Coordination Chemistry of a Modular N,C-Chelating Oxazole-Carbene Ligand and Its Applications in Hydrosilylation Catalysis§

Macarena Poyatos,† Aline Maisse-François,† Stéphane Bellemin-Laponnaz,*,† and Lutz H. Gade*,†,‡

Laboratoire de Chimie Organométallique et de Catalyse (UMR 7513), Institut Le Bel, Université Louis Pasteur, 4 Rue Blaise Pascal, 67070 Strasbourg, France, and Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Received February 21, 2006

Reaction of 1-mesitylimidazole with 2-chlorobenzoxazole gave the 2-benzoxazolyl imidazolium salt *bzoxcarbH*$^+$*Cl*$^-$ (**1**), which was converted to the silver N-heterocyclic carbene complex [Ag^I(bzoxcarb)-Cl] (**2**) by reaction with Ag_2O in dichloromethane. The crystal structure analysis confirmed the monomeric nature of complex **2**. The silver complex **2** was reacted with [$PdCl_2$(COD)] to yield the corresponding palladium complex [$PdCl_2$(bzoxcarb)] (**3**), for which an X-ray diffraction study established a distorted square planar configuration with the imidazolyl and the oxazolyl ring lying within the molecular plane. Upon direct reaction of the imidazolium salt **1** with $Pd(OAc)_2$/NaI, a bis-carbene palladium complex [PdI_2(bzoxcarb)$_2$] (**4**) was obtained. The rhodium complex [RhCl(bzoxcarb)(CO)] (**5**) was prepared in high yield in a one-step reaction of **1** with [Rh(acac)$(CO)_2$] (acac = acetylacetonate). The silver N-heterocyclic carbene complex **2** was also used as carbene transfer reagent in the synthesis of the platinum complex [$PtCl_2$(bzoxcarb)] (**6**), which was found to be an active catalyst for the hydrosilylation of alkenes and alkynes.

Introduction

Ligand design for functional molecules is based on the exploitation of the specific binding properties of the ligating units to the metal centers and the targeting of a particular, well-defined molecular shape. It relies on the combination of the steric and electronic properties of the molecular building blocks of which a polydentate ligand system is composed. This "additive" approach is frequently employed in the development of novel molecular catalysts.

N-Heterocyclic carbenes have emerged as a new family of ancillary ligands for the development of homogeneous catalysts. They are strong σ-donors and in many respects resemble phosphorus donor ligands rather than classical Fischer or Schrock type carbenes.[1] Their bonding to many of the late transition metals has proved to be kinetically inert, thus rendering them "anchors" for the attachment of polyfunctional ligands to such metals.

Metal complexes bearing these ligands have been employed as catalysts in a wide variety of chemical transformations.[2,3] Among the systems developed to date, ligands that combine the strongly coordinating anchor N-heterocyclic carbene function with a more labile ligating unit, which modulates the electronic properties of the metal center or imposes a particular stereochemical environment in the ligand sphere, have considerable potential.[4] Robust catalysts for C−C coupling reactions have been developed following this strategy,[5] while the combination of the carbene fragment with a chiral donor function has led to efficient enantioselective catalysts. These have been successfully applied in catalytic alkylations,[6] hydrogenations,[7] hydrosilylations,[8] or olefin metathesis reactions.[9]

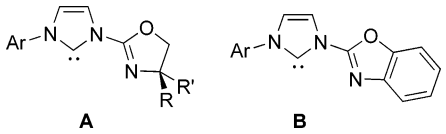


Figure 1. Comparison of the related bidentate C,N-chelating ligands. Left: oxazolinyl-carbene (**A**). Right: benzoxazole-carbene (**B**).

We recently reported the synthesis of oxazolinyl-carbene ligands of type **A** (Figure 1), which are readily obtained by the direct coupling between the two heterocycles. This modular approach, which assembles both the "anchor" and the stereo-

* Corresponding author. Fax: (+49) 6221-545609. E-mail: lutz.gade@uni-hd.de, bellemin@chimie.u-strasbg.fr.

§ Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 65th birthday.

† Université Louis Pasteur.

‡ Universität Heidelberg.

(1) Reviews: (a) Bourissou, D.; Guerret, O.; Gabbaï, F.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(2) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

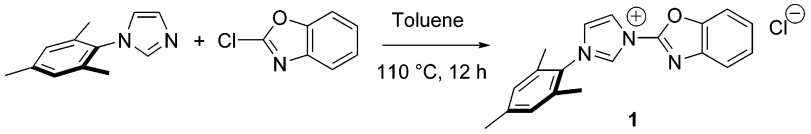
(3) Reviews on N-heterocyclic carbene-transition metal complexes in asymmetric catalysis: (a) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951. (b) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, 619.

(4) Selected references: (a) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162. (b) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274. (c) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473. (d) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376. (e) Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2003**, 699. (f) Frøseth, M.; Netland, K. A.; Rømming, C.; Tilset, M. *J. Organomet. Chem.* **2005**, *690*, 6125. (g) Edworthy, I. S.; Rodden, M.; Mungur, S. A.; Davis, K. M.; Blake, A. J.; Wilson, C.; Schröder, M.; Arnold, P. L. *J. Organomet. Chem.* **2005**, *690*, 5710. (h) Dastgir, S.; Coleman, K. S.; Cowley, A. R.; Green, M. L. H. *Organometallics* **2006**, *25*, 300.

(5) (a) Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247. (b) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201. (c) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. (d) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270. (e) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700.

10.1021/om060166u CCC: $33.50
Publication on Web 04/04/2006

Scheme 1. Synthesis of the Oxazolyl-Imidazolium Salt 1



directing units in a single reaction step, was found to be an efficient strategy in the development of novel (chiral) catalysts.[8,10]

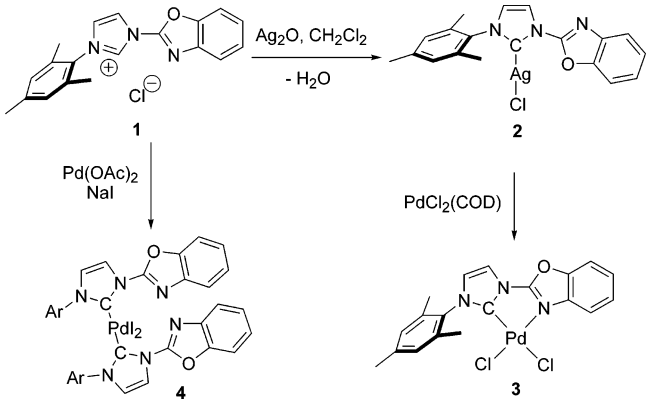
In this paper we report the synthesis of a new type of bidentate nitrogen donor-carbene ligand **B**, which is closely related to oxazolinyl carbene ligands **A**. In it the chiral, but relatively labile oxazoline ring of the latter is replaced by the achiral and robust benzoxazol unit. We report on the coordination chemistry of the oxazolyl carbene ligand **B** with silver, palladium, rhodium, and platinum, the latter having been employed as a catalyst in the hydrosilylation of alkynes and alkenes.

