ORGANIC LETTERS

2000
Vol. 2, No. 8
1125−1128

First Chelated Chiral *N*-Heterocyclic *Bis*-Carbene Complexes

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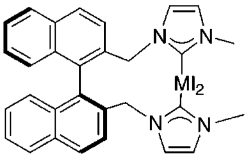
Received February 19, 2000

ABSTRACT



1 (**a** trans, **b** cis) M = **Pd**
2 (**a** trans) M = Ni

First chiral bidentate *bis*-carbene complex of Pd(II) prepared from a *bis*-imidazolium salt derived from (*S*)-2,2′-bromomethyl-1,1′-binaphthyl exists in both *cis*- and *trans*-square planar geometry. These and the corresponding *trans*-Ni(II) complexes are remarkably resistant to high temperature, air, water, and silica gel chromatography. The Pd complexes catalyze Heck reactions.

The pioneering works of Öfele and Wanzlick, who prepared the first authentic metal complexes of *N*-heterocyclic carbenes,[1] received little attention until the report of the synthesis of a stable, free carbene by Arduengo and coworkers in 1991.[2] New protocols for the synthesis of these carbenes and their metal complexes have spurred extensive research into applications of these complexes in homogeneous catalysis.[3] In contrast to the widely used phosphine complexes, several complexes formed with these ligands have been shown to be remarkably stable toward heat, air, and moisture. The metal−carbon bonds in the carbene complexes are much stronger than the metal−phosphorus bonds of typical phosphine complexes, thereby eliminating the problems associated with weak ligand−metal interactions including deposition of free metal under catalytic conditions.[3,4] The *N*-heterocyclic carbene complexes have been applied to a broad spectrum of catalytic reactions including Heck, Suzuki, and Kumada couplings,[5] olefin metathesis,[6] and hydrosilylation[7] processes. Herrmann and Fehlhammer have subsequently reported methylene-bridged chelated carbene complexes.[8] Carbene complexes with chiral ligands have also been prepared by a number of groups.[9]

Conspicuously absent from the studies reported thus far are chelated *bis*-carbene complexes of transition metals with a chiral backbone. Known chiral carbene complexes are of the type L*$_2$M (M = Rh,[9a] Ni,[9c] Pd;[9d] L* = monocarbene bearing a chiral group on the imidazoline-*N*) or a hybrid (oxazoline/imidazoline-2-ylidene)M (M = Rh).[9f] Lappert[9a]

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[1] (a) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42. (b) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141. (c) For contributions of the Lappert group, see: Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185. (d) For an historical account, see: Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725.

[2] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

[3] For a review, see: Herrmann; W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

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[5] (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371. (b) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93. (c) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (d) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348. (e) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889.

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[7] (a) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2805. (b) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217.

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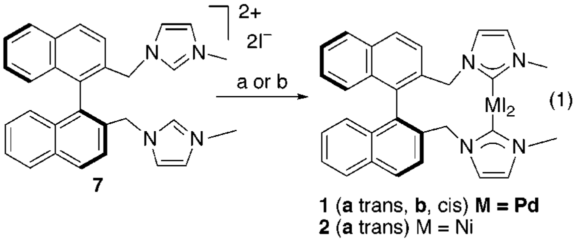
10.1021/ol005694v CCC: $19.00

