RESEARCH FRONT

CSIRO PUBLISHING

Full Paper

www.publish.csiro.au/journals/ajc

Aust. J. Chem. **2009**, *62*, 983–987

Synthesis and Structural Characterization of Palladium Dicarbene Complexes Bearing Labile Co-Ligands

Han Vinh Huynh[A,B] *and Hui Xian Seow*[A]

[A]Department of Chemistry, National University of Singapore, 3 Science Drive 3,
Singapore 117543, Singapore.
[B]Corresponding author. Email: chmhhv@nus.edu.sg

Dicarbene complexes [Pd(OAc)$_2$(diNHC)] (**2**), [Pd(O$_2$CCF$_3$)$_2$(diNHC)] (**3**), and [Pd(CNCH$_3$)$_2$(diNHC)](SO$_3$CF$_3$)$_2$ (**4**) bearing labile acetato, fluoroacetato, and acetonitrile co-ligands have been synthesized via metathesis reaction of the respective precursor [PdBr$_2$(diNHC)] (**1**) with Ag-salts. All complexes are stable towards air and moisture and have been fully characterized by spectroscopic and spectrometric methods. Notably and in comparison to diphosphine analogues, they resist ligand disproportionation in solution. Their molecular structures have also been determined by single crystal X-ray diffraction. A preliminary catalytic study showed low activity in the hydroamination reaction, but revealed an interesting co-ligand influence.

Manuscript received: 11 March 2009.
Manuscript accepted: 8 April 2009.

Introduction

Transition metal complexes of *N*-heterocyclic carbenes (NHCs) have been investigated in recent years with great intensity due to their unique properties especially in the field of organometallic chemistry and catalysis.[1,2] In particular, mono and bis(carbene) complexes of transition metals with chloro, bromo, and iodo ligands have been studied in more detail, while other anionic co-ligands remain relatively rare in NHC chemistry. Notably, NHC research is also commonly centred on imidazolium- and imidazolinium-based systems and less attention has been paid on complexes with benzannulated carbenes, although these may exhibit interesting properties due to their intermediate position between saturated and unsaturated NHCs.[3,4] Besides via in-situ deprotonation of benzimidazolium salts with basic metal precursors, such complexes can also be obtained by less common, but interesting routes, such as metal insertion into the C=C bond of dibenzotetraazafulvalenes[5] or template-assisted synthesis through intramolecular, nucleophilic attack on coordinated *ortho*-functionalized phenyl isocyanides.[6–8] Recently, we have reported the straightforward synthesis of carboxylato-Pd(II) complexes stabilized by two monodentate benzannulated carbenes and their application as catalyst precursors for the Mizoroki-Heck reaction.[9,10] These complexes also showed an interesting *trans-cis* isomerism. A detailed comparison of related *cis* and *trans*-complexes revealed that a *cis*-arrangement of NHC ligands in such complexes translates into a faster catalyst-initiation due to their strong *trans*-effect.[11] In addition, it is expected that the presence of labile co-ligands also contributes to a faster initiation. However, it has also been reported that related diphosphine complexes especially with labile co-ligands are unstable and tend to undergo ligand disproportionation (autoionization) to give cationic bis(chelate) complexes.[12,13] In search for *cis*-NHC complexes with labile co-ligands that resist autoionization, we herein describe the synthesis and structural characterizations of *cis*-chelating dibenzimidazolin-2-ylidene complexes bearing weakly coordinating carboxylato and acetonitrile co-ligands.