Results and Discussion

Synthesis of the Ligand Precursor and its Coordination to Silver(I) and Palladium(II). The synthesis of the imidazolium salt precursor of the new bidentate ligand was carried out by direct coupling of the oxazole unit and the imidazole. Adding 1-mesitylimidazole to a solution of the commercially available 2-chlorobenzoxazole in toluene under nitrogen and stirring at 110 °C overnight led to the precipitation of the 2-benzoxazolyl imidazolium salt *bzoxcarbH*$^+$Cl$^-$ (**1**) (Scheme 1), which was isolated as a white solid in 85% yield.

For the coordination of **1** as an N-heterocyclic carbene to palladium, we followed the strategy based on the ligand transfer with the aid of a silver N-heterocyclic carbene complex.[11] Stirring the imidazolium salt *bzoxcarbH*$^+$*Cl*$^-$ (**1**) with Ag_2O in dichloromethane at room temperature for 3 h afforded the silver N-heterocyclic complex [Ag^I(bzoxcarb)Cl], **2** (Scheme 2), the

Scheme 2. Synthesis of the Silver Complex 2 and Palladium Complexes 3 and 4



formulation of which was confirmed by elemental analysis. A high-resolution FAB mass spectrum of the solution of **2** in acetonitrile displayed a molecular ion peak at 714.8 amu, which corresponds to the silver bis(carbene) monocation. This suggests that a conversion of [Ag(bzoxcarb)Cl] to [Ag(bzoxcarb)$_2$]$^+$ occurs under the sampling conditions since no such redistribution was observed in the NMR spectra recorded in solution at low temperature. The formation of the chloro(carbene) complex was established by the observation of a signal at δ 187.3 ppm in the ^{13}C NMR spectrum, which was assigned to the 2C-imidazol-2-ylidene carbon nucleus and by the absence of the resonance for the 2H-imidazolium proton in the ^{1}H NMR spectra. The details of the molecular structure of the silver carbene complex **2** in the solid state were established by an X-ray diffraction study. The molecular structure of complex **2** is represented in Figure 2 along with the principal bond lengths and interbond angles.

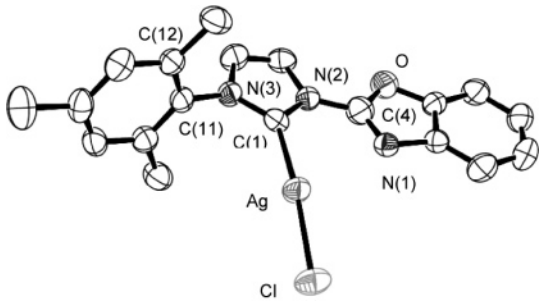


Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Ag−C(1), 2.104(4); Ag−Cl, 2.354(2); C(1)−N(2), 1.351(4); C(1)−N(3), 1.346(4); Ag−N(1), 2.97; C(1)−Ag−Cl, 168.5(1); C(1)−N(3)−C(11)−C(12), 95.7(4); C(1)−N(2)−C(4)−N(1), 2.4(6).

The crystal structure analysis established the monomeric nature of complex **2**. The coordination around the metal is quasi-linear with a C(1)−Ag−Cl bond angle of 168.5(1)°. The Ag−C(1) bond length of 2.104(4) Å is comparable to previously characterized examples of linear Ag(I)-NHC complexes.[12] The mesityl ring is oriented almost orthogonally to the imidazolyl ring [dihedral angle C(1)−N(3)−C(11)−C(12) 95.7°], while the oxazole unit is arranged with the N atom pointing toward the metal center. The Ag-bonded imidazolyl ring and the adjacent oxazole ring are slightly twisted with respect to each other, the dihedral angle C(1)−N(2)−C(4)−N(1) being 2.4°. The Ag−N(1) distance of 2.97 Å does not indicate a significant interaction of the benzoxazole with the silver atom.

The silver complex **2** was reacted with [PdCl$_2$(COD)] to yield the corresponding chelating oxazole-carbene-palladium(II) complex [PdCl$_2$(bzoxcarb)] (**3**) in ca. 40% yield (Scheme 2). The use of other palladium precursors (such as [(PhCN)$_2$PdCl$_2$]) did not improve the yield of the transmetalation reaction. The ^{1}H and ^{13}C NMR spectra of **3** are consistent with its formulation as a mononuclear complex. The molecular structure of the

(6) (a) Bonnet, L. G.; Douthwaite, R. E.; Kariuki, B. M. *Organometallics* **2003**, *22*, 4187. (b) Larsen, A. O.; Leu, W.; Nieto Oberhuber, C.; Campbell, J. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 11130. (c) Van Velhuizen, J. J.; Campbell, J. E.; Guidici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877. (d) Clavier, H.; Coutable, L.; Guillemin, J. C.; Mauduit, M. *Tetrahedron: Asymmetry* **2005**, *16*, 921.

(7) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113.

(8) César, V.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem. Eur. J.* **2005**, *11*, 2862.

(9) (a) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954. (b) Gillingham, D. G.; Kataoka, O.; Garber, S. B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 12288.

(10) (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204. (b) Gade, L. H.; César, V.; Bellemin-Laponnaz, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1014.

(11) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(12) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

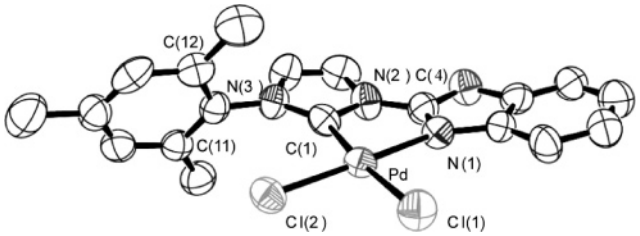


Figure 3. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Pd−C(1), 1.997(8); Pd−N(1), 2.073(6); Pd−Cl(1), 2.328(2); Pd−Cl(2), 2.262(2); C(1)−Pd-N(1), 80.6(3); Cl(1)−Pd−Cl(2), 91.42(8); C(1)−N(2)−C(4)−N(1), 0(2); C(1)−N(3)−C(11)−C(12), 74(1).

complex in the solid state was determined by X-ray diffraction and is depicted in Figure 3 along with the principal bond lengths and angles.