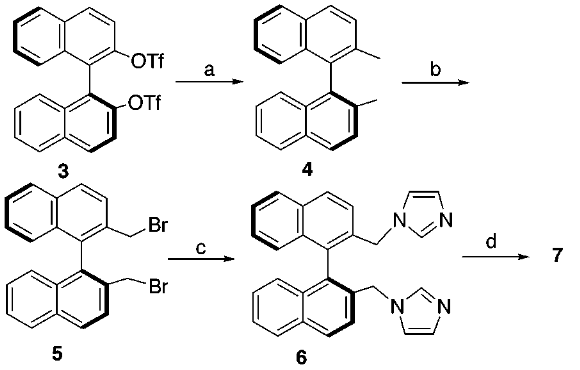
and Grubbs[9g] have described chiral 1,3-dialkyl-4,5-dihydroimidazol-2-ylidene complexes of Rh and Ru. Hydrosilylation[9b] and Heck reactions[9d] conducted with some of these complexes have given only marginal asymmetric induction. Since it is well-known that bidentate bisphosphine complexes generally give much superior asymmetric induction in many reactions vis-á-vis the corresponding monodentate phosphine complexes, we wondered whether a similar structural motif could be constructed with chelating *bis*-carbenes.[10] We have recently completed a study of the synthesis, structure, and reactivity of a new diimidazolin-2-ylidene ligand with a 2,2′-binaphthyl backbone.[11] In this paper we report the synthesis and potential utility of novel chiral, chelated *bis*-carbene complexes of palladium and nickel (**1** and **2**, eq 1) prepared with this ligand.



(a) MX, DMSO, Δ; (b) KO*t*-Bu, THF; MX

The preparation of the ligand began with the reaction of enantiomerically pure (*S*)-1,1′-bi-2-naphthol bis(trifluoromethanesulfonate) (**3**) with a solution of methylmagnesium bromide under (dppp)$NiCl_2$-catalyzed Kumada coupling conditions to give dimethyl compound **4** (Scheme 1).[12] Photolysis in carbon tetrachloride with *N*-bromosuccinimide gave dibromomethyl compound **5**. Bis-alkylation with the anion of imidazole followed by quaternization of the imidazole ring at the 3-position with methyl iodide completed the synthesis of the desired diimidazolium salt **7** in an overall yield of greater than 65% for the four steps.[13]

Scheme 1. Synthesis of Diimidazolium Salts



(a) MeMgBr, (dppp)$NiCl_2$, Et_2O, rt, 99%; (b) NBS, CCl_4, hν, rt, 90%; (c) NaH, imidazole, DME, 0 °C to rt, 80%; (d) MeI, CH_2Cl_2, 93%. (dppp = 1,3-bis(diphenylphosphino)propane).

A variety of conditions, which can be grouped into two main categories,[3] were examined for the preparation of the organometallic carbene complexes (eq 1). (1) In situ formation of the ligand by reaction with a metal salt (MX) where the X^- counterion of the salt functions as the base required for the carbene formation. (2) A two-step process where a solution of the putative *bis*-carbene of the ligand was generated under basic conditions and subsequently reacted with the metal salt.

The reaction of $Pd(OAc)_2$ with imidazolium salt **7** in DMSO at 140 °C gave both the *trans* and the *cis* Pd complexes **1a** and **1b** as yellow solids in 41% and 33% yields after chromatography.[14] The X-ray crystal structure analysis confirmed the geometry of these Pd complexes (vide infra). The absence of the signal for the imidazolium C-2 methine protons in the ^1H NMR spectra of the *cis* and *trans* complexes indicated successful transformation of the salt into the carbene. The NMR spectra indicated that the *trans* complex was C_2-symmetric, while the *cis* Pd complex **1b** had a more complex structure.[13] A single downfield signal in the ^{13}C spectrum of **1a** at 170.95 ppm for C-2 of the imidazole moieties was present for the carbene carbons. The

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(9) (a) Coleman, A. W.; Hitchcock, P. B.; Lappert, M. F.; Maskell, R. K.; Müller, J. H. *J. Organomet. Chem.* **1983**, *250*, C9. (b) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2805. (c) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472. (d) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483. (e) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1997**, *130*, 1253. (f) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162. (g) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (h) Other axial−chiral metal carbenes: Dötz, K. H.; Tomuschat, P.; Nieger, M. *Chem. Ber.* **1997**, *130*, 1605.

(10) All chelated carbene complexes prepared previously have an *N*,*N*′-methylene link between the imidazolines. Attempts to prepare other bridged *N*,*N*′-complexes (C_2, C_3, C_4, and *o*-xylylene) have not been successful. See ref 8b.

