Organometallics **2001,** *20,* 5485−5488 5485

Notes

Tridentate Carbene CCC and CNC Pincer Palladium(II) Complexes: Structure, Fluxionality, and Catalytic Activity

Stephan Gründemann, Martin Albrecht, Jennifer A. Loch, Jack W. Faller,* and Robert H. Crabtree*

Yale Chemistry Department, PO Box 208107, New Haven, Connecticut 06520-8107

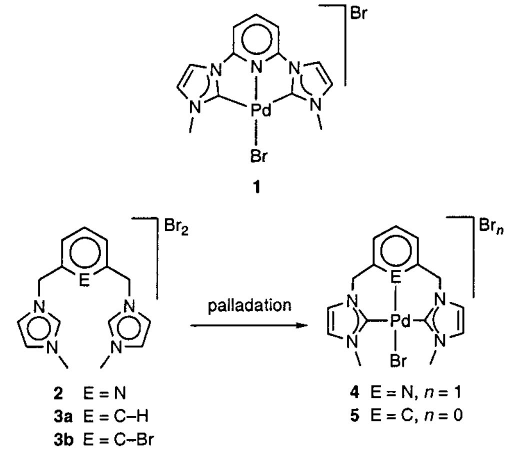
Received July 17, 2001

Summary: Air and thermally stable palladium(II) complexes of CNC and CCC bis-carbene pincer ligands have a twisted conformation and catalyze Heck olefination of activated aryl chlorides.

Two key ideas—heterocyclic carbenes and pincer ligands—have shown their power in recent work in homogeneous catalysis. Heterocyclic carbenes[1] are attractive in being a rare class of nonphosphine ligand that can give highly active catalysts.[2] They can undergo decomposition pathways, however.[3] Since pincer (*mer*, tridentate) frameworks enhance the stability of M−L bonds, we thought they could usefully be applied to stabilizing carbene complexes. While pincer phosphines and amines are well known,[4] pincer carbenes are rare.[5] Carbenes have a much higher trans effect than N- or P-donors and are more tightly bound to the metal, so they should give pincer derivatives having usefully different properties.

We recently reported the first palladium pincer carbene complex (**1**) which is an active catalyst for the Heck reaction.[5a] The molecule is essentially flat and has inconveniently low solubility. We now find that a CH_2 spacer between the rings enhances solubility and leads to an unusual twisted geometry.

Scheme 1. Palladation of Carbene Pincer Ligands with $[Pd(OAc)_2]$ (for 2) or $[Pd_2(dba)_3]$ (for 3)



The ligand precursor **2** (Scheme 1) was readily accessible in one step from *N*-methyl imidazole and bis-2,6-(bromomethyl)pyridine. Since bis-1,3-(bromomethyl)-benzene is also available, we were able to make the analogous precursor **3** with a CH replacing the pyridine N. The two ligands are nearly isosteric, but their central fragments are very different electronically.

Synthesis of **4** from the CNC carbene pincer **2** followed the known route from Pd(II) acetate at 160 °C. Palladation of the CCC precursor **3a** proved unsuccessful.[6] This suggests initial coordination of the pyridine of **2** is essential to direct the C−H bond activation needed in the formation of **4**. We therefore moved to the bromoaryl precursor **3b**, where oxidative addition to Pd(0) was expected to establish the initial M−L bond. Reaction of **3b** with $[Pd_2(dba)_3]$ indeed gave the desired complex **5** in moderate yields. **5** appears to be the first CCC pincer complex. Both **4** and **5** decompose only above 230 °C in the solid state. Complexes closely related to **4**, in which the peripheral methyl groups were substituted by mesityl or 2,6-diisopropylphenyl groups, have very recently been reported, together with their catalytic activity.[7]

Spectroscopic characterization of **4** and **5** in solution revealed a significant downfield shift of the carbene

---

[1] (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

[2] (a) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Heringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773. (b) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307. (c) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255. (d) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903. (e) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (f) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

[3] McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029.