In complex **3,** the geometry around the metal is distorted square planar, with the imidazolyl and the oxazolinyl ring lying in the molecular plane. The mesityl ring plane is twisted out of the plane of the central molecular unit [C(1)−N(3) C(11)−C(12) 74°], while the two heterocycles of the bidentate ligand are coplanar [C(1)−N(2)−C(4)−N(1) 0°]. The strong *trans* influence of the N-heterocyclic carbene ligand is reflected in the lengthening of the Pd−Cl bond in *trans* disposition to the carbene ligand compared to the Pd−Cl distance *trans* to the oxazoline-N donor atom [2.328(2) vs 2.262(2) Å]. This is consistent with previous structural studies on related complexes.[5e,10a]

In contrast to the reactive behavior of the previously reported oxazolinyl imidazolium salts of type **A**, we found that it is possible to carry out the complexation of the oxazole imidazolium protioligand **B** by the direct synthetic route used in the preparation of many NHC-Pd complexes. However, in the case at hand, the reaction product proved to be different from the one obtained via the silver carbene method. Reaction of imidazolium salt **1** with $Pd(OAc)_2$ in THF at room temperature in the presence of sodium iodide led to the stable palladium bis-carbene complex $[PdI_2(bzoxcarb)_2]$ (**4**) in moderate yield (35%) as the only identifiable reaction product. The molecular structure of complex **4** was established by X-ray diffraction and is depicted in Figures 4a and 4b along with a listing of the principal bond lengths and angles.

As is apparent in the molecular structure shown in Figure 4, the palladium complex was formed as the *trans* isomer. Within the square planar coordination geometry the two iodine ligands are tilted away from the sterically demanding mesityl rings (I−Pd−I angle of 172.8°). In the crystal, the molecule adopts a conformation in which the two oxazole rings in the *trans*-disposed oxazole-carbene units lie on the same side with respect to the coordination plane. Unlike compound **2**, the oxazole units are arranged with the nitrogen atoms pointing away from the metal center. Due to interligand repulsion between the mesityl units and the benzoxazol rings, the NHC rings are twisted, the dihedral angle between the two Pd-linked diaminocarbene subunits being 40.1°. The palladium−carbene bond length was found to be 2.016(5) Å and is consistent with related structures.[13]

As for the reactive potential of the two NHC-palladium complexes **3** and **4**, we tested both compounds for activity in the Suzuki cross-coupling reaction, using a set of standard substrates.[14] For both complexes, standardized reaction conditions concerning solvent and the choice of the base were applied (dioxane, Cs_2CO_3, 80 °C).[10a,15] The coupling of 4-bromoacetophenone or 4-methoxybromobenzene with phenylboronic acid was found to proceed in good yield with a catalyst loading of 0.2 mol % of **3** (87 and 90% isolated yield, respectively, after 3 h). However, under the same conditions, complex **4** did not exhibit any activity. We also failed in the coupling of chloroarenes even with a higher catalyst loading of **3**. Since the palladium oxazole-carbene complex **3** appeared to be less efficient than the previously studied palladium oxazoline-carbene complex bearing ligand type **A**, this investigation was not carried any further.[10a]

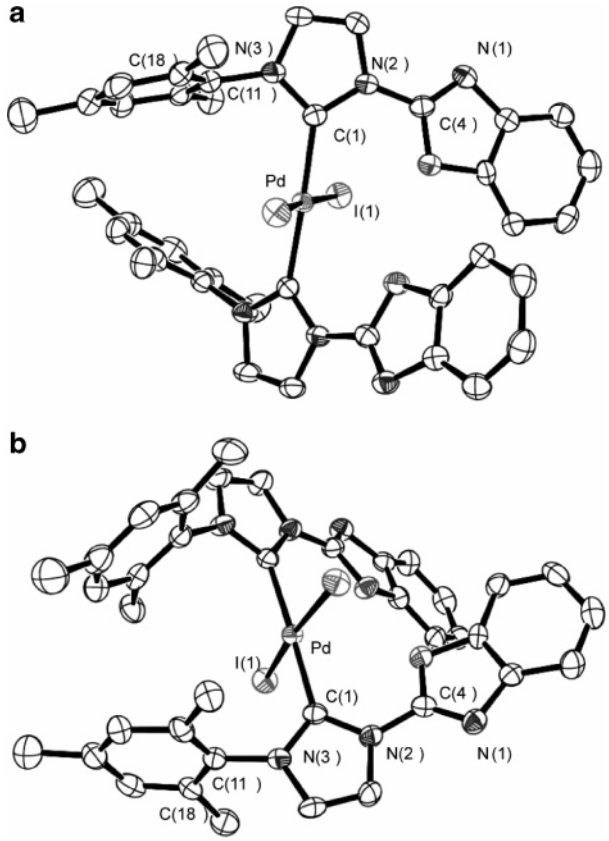
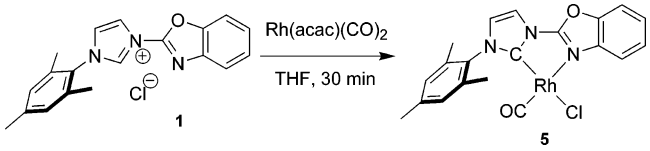


Figure 4. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Pd−C(1), 2.016(5); Pd−I(1), 2.618(1); I(1)−Pd−I(1), 172.8(1); C(1)−Pd−C(1), 178.1(2); C(1)−Pd−I(1), 90.1(2); C(1)−N(3)−C(11)−C(18), 104.4(6); C(1)−N(2)−C(4)−N(1), 159.9(5).

Scheme 3. Synthesis of the Neutral Four-Coordinate Complex [RhCl(ligand)(CO)], 5



Synthesis and Structural Characterization of the Rhodium(I) Complex [RhCl(bzoxcarb)(CO)] (5). A rhodium carbonyl derivative of the oxazole-carbene [RhCl(bzoxcarb)(CO)] (**5**) was prepared by direct reaction of the imidazolium precursor **1** with $[Rh(acac)(CO)_2]$ in THF at room temperature (Scheme 3). The synthesis is based on the protonation of the acetylace-

(13) (a) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K. H.; Wurst, K. *J. Organomet. Chem.* **1998**, *552*, 45. (b) Xu, L.; Chen, W.; Bickley, J. F.; Steiner, A.; Xiao, J. *J. Organomet. Chem.* **2000**, *598*, 409. (c) Glas, H.; Herdtweck, E.; Spiegler, M.; Pleier, A. K.; Thiel, W. R. *J. Organomet. Chem.* **2001**, *626*, 100. (d) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, *22*, 2704. (e) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

(14) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(15) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866.

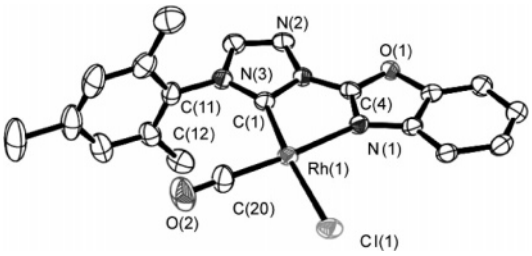
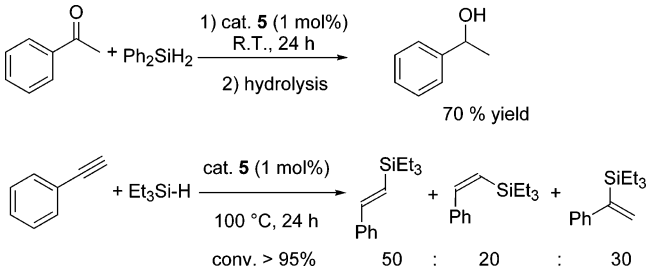


Figure 5. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Rh(1)−Cl(1), 2.370(2); Rh(1)−C(20), 1.811(4); Rh(1)−N(1), 2.113(3); Rh(1)−C(1), 1.957(4); C(1)−Rh(1)−N(1), 78.8(2); C(1)−N(3)−C(11)−C(12), 84.0(5); C(1)−N(2)−C(4)−N(1), 0(1).