(11) This work was presented by D.S.C. at the 218th National Meeting of the American Chemical Society (New Orleans, August 1999), Paper ORGN 167.

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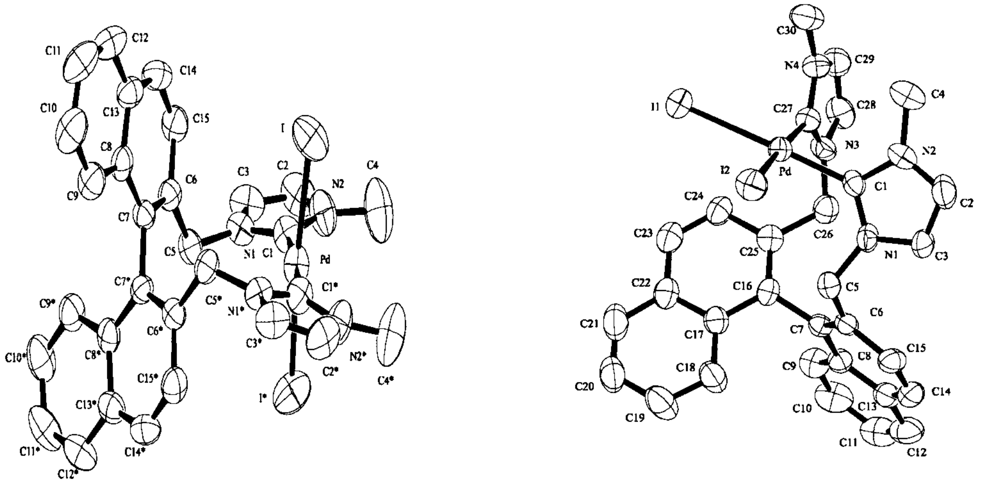
(13) See Supporting Information for details.

(14) **1a** and **1b**: imidazolium salt **7** (358 mg, 0.512 mmol) and palladium acetate (125 mg, 0.559 mmol) were stirred in DMSO (30 mL) at 140 °C for 6 h. The solvent was removed by distillation under high vacuum, and the residue was dissolved in CH_2Cl_2. Chromatography of the residue with CH_2Cl_2 as eluant gave complex **1a** (167 mg, 41%), and with ethyl acetate gave complex **1b** (135 mg, 33%) both as yellow solids. **1a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, $J = 7.8$ Hz, 2H), 7.94 (d, $J = 7.5$ Hz, 2H), 7.48 (dd, $J = 7.3$, 7.5 Hz, 2H), 7.36 (dd, $J = 7.3$, 8.7 Hz, 2H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 1.8$ Hz, 2H), 6.90 (d, $J = 1.8$ Hz, 2H), 5.70 (d, $J = 16.5$ Hz, 2H), 4.70 (d, $J = 16.5$ Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75.469 MHz, $CDCl_3$) δ 170.95 (2), 133.72 (2), 133.43 (2), 132.92 (2), 132.71 (2), 129.00 (2), 128.86 (2), 126.92 (2), 126.01 (2), 125.93 (2), 125.38 (2), 123.71 (2), 121.61 (2), 53.37 (2), 38.60 (2); MSFAB (SIMS-(+)) *m*/*z* (relative intensity) 803 ($C_{30}H_{26}N_4PdI_2$, $M^+ + 1$, 42), 802 (M^+, 26), 675 (100); rev. phase HPLC (10% water in methanol, 1 mL/min, Zorbax ODS, 300 nm) 3.87 min (100%). **1b**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, $J = 8.7$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 7.5$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.51 (dd, $J = 7.5$, 7.5 Hz, 1H), 7.47 (dd, $J = 7.8$, 8.4 Hz, 1H), 7.35 (d, $J = 1.8$ Hz, 1H), 7.30−7.35 (m, 2H), 7.22 (dd, $J = 7.8$, 8.7 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 6.98 (d, $J = 1.8$ Hz, 1H), 6.80 (d, $J = 8.7$ Hz, 1H), 6.41 (d, $J = 1.8$ Hz, 1H), 5.98 (d, $J = 1.8$ Hz, 1H), 5.80 (d, $J = 17.1$ Hz, 1H), 5.71 (d, $J = 15.6$ Hz, 1H), 4.87 (d, $J = 17.1$ Hz, 1H), 4.69 (d, $J = 15.6$ Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.21, 163.71, 134.03, 133.18, 133.08 (2), 133.02, 131.91, 131.44, 130.78, 129.91, 128.86, 128.77, 128.21, 127.47, 126.93, 126.65, 126.30, 126.14, 125.20, 124.28, 124.01, 123.34, 122.60, 121.27, 113.15, 55.31, 52.89, 39.58, 39.52; MSFAB (SIMS-(+)) *m*/*z* (relative intensity) 803 ($C_{30}H_{26}N_4PdI_2$, $M^+ + 1$, 6), 802 (M^+, 12), 675 (100); rev. phase HPLC (10% water in methanol, 1 mL/min, Zorbax ODS, 300 nm) 3.83 min (100%).