[4] (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (c) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (d) Jensen, C. M. *Chem. Commun.* **2000**, 2443.

[5] (a) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201. (b) Babu, R. P. K.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226. (c) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Chem. Comm.* **2000**, 481.

[6] Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*−*618*, 546.

[7] 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.

10.1021/om010631h CCC: $20.00
Publication on Web 11/10/2001

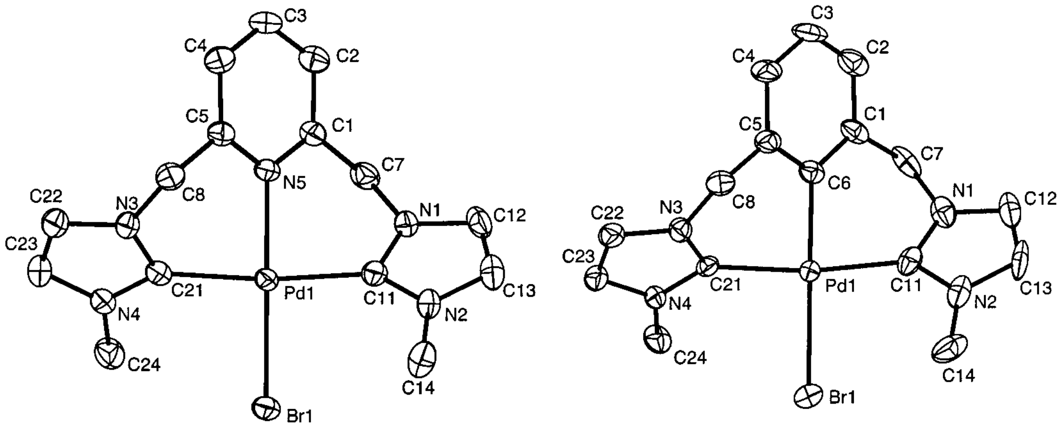
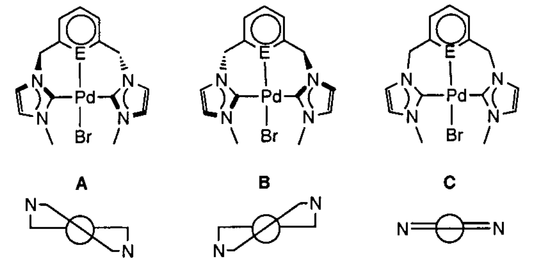


Figure 1. Perspective view (50% probability level) of the structures of **4** (left) and **5** (right). Hydrogen atoms in both structures and the noncoordinating bromide anion and the two cocrystallized MeOH molecules (**4**) are not shown.

carbon in the ^{13}C NMR spectrum and the absence of a proton attached to this nucleus (located at ca. δ 9 in the ligand precursors; DMSO-d_6 solution). These are diagnostic for metalation of the imidazolium salts and formation of the carbene complexes. Interestingly, the benzylic CH_2 protons in **4** appear as a broad singlet in the ^{1}H NMR spectrum, while in **5** they appear as a sharp AB pattern at δ 5.47 and 4.66 ($CDCl_3$). Variable-temperature studies showed that these protons are involved in a dynamic process. The twisted conformation adopted (see below) led us to assign this process to interconversion between the left- and right-hand twisted forms with a corresponding chirality change of the complex (**A**, **B** in Scheme 2). This atropisomerization includes a reorientation of all three rings. At the fast exchange limit, only an average structure **C** is observed, which has C_{2v} symmetry with equivalent benzylic protons.