Scheme 4. Hydrosilylation of Acetophenone (top) or Phenylacetylene (bottom) Catalyzed by Rhodium Complex 5



tonate by the imidazolium precursor and on trapping the resulting carbene by coordination to the metal. The detection of a signal at δ 186.9 ppm in the ^{13}C NMR spectrum, with a characteristic coupling constant J(Rh−C) of 59 Hz, established the formation of the carbene complex, while the $\nu_{(C=O)}$ band of the carbonyl ligand was observed in the IR spectrum at 1976 cm^{-1}.

The single-crystal X-ray diffraction study of compound **5** confirmed the square planar coordination geometry (Figure 5). The carbonyl ligand is disposed *trans* to the oxazoline unit, whereas the chloride is coordinated *trans* to the carbene. This arrangement is similar to that found in the previously reported bromo(1-(4,4-dimethyloxazolyl)-3-mesitylimidazol-2-ylidene)-(carbonyl)rhodium(I) complex bearing ligand type **A**.[16] The rhodium carbene distance [Rh(1)−C(1) = 1.957(4) Å] and the rhodium nitrogen distance [Rh(1)−N(1) = 2.113(3) Å] lie within the expected range.

To test the catalytic activity of compound **5**, we investigated the hydrosilylation of acetophenone with diphenylsilane (Scheme 4). The reaction was carried out at room temperature with 1.0 mol % of **5**. After 24 h and after hydrolysis, the corresponding secondary alcohol was isolated with 70% yield.

Since vinylsilanes are important intermediates in organic synthesis[17] and can be prepared by addition of silanes to alkynes, we also tested **5** for activity in this transformation. One major point of interest in this reaction is the regioselectivity, since hydrosilylation of monosubstituted or unsymmetrically substituted alkynes may give mixtures of isomeric products. For terminal alkynes in particular, three vinylsilane derivatives may be obtained as reaction products.[18]

The hydrosilylation of phenylacetylene with 1 equiv of triethylsilane was carried out at 100 °C, using 1.0 mol % of catalyst **5** and toluene as solvent. After 24 h, the complete catalytic transformation of the alkyne into the vinylsilanes was

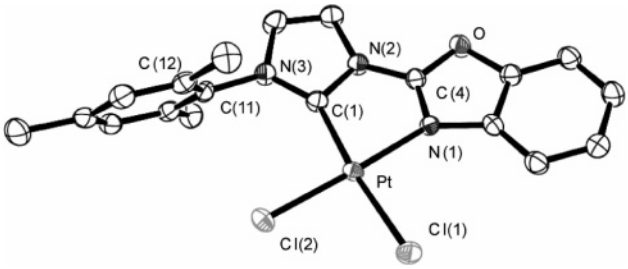
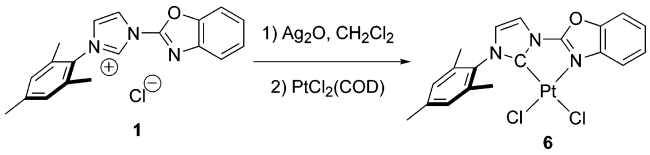


Figure 6. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Pt−Cl(1), 2.361(2); Pt−Cl(2), 2.294(1); Pt−C(1), 1.979(4); Pt−N(1), 2.056(3); C(1)−Pt−N(1), 80.8(2); C(1)−N(3)−C(11)−C(12), 74.4(6); C(1)−N(2)−C(4)−N(1), 0.3(6).

Scheme 5. Synthesis of the Platinum Complex 6 via Transmetalation with Ag_2O



observed (Scheme 4). The β-(*E*)-isomer, the β-(*Z*)-isomer, and the α-isomer were isolated in a ratio of 50/20/30.[19]

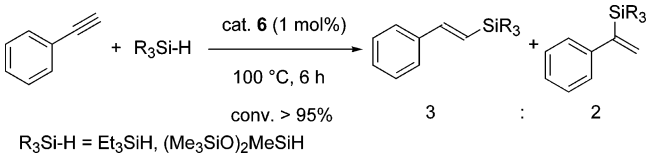
Synthesis and Structural Characterization of the Platinum Complex [$PtCl_2$(bzoxcarb)], 6. The silver complex **2** was also found to be an efficient starting material for the synthesis of platinum(II) complexes. Reaction of the imidazolium salt **1** with Ag_2O in situ prior to the addition of a solution of [$PtCl_2$(COD)] to the reaction mixture yielded the corresponding benzoxazole-carbene-platinum complex [$PtCl_2$(bzoxcarb)] (**6**) in good yield (Scheme 5).

Suitable crystals of **6** for an X-ray diffraction study were obtained from dichloromethane/hexanes. The molecular structure of **6**, which is very similar to that of the Pd analogue **3**, is depicted in Figure 6 along with the principal bond lengths and angles. The imidazole and benzoxazole rings are almost coplanar, whereas the mesityl ring slightly deviates from the orthogonal position to the imidazol ring (dihedral angle: C(1)−N(3)−C(11)−C(12) of 74.4°). As in the palladium complex **3**, the strong *trans* influence of the N-heterocyclic carbene ligand induces an increase in the Pt−Cl bond length in *trans* disposition to the carbene ligand compared to the chloro ligand *trans* to the oxazoline-N donor atom [2.361(2) vs 2.294(1) Å]. The platinum carbene distance of Pt−C(1) = 1.979(4) Å is within the expected range.[4f]

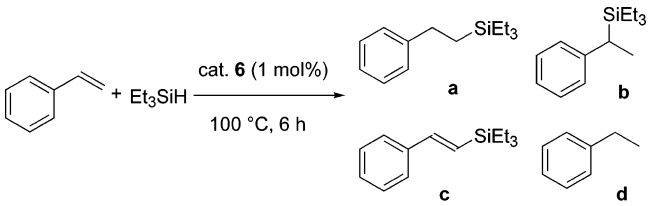
Catalytic Hydrosilylation of Alkenes and Alkynes with the Platinum Complex [$PtCl_2$(bzoxcarb)], 6. The hydrosilylation of C−C multiple bonds with platinum as catalyst is an important reaction for the production of intermediates for silicon-based polymers. Classical systems such as the Karstedt[20] or the Speier catalysts[21] display very high activity for that reaction, however, with a fairly rapid formation of inactive colloidal platinum. The development of new hydrosilylation catalysts is thus of interest, and several other active catalysts have been reported.[22] Very recently, platinum complexes that contain N-heterocyclic carbene ligands have been applied for the hydrosilylation of alkenes; high efficiency along with an uncommon selectivity was observed for these systems.[23]