1a

1b

Figure 1. ORTEP drawings of the molecular structure of *trans* Pd complex **1a** and *cis* Pd complex **1b** (thermal ellipsoids at the 50% probability level). **1a**: the atoms marked with an asterisk (*) are related to the unmarked atoms by a crystallographic 2-fold axis. Selected bond lengths [Å] and angles [deg]: Pd−C1 2.016 (6), Pd−I 2.6011 (6), C1−Pd−C1* 175.6 (4), I−Pd−I* 174.64 (4), I−Pd−C1 90.1 (2). **1b**, selected bond lengths [Å] and angles [deg]: Pd−C1 1.986 (6), Pd−C27 1.994 (7), Pd−I1 2.6890 (8), Pd−I2 2.6416 (7), C1−Pd−C27 89.7 (3), I1−Pd−I2 92.64 (2), I2−Pd−C1 86.5 (2), I1−Pd−C27 91.1 (2).

methylenes connecting the aromatic backbone to the heterocyclic rings were visible as an AX system of doublets at 5.70 and 4.70 ppm. The geometry of the 11-membered chelated ring was such that these geminal protons occupied quite different environments as indicated by the large $\Delta\delta$ of 1.00 ppm. The ^{13}C NMR spectrum for *cis* Pd complex **1b** contained two downfield signals at 161.23 and 159.28 ppm for the carbene carbons. In the ^{1}H NMR spectrum, four signals for the bridging benzylic methylene protons were visible as doublets at 5.80, 5.71, 4.87, and 4.69 ppm. The *N*-methyl groups appeared as a pair of singlets at 3.89 and 3.73 ppm.

The formation of the *bis*-carbene of the ligand was attempted with a variety of base and solvent combinations. It was found that reaction in THF at rt with potassium *tert*-butoxide under dilute conditions gave the *bis*-carbene cleanly, and in high yield.[13] Reaction of a THF solution of the *bis*-carbene of the ligand with $Pd(OAc)_2$ gave *exclusively* the *trans* palladium complex in 21% yield with spectral properties identical to those of the material prepared in hot DMSO. Reaction of $(Ph_3P)_2PdCl_2$ under similar conditions gave none of the desired Pd complexes. Here, the larger ring size of the chelate allowed for the *trans* configuration of the complex in contrast to previous observations where only the *cis* configuration of a methylene bridged *bis*-carbene Pd complex was formed.[8] Metal complexes with *trans*-spanning chelating ligands are rare, and some have been shown to possess unique catalytic properties.[15]

Single crystals of the Pd complexes were obtained by diffusion of hexane into a solution of the complex in CH_2Cl_2. X-ray analysis of these crystals showed the geometry of the ligands around the metal to be distorted square planar (Figure 1).[16] The Pd−C bond lengths were 2.016 Å for the *trans* Pd complex and slightly shorter at 1.986 and 1.994 Å for the *cis* Pd complex, indicating a more congested environment at the metal center for complex **1b**. The C−Pd−C bond angles were determined to be 175.6° and 89.7°, respectively. It was hoped that the highly asymmetric nature of the complexes would result in efficient chirality transfer from the BINAP backbone in stereodifferentiating reactions.