Results and Discussion

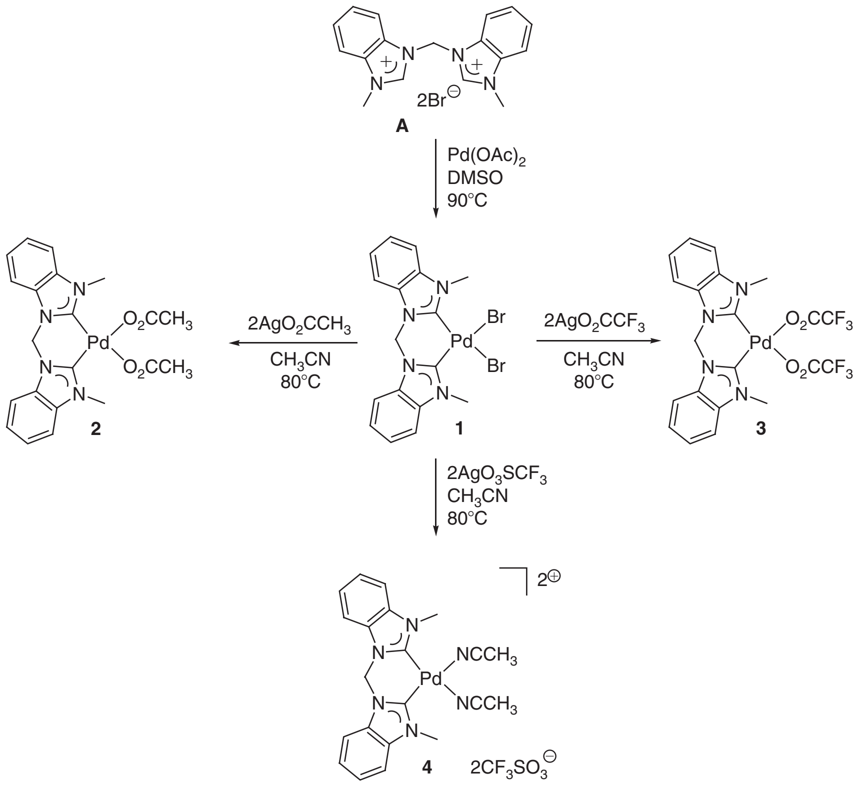
Syntheses and Characterizations

The syntheses of all compounds are summarized in Scheme 1. The reaction of dicarbene precursor diNHC·2HBr (**A**)[14] with one equiv of Pd(OAc)$_2$ in DMSO at 90°C afforded the respective dibromo-dicarbene complex [PdBr$_2$(diNHC)] (**1**) in 82% yield.[15] Successful coordination of the dicarbene ligand to Pd(II) was corroborated by the absence of the downfield signal for the NCHN proton characteristic for **A** in the ^{1}H NMR spectrum of **1**. In addition, the protons for the methylene bridge become diastereotopic upon coordination and split into two slightly broad doublets at 7.35 and 6.78 ppm with a geminal, homonuclear coupling constant of $^2J(\mathrm{H,H}) = 14.1$ Hz. Its formation is also supported by a base peak at $m/z = 503$ for the $[\mathrm{M} - \mathrm{Br} + \mathrm{MeCN}]^+$ fragment in the positive mode electrospray ionization (ESI) mass spectrum.

The introduction of labile co-ligands can be straightforwardly achieved by metathesis reactions of complex **1** with various Ag salts in hot acetonitrile. Hence, the mixed carboxylato-dicarbene complexes [Pd(OAc)$_2$(diNHC)] (**2**) and [Pd(O$_2$CCF$_3$)$_2$(diNHC)] (**3**) as well as the acetonitrile-dicarbene complex [Pd(diNHC)(NCCH$_3$)$_2$](O$_3$SCF$_3$)$_2$ (**4**) were prepared by reacting precursor-complex **1** with AgO$_2$CCH$_3$, AgO$_2$CCF$_3$, and AgO$_3$SCF$_3$, respectively, as depicted in Scheme 1. The complexes were isolated as white and air-stable solids. Even in solution, the complexes are unusually stable and no palladium black was observed upon prolonged standing, even in polar solvents such as DMSO.

In general, the substitution of both bromo-ligands in **1** by carboxylato and acetonitrile ligands leads to an improved solubility.

10.1071/CH09143 0004-9425/09/090983



Scheme 1. Synthesis of dicarbene complexes **1**–**4** bearing various co-ligands.