(16) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Eur. J. Inorg. Chem.* **2004**, 3436.
(17) Langkopf, E.; Shinzer, D. *Chem. Rev.* **1995**, *95*, 1375.
(18) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 197.
(19) The products were unambiguously determined on the basis of the coupling constants of ^{1}H NMR spectra and GC-MS.
(20) Karstedt, B. D. US Patent 226928, 1972.
(21) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

Scheme 6. Hydrosilylation of Phenylacetylene Catalyzed by 6



Scheme 7. Hydrosilylation of Styrene with Triethylsilane Catalyzed by 6, along with Observed Byproducts



Time (h)	Yield (%)	selectivity a / b / c / d
2	25	89/2/4/5
10	62	88/2/4/6
20	70	85/2/5/8

While platinum(0) species are thought to be the active catalysts and zerovalent Pt complexes are thus used as catalysts for hydrosilylation, platinum(II) derivatives may also be employed with success as precursors to such species.[24] We therefore investigated the activity of the platinum(II) complex **6** in the hydrosilylation of various substrates.

The hydrosilylation of phenylacetylene with 1 equiv of triethylsilane or 1,1,1,3,5,5,5-heptamethyltrisiloxane was tested at 100 °C, using 1.0 mol % of catalyst **6** and toluene as solvent. After an induction period of ca. 1 h, the catalytic transformation of the alkyne to the vinylsilanes commenced, giving full conversion within 6 h (Scheme 6). Unlike for the reaction carried out with the rhodium catalyst **5**, the β-(*E*)-isomer and the α-isomer were the only two reaction products, which were formed in a ratio of 60 to 40, respectively.[19]

Hydrosilylation of alkenes is often accompanied by side-reactions such as isomerization or dehydrogenative silylation. For example, the hydrosilylation of styrene with triethylsilane generally yields a mixture of products **a**−**d** (Scheme 7). We carried out this reaction in toluene at 100 °C and in the presence of 1 mol % of **6**, and product **a** was detected as the major isomer. After 20 h, a 70% conversion to silylated products was obtained, with the linear product **a** being formed with 85% selectivity. While the activity of this system is thus lower than that of the platinum(0)-NHC complexes recently reported by Elsevier et al., its selectivity in the hydrosilane addition (**a** vs **b**) is within the same range.[25]

In another application of **6**, the hydrosilylation of styrene and 1-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane was tested (Scheme 8). The conversion of styrene into silylethylbenzene (**a** + **b**) was complete in the presence of 1% of catalyst precursor **6** within 20 h (entry 1), whereas using 0.1 mol % of catalyst required 48 h reaction time in order to obtain high conversion. The ratio between the 1-silylethylbenzene **a** and 2-silylethylbenzene **b** is high (ca. 9:1) under both conditions. Conversely, we noted in both cases that some dehydrogenative silylation, leading to the vinylsilane derivative, took place under the reaction conditions applied. Reaction with 1-octene as substrate gave 90% conversion after 13 h (entry 3), and the selectivity for 1-silyloctane is excellent, with only traces of 2-silyloctane and no dehydrogenative product being observed. Running the reaction with 0.1 mol % of catalyst gave 75% conversion after 13 h and identical selectivity (entry 4). However, the activity of catalyst **6** is considerably lower than that reported recently for the platinum(0)-carbene complexes studied by Markó et al.[20,26]

Conclusions

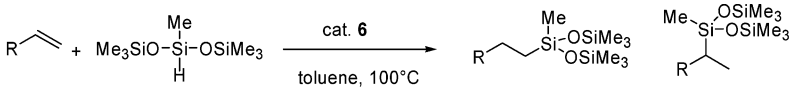
In summary, we have shown that the 2-benzoxazolyl imidazolium salt **1** is a readily accessible precursor for a new chelating C−N ligand system. Its coordination capabilities and its structural chemistry have been established in the synthesis of silver(I), palladium(II), rhodium(I), and platinum(II) complexes. First results in the platinum-catalyzed hydrosilylation of alkynes and alkenes indicate the potential of this new ancillary ligand in molecular catalysis.

Experimental Section

All manipulations were carried out under an inert gas atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified and dried by standard methods. 1-Mesitylimidazole,[27] $[PdCl_2(COD)]$,[28] and $[PtCl_2(COD)]$[28] were synthesized according to literature procedures. All other reagents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz and were referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra and elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department.

1-(Benzoxazol-2-yl)-3-mesitylimidazolium Chloride (1). 1-Mesitylimidazole (1.0 g, 5.4 mmol) was added to a solution of 2-chlorobenzoxazole (0.69 mL, 6.2 mmol) in toluene, and the mixture was heated at reflux overnight. During the course of the

Scheme 8. Hydrosilylation of Styrene or 1-Octene with Heptamethyltrisiloxane Catalyzed by 6



Entry	R	Cat. (%)	Time (h)	Conv. (%)	Yield of **a** (%)	Yield of **b** (%)
1	Ph	1	20	100	86	6
2	Ph	0.1	48	95	78	12
3	C_6H_{13}	1	13	90	89	<1
4	C_6H_{13}	0.1	13	75	74	<1

[a] Silane/alkene ratio 1.0, toluene, 100°C. Yield and selectivity were measured by ^{1}H NMR and GC using internal standard.

[a] Silane/alkene ratio 1.0, toluene, 100 °C. Yield and selectivity were measured by ^{1}H NMR and GC using internal standard.

reaction, a white precipitate formed and the product was isolated by filtration. The solid was washed twice with Et_2O (10 mL) and dried in vacuo, giving the desired imidazolium salt **1** (1.55 g, 85% yield). ^{1}H NMR (CD_2Cl_2): δ 12.21 (s, 1H, NC*H*N), 8.47 (pseudo-t, $^3J_{H-H}$ = 1.8 Hz, 1H, CH_{imid}), 7.88−7.85 (m, 2H, CH_{Ph}), 7.67 (pseudo-t, $^3J_{H-H}$ = 1.8 Hz, 1H, CH_{imid}), 7.79−7.83 (m, 2H, CH_{Ph}), 7.15 (s, 2H, CH_{mes}), 2.43 (s, 3H, $CH_{3\ para}$), 2.26 (s, 6H, $CH_{3\ ortho}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 150.0 (NCO), 148.9 ($C_{q\ benzox}$), 141.9 ($C_{q\ benzox}$), 139.6 (C_{mes}), 139.4 (N_2C), 134.2 (C_{mes}), 130.3 (C_{mes}), 129.9 (CH_{mes}), 127.2 (CH_{Ph}), 126.3 (CH_{Ph}), 125.5 (CH_{imid}), 120.7 (CH_{Ph}), 120.3 (CH_{imid}), 111.8 (CH_{Ph}), 20.9 ($CH_{3\ para}$), 17.7 ($CH_{3\ ortho}$). Anal. Calc for $C_{19}H_{18}ClN_3O$ (339.82): C, 67.15; H, 5.34; N, 12.37. Found: C, 66.98; H, 5.37; N, 12.46. MS(FAB) *m*/*z* (%): 304.1 (100) $[M]^+$. FT-IR (KBr): 1636 cm^{-1} ($\nu_{(C=N)}$).