Scheme 2. Limiting Structures of the Atropisomerization of 4 and 5 in Solution; Bottom Figures Represent the Newman-Projection along the Pd−E Bond



At 25 °C, the dynamic process of **4** is relatively fast on the ^{1}H NMR time scale and the benzylic protons appear as a broad singlet. Decoalescence of the signal is reached at 5 °C ($CDCl_3$ solution), and at −50 °C, the sharp AB pattern is observed, as in **5** at 25 °C. Heating of a DMSO-d_6 solution of **5** was required to achieve coalescence ($T_{\mathrm{coal}} = 77$ °C), and above 145 °C, the benzylic protons appear as a sharp singlet, indicating that atropisomerization is fast. The line broadening is independent of solvent ($CDCl_3$ vs DMSO) so DMSO does not coordinate to **5**, e.g., to give a cationic solvento complex [Pd(CCC)(DMSO)]Br.[8]

Table 1. Thermodynamic Parameters for the Atropisomerization of 4 and 5[a]

complex	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	k_{298}/s^{-1}
4	51.6 (1.9)	−5.5 (6.9)	2900 (150)
5	74.5 (5.8)	10.3 (16.9)	2 (0.6)

[a] esd's in parentheses.

Line-shape analysis of the temperature-dependent NMR spectra allowed us to extract the kinetic parameters (Table 1). As expected for intramolecular processes, $\Delta S^{\ddagger}$ is close to zero. Unexpectedly for such similar compounds, there is a large difference in $\Delta H^{\ddagger}$ for **4** vs **5**. The nearly isosteric character of **4** and **5** requires an electronic explanation. Future computational work is planned to try to understand these results. Single-crystal structure analyses of **4** and **5** showed that the metallacycles are strongly puckered (Figure 1 and Table 2).[9] For example, the dihedral angles (C1−E−Pd1−C11) are 40.5(4)° in **4** (i.e., E = N5) and 42.9(7)° in **5** (E = C6). These compare well to those observed in related Pt(II)-pyrazolyl complexes.[10] Notably, the lengths of the Pd−N bond in **4** and the Pd−C bond in **5** are virtually identical, so the ground-state structures are not dissimilar enough to provide a plausible origin for the very different fluxional behavior. The different trans influence of pyridine vs the aryl is shown by the difference in the Pd−Br bond distances trans to the aryl C (2.5388(10) Å in **5**) vs trans to the pyridine N (2.4250(5) Å in **4**).

Heck olefination often requires expensive ArI or ArBr and is rarer for the more readily available ArCl,[11] where high catalyst loadings of 2−10% are commonly needed.[12]

---

(8) Similar complexes have been detected in related pincer chemistry using NCN-platinum complexes and polar coordinating solvents: Gossage, R. A.; Ryabov, A. D.; Spek, A. L.; Stufkens, D. J.; Beck, J. A. M.; van Eldik, R.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 2488.

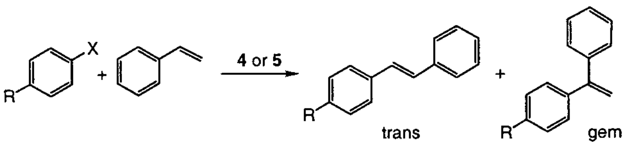
(9) Crystal data: **4**: $C_{15}H_{17}Br_2N_5Pd \times 2CH_3OH$, colorless prism (0.19 × 0.12 × 0.12 mm), $M = 597.62$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.3828(5)$ Å, $b = 17.3816(11)$ Å, $c = 13.5501(5)$ Å, $\beta = 91.534(3)°$, $V = 2209.1(2)$ Å^3, $Z = 4$, $D_c = 1.797$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 4.49 mm^{-1}, $\lambda = 0.71073$ Å, reflections $[I > 3\sigma(I)] = 3066$, $R_1 = 0.032$, $wR_2 = 0.038$, GOF = 1.105. **5**: $C_{16}H_{17}BrN_4Pd$, $M_r = 451.64$, colorless plate (0.12 × 0.12 × 0.05 mm), orthorhombic, space group *Aba*2 (no. 41), $a = 20.2868(8)$ Å, $b = 13.0587(5)$ Å, $c = 12.0237(4)$ Å, $V = 3185.3(2)$ Å^3, $Z = 8$, $D_c = 1.883$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 3.684 mm^{-1}, $\lambda = 0.71073$ Å, reflections $[I > 3\sigma(I)] = 1413$, $R_1 = 0.033$, $wR_2 = 0.048$, GOF = 0.983.

