *n*-dodecane as an internal standard (between 20 and 40 mg) are added via syringe and the reaction is stirred for 2 h. Workup and determination of the yields are performed as described above. No activity can be observed in any case.

Kinetic Experiment. In a Young-NMR tube, 0.35 mL of a similarly prepared solution of [Rh(dipiy)(COD)(PR$_3$)][OTf] in CD_2Cl_2 is cooled to −35 °C. A defined amount of dodecahydrotriphenylene (between 6.00 and 8.00 mg) as an internal standard and 42.0 mg (0.350 mmol) of acetophenone are added. Within 2 min 77.0 mg (0.420 mmol) of diphenylsilane is added by syringe. The cooled sample is then transferred to the precooled NMR spectrometer and ^{1}H NMR spectra are recorded immediately after constant time intervals. Conversion rates are determined by integration of the TMS signal of the product against dodecahydrotriphenylene as an internal standard.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **2a**, **2b**, **3a**, **4t**, **4m**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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