(1-(Benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene)silver(I) Chloride (2). A suspension of 1-(benzoxazol-2-yl)-3-mesitylimidazolium chloride (**1**) (50 mg, 0.147 mmol) and Ag_2O (24 mg, 0.103 mmol) in dichloromethane was stirred at room temperature under exclusion of light. After 3 h of reaction, a colorless and transparent solution was obtained. The mixture was filtered through Celite in order to remove unreacted Ag_2O and other insoluble solids, and the solvent was evaporated in vacuo. The residue was washed twice with Et_2O and dried in vacuo to yield the desired compound as a white, light-sensitive solid. Suitable crystals for X-ray diffraction study were obtained by slow diffusion of Et_2O into a dichloromethane solution of the compound. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, CH_{imid}), 7.80 (m, 1H, CH_{Ph}), 7.71 (m, 1H, CH_{Ph}), 7.49 (m, 2H, CH_{Ph}), 7.27 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, CH_{imid}), 7.11 (s, 2H, CH_{mes}), 2.64 (s, 3H, $CH_{3\ para}$), 2.11 (s, 6H, $CH_{3\ ortho}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 187.3 (N_2C), 153.1 (N=*C*O), 149.5 ($C_{q\ benzox}$), 140.4 (C_{mes}), 139.9 ($C_{q\ benzox}$), 135.1 (C_{mes}), 134.5 (C_{mes}), 129.6 (CH_{mes}), 125.9 (CH_{Ph}), 125.8 (CH_{Ph}), 124.3 (CH_{imid}), 120.2 (CH_{Ph}), 120.1 (CH_{Ph}), 111.0 (CH_{imid}), 21.2 ($CH_{3\ para}$), 17.9 ($CH_{3\ ortho}$). Anal. Calc for $C_{19}H_{17}AgClN_3O$ (446.679): C, 51.09; H, 3.84; N, 9.41. Found: C, 51.27; H, 4.01; N, 9.35. MS(FAB) *m*/*z* (%): 304.0 (60) $[L]^+$, 409.8 (90) $[LAg]^+$, 714.8 (94) $[L_2Ag]^+$. FT-IR (KBr): 1626 cm^{-1} ($\nu_{(C=N)}$).

Dichloro(1-(benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene)-palladium(II) (3). [$PdCl_2$(1,5-COD)] (90 mg, 0.31 mmol) was added to a solution of **2** (143 mg, 0.32 mmol) in CH_2Cl_2 with exclusion of light. The mixture became cloudy immediately. After one night at room temperature, the solution was filtered through Celite. The solvents were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexanes to yield **3** (52 mg, 35%) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.45 (dd, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H-H}$ = 2.3 Hz, 1H, CH_{Ph}), 7.65 (m, 2H, CH_{imid}, CH_{Ph}), 7.45−7.36 (m, 2H, CH_{Ph}), 6.96 (m, 3H; 2H CH_{mes}, 1H CH_{imid}), 2.37 (s, 3H, $CH_{3\ para}$), 2.30 (s, 6H, $CH_{3\ ortho}$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 153.2 (N=*C*O), 149.6 ($C_{q\ benzox}$), 140.2 (C_{mes}), 139.9 ($C_{q\ benzox}$), 134.8 (C_{mes}), 134.4 (C_{mes}), 129.4 (CH_{mes}), 127.3 (CH_{Ph}), 126.5 (CH_{Ph}), 126.1 (CH_{Ph}), 123.6 (CH_{Ph}), 120.4 (CH_{imid}), 111.8 (CH_{imid}), 21.0 ($CH_{3\ para}$), 18.8 ($CH_{3\ ortho}$), the carbene ^{13}C NMR resonance was not observed. Anal. Calc for $C_{19}H_{17}Cl_2PdN_3O$ (480.68): C, 47.47; H, 3.56; N, 8.74. Found: C, 46.95; H, 3.47; N, 8.58. FT-IR (KBr): 1630 cm^{-1} (s, $\nu_{(C=N)}$).

Bis(1-(benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene)diiodopalladium(II) (4). Solid $[Pd(OAc)_2]_3$ (50 mg, 0.074 mmol) was added to a solution of 1-(benzoxazol-2-yl)-3-mesitylimidazolium chloride (**1**) (76 mg, 0.222 mmol, 3 equiv) in THF, giving an orange suspension, which immediately turned dark after adding an excess of NaI (415 mg, 2.5 mmol). The suspension was stirred at room temperature for 2 h, and the solvent was removed in vacuo, leaving a dark oily material as residue. The substance was redissolved in dichloromethane, filtered, and then purified by column chromatography on silica. Elution with dichloromethane afforded the desired compound as an orange solid (25 mg, 35% yield). X-ray quality crystals were obtained by slow diffusion of hexanes into a solution of **4** in dichloromethane. ^{1}H NMR ($CDCl_3$): δ 8.05 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 7.72 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, CH_{Ph}), 7.59 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, CH_{Ph}), 7.36 (td, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, CH_{Ph}), 7.26 (td, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, CH_{Ph}), 6.92 (s, 2H, CH_{mes}), 6.91 (d, $^3J_{H-H}$ = 2.1 Hz, CH_{imid}), 2.47 (s, 3H, $CH_{3\ para}$), 2.03 (s, 6H, $CH_{3\ ortho}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.3 (N=*C*O), 149.6 ($C_{q\ benzox}$), 140.6 (C_{mes}), 138.6 ($C_{q\ benzox}$), 135.7 (C_{mes}), 135.5 (C_{mes}), 129.7 (CH_{mes}), 129.1 (CH_{imid}), 125.2 (CH_{Ph}), 125.1 (CH_{Ph}), 121.5 (CH_{Ph}), 120.3 (CH_{Ph}), 112.3 (CH_{imid}), 21.2 ($CH_{3\ para}$), 17.9 ($CH_{3\ ortho}$), the carbene ^{13}C NMR resonance was not observed. MS(FAB) *m*/*z* (%): 301.9 (53) $[L]^+$, 425.9 (68) $[LPd(H_2O)]^+$, 728.8 (18) $[L_2Pd(H_2O)]^+$, 837.3 (8) $[L_2PdI]^+$. Anal. Calc for $C_{38}H_{36}I_2N_6O_3Pd$ (984.96): C, 46.34; H, 3.68; N, 8.53. Found: C, 46.24; H, 3.78; N, 7.96. FT-IR (KBr): 1617 cm^{-1} ($\nu_{(C=N)}$).