(10) Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *599*, 195.

Table 2. Selected Bond Lengths and Angles for 4 and 5

	4 (E = N5)	**5** (E = C6)
	Bond Lengths (Å)	
Pd1−E	2.066(3)	2.014(8)
Pd1−C11	2.020(4)	2.00(1)
Pd1−C21	2.025(5)	2.055(12)
Pd1−Br1	2.4250(5)	2.5388(10)
C12−C13	1.328(7)	1.33(2)
C22−C23	1.329(7)	1.31(2)
	Bond Angles (deg)	
C11−Pd1−C21	173.2(2)	170.9(4)
E−Pd1−C11	86.5(2)	85.1(5)
E−Pd1−C21	86.7(2)	86.1(4)
E−Pd1−Br1	178.92(10)	179.6(3)

Table 3. Heck Activity of 4 and 5 with Different Aryl Halides[a]



entry	catalyst	R	X	reaction time (h)	yield (%)[b] (trans/gem)	TON[c]
1	**5**	CHO	Cl	19	70 (65/5)	350
2	**4**	CHO	Cl	0.5	90 (82/8)	450
3	**4**	C(O)CH_3	Br	0.25	97 (90/7)	485
4	**4**	OCH_3	Br	1	97 (84/13)	485
5	**4**	C(O)CH_3	Cl	0.25	98 (91/7)	490
6	**4**	OCH_3	Cl	18	11 (10/1)	55

[a] Reaction conditions: 1.4 molar equiv styrene, 1.1 molar equiv NaOAc, 20 mol % n-Bu_4NBr (for X = Cl only), 0.2 mol % catalyst, refluxing DMA. [b] ^{1}H NMR yield using di(ethylene glycol) dibutyl ether as standard. [c] TON = mol prod./mol Pd.

We find **4** and **5** are thermally very robust and active for high-temperature Heck olefination of aryl chlorides, albeit activated ones (Table 1).[5a] Neutral complex **5** is less active and the initial turnover frequency (TOF; mol substrate/mol Pd) for the olefination of chlorobenzaldehyde does not exceed 125 h^{-1}. Prolonged reaction times increased the product yield, and after 19 h, 70% conversion was observed (entry 1). In contrast, cationic complex **4** is more efficient: at 0.2 mol % catalyst loading, maximum conversion to products is noted after only 30 min at 165 °C, corresponding to a TOF of 900 h^{-1} (entry 2). This catalytic performance of **4** is significantly better than the one reported for related pincer carbene catalysts containing aryl substituents at the imidazole units.[7] Activated and deactivated aryl bromides are olefinated in a short time and in the absence of any additives such as Bu_4NBr (entries 3, 4). The turnover rates and numbers of **4** with deactivated aryl chlorides were low, however (entry 6). Despite **4** and **5** being nearly isosteric, the different electronic effects of aryl C vs pyridine N cause the fluxional and catalytic properties to differ strongly; **4** is more active than **5**. Both complexes are highly air and thermally stable.

Experimental Section

General Procedures. The 2-bromo-α,α′-dibromo-*m*-xylene was prepared according to a literature procedure;[13] other reagents are commercially available and were used as received. NMR spectra were recorded at 25 °C on Bruker spectrometers at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm, J in Hz). Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on heteronuclear shift correlation spectroscopy. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc. or Robertson Microlit Laboratories, Inc.; residual solvent molecules have been identified by ^{1}H NMR. Line-shape analyses were performed using in-house developed programs based on the quantum-mechanical density matrix formalism of Binsch.[14] The catalytic experiments were carried out according to procedures reported earlier.[5a]