We next turned our attention to the preparation of Ni complexes. The reaction of diimidazolium salt **7** with either $Ni(acac)_2$ or $(Ph_3P)_2NiCl_2$ in hot DMSO gave either no reaction or decomposition of starting materials with no trace of the desired complex. Surprisingly, the reaction of $Ni(acac)_2$ with the iodide salt in the higher boiling *N*-methylpyrrolidinone (NMP) at 200 °C was successful, giving after chromatography *trans* Ni complex **2a** as a red-colored solid in 26% yield. The reaction of $(Ph_3P)_2NiCl_2$ and a solution of the preformed *bis*-carbene in THF also gave *trans* Ni complex **2a** in 45% yield after chromatography. In contrast to the Pd complexes described above, only the *trans* Ni complex was obtained, even under the harsh NMP reaction conditions. Nickel tends to form *trans* complexes with monocarbenes,[17] and furthermore, no chelated bidentate

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(15) Sawamura, M.; Sudoh, M.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309 and references therein.

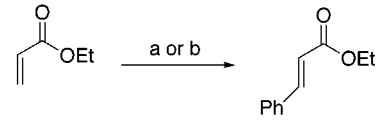
(16) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137339 (**1a**), CCDC-137340 (**1b**), and CCDC-137338 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk). See Supporting Information for details of the crystal structure analysis.

(17) Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209.

[carbene]NiX_2 complexes have been reported even though attempts to synthesize such complexes have been documented.[8a]

The ^{13}C NMR spectrum of Ni complex **2a** contained 15 signals with one signal downfield at 176.41 ppm for the C-2 carbene of the imidazole moieties. The ^{1}H NMR spectrum in $CDCl_3$ contained signals between 6.78 and 8.00 ppm for the aromatic backbone and imidazole portions of the complex. The bridging methylene protons were visible as an AX system of doublets at 6.20 and 4.78 ppm. The imidazole *N*-methyl groups appeared as a singlet at 4.07 ppm. Single crystals of Ni complex **2a** were obtained by diffusion of hexane into a solution of the complex in CH_2Cl_2. X-ray analysis of these crystals confirmed the *trans* configuration of the ligand and further showed the geometry of the ligands around the metal to be distorted square planar.[18] The Ni−C bond lengths were 1.889 and 1.901 Å, and the C1−Ni−C27 bond angle was determined to be 177.7°. Taking into account the shorter Ni−C bonds, the geometric parameters are comparable to those of the *trans* Pd complex **1a**.

As can be inferred from the method of preparation (polar solvents and high temperature), analysis (reverse phase HPLC with water/methanol solvent), and purification (silica chromatography with no special attention to exclude air),[13] these are remarkably stable complexes. Preliminary catalytic studies support these conclusions. Complexes **1a** and **1b** were found to catalyze Heck coupling between ethyl acrylate and bromo- or iodobenzene in 79% and 95% yields, respectively, at 1−2 mol % of catalyst loading (eq 2).



(2)

(a) **1b**, PhI, NaOAc, DMA, 140 °C, 38 h, 95%;
(b) **1b**, PhBr, Cs_2CO_3, Bu_4NBr, NMP, 130 °C, 24 h, 79%.

In summary we have prepared the first catalytically competent monomeric, chiral *bis*-carbene complexes of Pd and Ni possessing a binaphthyl backbone. Further examination of this ligand motif and its structural variants as well as the applications of these materials as enantioselective catalysts are under investigation and will be reported in due course.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9706766) and The Ohio State University (postdoctoral fellowship, D.S.C.). We thank Johnson Matthey for a gift of precious metals in support of our research programs.

Supporting Information Available: Details of the preparation of the imidazolium salts and Ni complex **2a** and ORTEP diagram of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] See Supporting Information for details of the preparation and for an ORTEP drawing of the complex with selected bond lengths and bond angles.