Chlorocarbonyl(1-(benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene)rhodium(I) (5). Solid Rh(acac)$(CO)_2$ (50 mg, 0.194 mmol) and 1-(benzoxazol-2-yl)-3-mesitylimidazolium chloride (65.9 mg, 0.194 mmol) were weighed in a Schlenk tube in a glovebox. THF (10 mL) was then added, and the color of the solution immediately turned yellow. After stirring for 1 h at room temperature, the solvent was removed in vacuo, and the crude product was twice washed with Et_2O, giving the rhodium complex as a yellow solid (77 mg, 85% yield). Crystallization from CH_2Cl_2/Et_2O gave suitable crystals for X-ray diffraction studies. ^{1}H NMR ($CDCl_3$): δ 8.65 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, CH_{Ph}), 7.64 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 7.57 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, CH_{Ph}), 7.48−7.36 (m, 2H, CH_{Ph}), 7.01 (s, 2H, CH_{mes}), 6.87 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 2.35 (s, 3H, $CH_{3\ para}$), 2.15 (s, 6H, $CH_{3\ ortho}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 186.9 (d, $^1J(^{103}Rh-^{13}C)$ = 81 Hz, CO), 184.1 (d, $^1J(^{103}Rh-^{13}C)$ = 59 Hz, Rh−$C_{carbene}$), 157.2 (NCO), 149.8 ($C_{q\ benzox}$), 140.7 (C_{mes}), 138.0 ($C_{q\ benzox}$), 135.0 (C_{mes}), 133.9 (C_{mes}), 129.5 (CH_{mes}), 127.1 (CH_{Ph}), 125.4 (CH_{Ph}), 124.6 (CH_{imid}), 121.1 (CH_{Ph}), 114.2 (CH_{imid}), 110.7 (CH_{Ph}), 21.2 ($CH_{3\ para}$), 17.9 ($CH_{3\ ortho}$). Anal. Calc for $C_{20}H_{17}ClN_3O_2Rh$ (469.726): C, 51.14; H, 3.65; N, 8.95. Found: C, 50.69; H, 3.74; N, 8.72. MS(FAB) *m*/*z* (%): 469.0 (13.6) $[LRhCOCl]^+$, 434.1 (31.8) $[LRhCO]^+$, 404.0 (61.4) $[LRh]^+$. FT-IR (KBr): 1976 cm^{-1} ($\nu_{(C=O)}$), 1626 cm^{-1} ($\nu_{(C=N)}$).

Dichloro(1-(benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene)-platinum(II) (6). A suspension of 1-(benzoxazol-2-yl)-3-mesitylimidazolium chloride (**1**) (91 mg, 0.27 mmol) and Ag_2O (44 mg, 0.189 mmol) in dichloromethane was stirred at room temperature under exclusion of light. After 3 h, a colorless and transparent solution of the Ag(I)-carbene compound was obtained. [Pt(COD)-Cl_2] (100 mg, 0.27 mmol) was then added to the solution, and the mixture immediately became cloudy. After stirring overnight at room temperature, the mixture was filtered through Celite and the solvent removed in vacuo. The residue was washed twice with pentane and dried under vacuum to yield the product (156 mg, 67% yield) as a pale yellow solid. X-ray quality crystals were obtained by vapor diffusion of hexane into a dichloromethane solution of **6**. ^{1}H NMR ($CDCl_3$): δ 9.00 (dd, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.8 Hz,

(22) See for example: (a) Steffanut, P.; Osborn, J. A.; De Cian, A.; Fisher, J. *Chem. Eur. J.* **1998**, *4*, 2008. (b) Jagadeesh, M. N.; Thiel, W.; Köhler, J.; Fehn, A. *Organometallics* **2002**, *21*, 2076. (c) Sprengers, J. W.; de Greef, M.; Duin, M. A.; Elsevier, C. J. *Eur. J. Inorg. Chem.* **2003**, 3811. (d) Sprengers, J. W.; Agerbeek, M. J.; Elsevier, C. J.; Kooijman, H.; Spek, A. L. *Organometallics* **2004**, *23*, 3117.

(23) Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J. P. *Science* **2002**, *298*, 204.

(24) Roy, K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510.

(25) Sprengers, J. W.; Mars, M. J.; Duin, M. A.; Cavell, K. J.; Elsevier, C. J. *J. Organomet. Chem.* **2003**, *679*, 149.

(26) (a) Markó, I. E.; Stérin, S.; Buisine, O.; Berthon, G.; Michaud, G.; Tinant, B.; Declercq, J. P. *Adv. Synth. Catal.* **2004**, *346*, 1429. (b) Buisine, O.; Berthon-Gelloz, G.; Brière, J. F.; Stérin, S.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J. P.; Markó, I. E. *Chem. Commun.* **2005**, 3856.

(27) Arduengo, A. J., III; Gentry, F. P., Jr.; Taverkere, P. K.; Simmons, H. E., III. US Patent 6,177,575 (January 2001).

(28) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 348.

Table 1. X-ray Experimental Data of Compounds 2−6

	2	3	4	5	6
formula	$C_{19}H_{17}AgClN_3O$	$C_{20}H_{19}Cl_4N_3OPd$	$C_{38}H_{34}I_2N_6O_2Pd$	$C_{60.75}H_{52}Cl_{4.5}N_9O_6Rh_3$	$C_{20}H_{19}Cl_4N_3OPt$
M_w	446.68	565.58	966.91	1472.37	654.27
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$Pbcn$	$P2_1/c$	$P2_1/c$
a (Å)	8.562(1)	11.615(1)	15.941(1)	22.860(1)	11.5920(6)
b (Å)	22.453(1)	14.779(1)	17.114(1)	9.520(1)	14.8230(8)
c (Å)	10.082(1)	13.821(1)	13.240(1)	31.005(2)	13.7950(9)
α (deg)	90.00	90.00	90.00	90.00	90.00
β (deg)	114.35(1)	108.41(1)	90.00	109.26(5)	108.439(2)
γ (deg)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	1765.7(1)	2251.0(2)	3612.1(4)	6370(3)	2248.7(2)
Z	4	4	4	4	4
ρ_{calc} (g cm^{-3})	1.68	1.67	1.78	1.53	1.93
$F000$	896	1128	1888	2956	1256
μ (mm^{-1})	1.304	1.316	2.266	1.012	6.732
temperature (K)	173	173	173	173	173
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
radiation			Mo Kα graphite monochromated		
no. of data measd	5230	5058	5280	18 628	6422
no. of data with $I > 2\sigma(I)$	2775	2275	2466	12 540	4682
no. of variables	214	262	222	752	262
R1	0.0464	0.0658	0.0464	0.0554	0.0355
wR2	0.1112	0.2115	0.1209	0.1895	0.0712
GOF	1.000	0.957	0.952	0.911	1.026
largest peak in final diff (e Å^3)	0.601	1.164	1.621	3.124	2.592