Synthesis of 2. A solution of 2,6-bis(bromomethyl)pyridine (1.337 g, 5.0 mmol) and 1-methylimidazole (0.831 g, 10.0 mmol) was stirred in dioxane (80 mL) at 100 °C for 12 h. After cooling, the formed solid was collected and purified by repetitive precipitation from MeOH/Et_2O mixtures and finally by recrystallization from CH_2Cl_2/Et_2O. Yield: 1.97 g (91%). ^{1}H NMR (DMSO-d_6): δ 9.22 (s, 2H, NC*H*N), 7.97 (d, 2H, $^3J_{HH} = 8.0$ Hz, py-*H*), 7.78 (s, 2H, im-*H*), 7.74 (s, 2H, im-*H*), 7.51 (t, 1H, $^3J_{HH} = 8.0$ Hz, py-*H*), 5.59 (s, 4H, pyCH_2N), 3.93 (s, 6H, NCH_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 153.42 (N*C*HN), 138.57 (C_{ortho}), 137.00 (C_{para}), 123.16 (C_{im}), 122.90 (C_{im}), 121.87 (C_{meta}), 52.27 (pyCH_2N), 35.74 (NCH_3); mp 140 °C (dec). Anal. Calcd for $C_{15}H_{19}Br_2N_5$ (429.15) × $0.5CH_2Cl_2$: C, 39.47; H, 4.27; N, 14.85. Found: C, 39.46; H, 4.64; N, 14.72.

Synthesis of 3b. The procedure was analogous to the preparation of **2**, starting from 2-bromo-α,α′-dibromo-*m*-xylene (3.38 g, 9.9 mmol) and 1-methylimidazole (2.6 mL, 32.5 mmol). The crude product was repetitively washed with dioxane and ether and dried in vacuo to give **3b** (4.41 g, 88%) as a colorless solid, which was recrystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (DMSO-d_6): δ 9.28 (s, 2H, NC*H*N), 7.79 (m, 4H, im-*H*), 7.54 (t, 1H, $^3J_{HH} = 7.6$ Hz, Ar-*H*), 7.40 (d, 2H, $^3J_{HH} = 7.6$ Hz, Ar-*H*), 5.59 (s, 4H, ArCH_2N), 3.89 (s, 6H, NCH_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 137.26 (N*C*N), 135.12 (C_{ortho}), 130.98 (C_{meta}), 128.89 (C_{para}), 124.48 (C_{ipso}), 124.08 (im-*C*), 122.74 (im-*C*), 52.42 (Ar-CH_2-N), 36.02 (NCH_3); mp 230 °C (dec). Anal. Calcd for $C_{16}H_{19}Br_3N_4$ (507,06) × H_2O: C, 36.60; H, 4.03; N, 10.67. Found: C, 36.65; H, 3.93; N, 10.64.

Synthesis of 4. A solution of **2** (870 mg, 2.0 mmol) and [Pd(OAc)$_2$] (448 mg, 2.0 mmol) was stirred in DMSO (8 mL) for 2 h at 25 °C, then for 12 h at 50 °C, and finally for 1 h at 150 °C. The mixture was subsequently diluted with CH_2Cl_2 (20 mL) and Et_2O (200 mL). The precipitate that formed was collected, suspended in $CHCl_3$ (30 mL), and filtered over Celite. Upon addition of Et_2O (150 mL), **4** formed as a yellowish precipitate, which was isolated by filtration and dried in vacuo (0.68 g, 64%). Powderous **4** appeared to be very hygroscopic and rapidly became sticky when exposed to air (cf. elemental analysis).[15] Crystals that were suitable for a single-crystal structure determination were grown by slow diffusion of an Et_2O solution into a solution of **4** in MeOH. ^{1}H NMR (DMSO-d_6): δ 8.20 (t, 1H, $^3J_{HH} = 7.7$ Hz, py-*H*), 7.86 (d, 2H, $^3J_{HH} = 7.7$ Hz, py-*H*), 7.58 (s, 2H, $^3J_{HH} = 1.6$ Hz, im-*H*), 7.37 (s, 2H, $^3J_{HH} = 1.6$ Hz, im-*H*), 5.68 (br s, 4H, pyCH_2N), 3.94 (s, 6H, NCH_3); ^{13}C{^{1}H} NMR (DMSO-d_6): δ 164.06 (C−Pd), 155.03 (C_{ortho}), 141.55 (C_{meta}), 125.20 (C_{meta}), 123.43 (C_{im}), 121.62 (C_{im}), 54.30 (pyCH_2N), 37.86 (NCH_3); mp 230−240 °C (dec). Anal. Calcd for $C_{15}H_{17}$-