1H, CH_{Ph}), 7.81 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 7.65 (m, 1H, CH_{Ph}), 7.54−7.50 (m, 2H, CH_{Ph}), 6.98 (s, 3H; 2H CH_{mes}; 1H CH_{imid}), 2.35 (s, 3H, $CH_{3\ para}$), 2.17 (s, 6H, $CH_{3\ ortho}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.6 (N═*C*O), 147.3 ($C_{q\ benzox}$), 140.3 (C_{mes}), 139.3 ($C_{q\ benzox}$), 137.1 (C_{mes}), 134.2 (C_{mes}), 129.3 (CH_{mes}), 127.9 (CH_{Ph}), 126.8 (CH_{Ph}), 126.5.3 (CH_{Ph}), 121.1 (CH_{imid}), 114.8.1 (CH_{Ph}), 111.3 (CH_{imid}), 21.3 ($CH_{3\ para}$), 17.9 ($CH_{3\ ortho}$), the carbene ^{13}C NMR resonance was not observed. Anal. Calc for $C_{19}H_{17}Cl_2N_3OPt-CH_2Cl_2$ (569.34): C, 36.71; H, 2.93; N, 6.42. Found: C, 37.93; H, 3.19; N, 6.41. The deviation from the calculated values is due to variable amounts of lattice solvent CH_2Cl_2 in the crystalline sample. MS(FAB) *m*/*z* (%): 303.9 (25) $[L]^+$, 378.9 (37) $[(L\text{-}Mes)Pt]^+$, 499.9 (77) $[LPt]^+$. FT-IR (KBr): 1631 cm^{-1} ($\nu_{(C=N)}$).

Catalytic Hydrosilylation with Precatalyst 5 (Scheme 4). Hydrosilylation of Acetophenone. In a Schlenk tube, a solution of complex **5** (4.7 mg, 0.01 mmol) in dry toluene (5 mL) was prepared. After addition of the acetophenone (1.0 mmol), diphenylsilane (2.0 mmol) was added dropwise, and the bright yellow reaction mixture was stirred at room temperature for 24 h. A solution of NaOH in methanol was then added, and the resulting mixture was stirred for 1 h at room temperature. After evaporation of the solvents, the product was purified by column chromatography, giving pure 1-phenylethanol in 70% yield (85 mg).

Hydrosilylation of Phenylacetylene. In a Schlenk tube, a solution of complex **5** (2.4 mg, 0.005 mmol) in dry toluene (1.5 mL) was prepared, and phenylacetylene (0.5 mmol), triethylsilane (0.55 mmol), and *n*-dodecane (100 μL) were added in quick succession via syringes. The bright yellow reaction mixture was stirred at 100 °C for 24 h, and the crude mixture was subsequently filtered through alumina and analyzed by GC-MS (*m*/*z* = 218.1). After evaporation of the solvent, the products were purified by flash chromatography through a short plug of silica and analyzed by ^1H NMR spectroscopy. The three reaction products were unambiguously determined on the basis of the olefinic coupling constants in the ^1H NMR spectra: β-(*Z*)-isomer ^1H NMR ($CDCl_3$) δ 7.45 (d, J = 15.0 Hz), 5.75 (d, J = 15.0 Hz); β-(*E*)-isomer ^1H NMR ($CDCl_3$) δ 6.89 (d, J = 19.3 Hz), 6.43 (d, J = 19.2 Hz); α-isomer ^1H NMR ($CDCl_3$) δ 5.87 (d, J = 3.0 Hz), 5.58 (d, J = 3.0 Hz).

Catalytic Hydrosilylations with Precatalyst 6. Hydrosilylation of Phenylacetylene (Scheme 6). The same procedure as with precatalyst **5** was followed. The products were unambiguously determined on the basis of the coupling constants of the olefinic protons in the ^1H NMR spectra and by GC-MS (see above). ^1H NMR data of the products from hydrosilylation of phenylacetylene with 1,1,1,3,5,5,5-heptamethyltrisiloxane (olefinic region): β-(*E*)-isomer ^1H NMR ($CDCl_3$) δ 7.05 (d, J = 19.2 Hz), 6.69 (d, J = 19.2 Hz); α-isomer ^1H NMR ($CDCl_3$) δ 5.97 (d, J = 3.0 Hz), 5.57 (d, J = 3.0 Hz). GC-MS: *m*/*z* = 324.1.

Hydrosilylation of Alkenes (Schemes 7 and 8). In a Schlenk tube, a solution of complex **6** (2.0 mg, 0.0035 mmol) in dry toluene (1.5 mL) was prepared, and the respective substrate (0.35 mmol), the silane (0.36 mmol), and *n*-dodecane (100 μL) were added in quick succession via syringes. The Schlenk tube was heated in an oil bath at 100 °C. Samples were taken periodically for GC-MS analysis. At the end of the reaction, the products were purified by filtration through a short plug of silica and analyzed by ^1H NMR. The products from the hydrosilylation of styrene with triethylsilane (Scheme 7) have been reviously reported in the literature.[29]

3-Ethylbenzyl(1,1,1,3,5,5,5-heptamethyltrisiloxane) (Scheme 8, entries 1, 2). ^1H NMR ($CDCl_3$): δ 7.3 (m, 5H), 2.67 (m, 2H), 0.87 (m, 2H), 0.16 (s, 18H), 0.10 (s, 3H). GC-MS (EI): *m*/*z* 311.1 ($M^+ - CH_3$), 221.1 $[SiMe(OSiMe_3)_2^+]$.

3-Octyl(1,1,1,3,5,5,5-heptamethyltrisiloxane) (Scheme 8, entries 3, 4). ^1H NMR ($CDCl_3$): δ 1.4−1.2 (12H), 0.87 (t, 3H), 0.47 (m, 2H), 0.09 (s, 18H), 0.00 (s, 3H). GC-MS (EI): *m*/*z* 334.1 (M^+), 319.2 ($M^+ - CH_3$), 221.1 $[SiMe(OSiMe_3)_2^+]$.

X-ray Diffraction Study of 2−6. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[30] The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reduction. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C−H: 0.95 Å) and isotropic temperature factors (U(H) = 1.3U_{eqv}(C) Å^2) but not refined. Full least-squares refinements were on F^2. A final difference map revealed no significant maxima of residual electron density. The scattering factor coefficients and the anomalous

(29) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098.
(30) *Nonius OpenMoleN*, Interactive Structure Solution; Delft, 1997.
(31) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, 1974.

dispersion coefficients were taken from ref 31. Crystal data and experimental details for the crystals of **2**−**6** are given in Table 1.

Acknowledgment. We thank the CNRS (France), the Deutsche Forschungsgemeinschaft (SFB 623), and the EU (RTN Network AC3S). We thank the Service Commun des Rayons X, Strasbourg, for the X-ray diffractions studies.

Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, the positional and thermal parameters, and interatomic distances and angles for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060166U