---

(11) (a) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. (b) Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10. (c) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1473. For a catalyst system that works efficiently at room temperature, see: (d) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6869.

(12) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(13) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468.

(14) Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304.

(15) Related ionic Pd(CNC) complexes were found to be hygroscopic as well: Miecznikowski, J. R.; Crabtree, R. H. unpublished results.

Br_2N_5Pd (533.56) × $2H_2O$: C, 31.63; H, 3.72; N, 12.30. Found: C, 31.78; H, 3.68; N, 12.29.

Synthesis of 5. A solution of **3b** (1.11 g, 2.18 mmol), $[Pd_2(dba)_3]$ (1.00 g, 1.09 mmol), and Na_2CO_3 (930 mg, 8.74 mmol) was stirred in degassed DMSO (30 mL) for 6 h at 25 °C and then 18 h at 125 °C. Then brine (270 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The brown solid was purified by column chromatography (SiO_2; elutant first CH_2Cl_2, then CH_2Cl_2/acetone, 3:2), yielding **5** as an off-white solid (428 mg, 43%). Analytically pure **5** suitable for a single-crystal structure determination was obtained by slow diffusion of Et_2O into a solution of **5** in CH_2Cl_2. ^1H NMR ($CDCl_3$): δ 7.02 (d, 2H, $^3J_{HH} = 7.3$ Hz, Ar-*H*), 6.98 (d, 2H, $^3J_{HH} = 1.5$ Hz, im-*H*), 6.90 (t, 1H, $^3J_{HH} = 7.3$ Hz, Ar-*H*), 6.72 (d, 2H, $^3J_{HH} = 1.5$ Hz, im-*H*), 5.47 (d, 2H, $^3J_{HH} = 13.6$ Hz, ArCH*H*N), 4.66 (d, 2H, $^3J_{HH} = 13.6$ Hz, ArC*H*HN), 4.08 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.54 (N*C*N), 151.44 (C_{ipso}), 140.96 (C_{ortho}), 125.11 (C_{meta}), 123.12 (C_{para}), 121.41 (im-*C*), 120.16 (im-*C*), 58.70 (Ar-CH_2-N), 39.33 (N*C*H_3); mp 290 °C (dec). Anal. Calcd for $C_{16}H_{17}BrN_4Pd$ (451.66): C, 42.55; H, 3.79; N, 12.40. Found: C, 43.20; H, 3.85; N, 12.37. Despite several attempts, no better elemental analysis could be obtained even using different laboratories. All samples, including crystals from the batch used for the X-ray structure determination of **5**, gave the correct C/H/N *ratio*; however the absolute percentages were irreproducible and always too high. Triple analysis on a single sample revealed that the combustion data are inhomogeneous. Similar combustion analysis problems with carbene complexes have been reported previously.[16]

Acknowledgment. We gratefully acknowledge financial support from the Swiss National Foundation (M.A.), Deutsche Akademie der Naturforscher Leopoldina (BMBF-LPD 9901/8-37; S.G.), and the US DOE and NSF (J.W.F., R.H.C.). Prof. Limbach (FU Berlin, Germany) is kindly acknowledged for providing the programs for line-shape analyses.

Supporting Information Available: ^1H and $^{13}C\{^1H\}$ NMR of **5** and crystallographic details for **4** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM010631H

---

[16] Voges, M. H.; Rømming, C.; Tilset, M. *Organometallics* **1999**, *18*, 529.