All novel complexes **2**–**4** are soluble in acetone, CH_3CN, DMSO, DMF and insoluble in non-polar solvents such as diethyl ether, hexane, or toluene. However, their solubility is still inferior compared with their analogues which contain monodentate carbene ligands.[9] The ^1H NMR resonances recorded in d_6-DMSO of the chelating dibenzimidazolin-2-ylidene ligand in **2**–**4** remain largely unaffected upon ligand exchange. The only difference noted is the broadness of the resonances for the diastereotopic protons of the methylene bridge indicating a different rate of fluxionality due to different co-ligands. For example, only two very broad singlets are observed for complex **2**, whereas the spectra of **3** and **4** show two defined doublets for these methylene protons. However, the influence of the various co-ligands has more impact on the ^{13}C NMR chemical shift of the carbene carbon. The coordination of the acetato ligand leads to a slight upfield shift from 171.4 ppm in **1**[15] to 169.8 ppm in **2**. This shielding effect is even greater when the weaker coordinating anions such as fluoroacetates and triflates are employed, where upfield shifts of the carbenoid signal to 159.4 ppm and 159.1 ppm, respectively, are observed. We have observed a similar but much more pronounced upfield shift in methylene bridged imidazolin-2-ylidene analogues previously.[16] The ^{13}C NMR signals for the CF_3 groups of the fluoroacetato ligand in **3** (116.4 ppm, q) and the triflate anions in **4** (120.7 ppm, q) show the expected splitting pattern due to ^{13}C-^{19}F heteronuclear couplings with $^1J(C,F) = 290$ and 323 Hz, respectively. In the ^{19}F NMR spectra, broad singlets are observed at 2.55 ppm (**3**) and -1.80 ppm (**4**) for these CF_3 groups. More importantly, even in the polar solvent d_6-DMSO we did not find any NMR evidence for the formation of bis(chelates) due to possible autoionization processes as observed for diphosphine analogues.[12,13] To this point, it is worth noting that we have recently reported such autoionization behaviour in a Ni(II) system, which resulted in a dicationic bis(chelate) complex with the same dicarbene ligand.[17] ^1H NMR spectroscopy also showed no indication for a bridging or bidentate coordination mode of the carboxylato ligands in **2** and **3**.

Molecular Structures

Single crystals of complexes **2**–**4** suitable for X-ray diffraction studies were obtained by slow diffusion of dichloromethane (**2**·CH_2Cl_2·H_2O) or diethyl ether (**3**, **4**·$2CH_3CN$) into concentrated acetonitrile solutions at ambient temperature. For the purpose of comparison, X-ray analysis was also carried out for single crystals of the dibenzimidazolium salt **A** obtained as solvate **A**·$2H_2O$ by slow evaporation of a concentrated methanol/ethyl acetate solution at ambient temperature.

The molecular structures of salt **A** and complexes **2**–**4** are depicted in Figs 1–4 along with selected bond parameters. Selected crystallographic data are listed in Table 1. All three complexes crystallized as mononuclear complexes, in which the palladium centre is coordinated by the chelating dicarbene and two monodentate co-ligands in a nearly perfect square-planar geometry. Upon coordination, the NCN angle of the heterocyclic ring decreases from 110.55° in **A** to ~107° in all complexes **2**–**4**. This change is accompanied by a slight lengthening of the average N-$C_{carbene}$ bond from 1.327 Å in **A** (N-$C_{precarbene}$) to 1.348, 1.347, and 1.345 Å in the complexes **2**–**4**, respectively. The similarity of these bond distances in the three complexes indicates the absence of any co-ligand influence. The short methylene bridge of the dicarbene ligand prevents the favourable perpendicular orientation of the carbene ring planes with respect to the PdC_2L_2-coordination plane, which results in small dihedral angles ranging from 39° to 47°. More importantly, a comparison of the average Pd-C bonds in **2**–**4** reveals that those in **2** and **4** are almost identical (~1.9645 Å), whereas those in **3** are

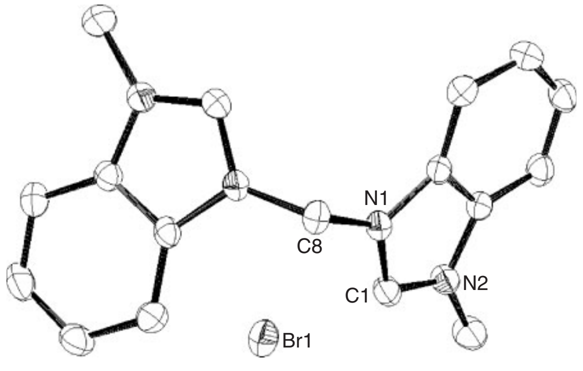


Fig. 1. Molecular structure of salt **A** showing 50% probability ellipsoids with the crystallographic numbering scheme; solvent molecules and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: N1-C1 1.343(3), N2-C1 1.311(3), N1-C8 1.455(2); N1-C1-N2 110.55(19), N1-C8-N1A 113.2(2).

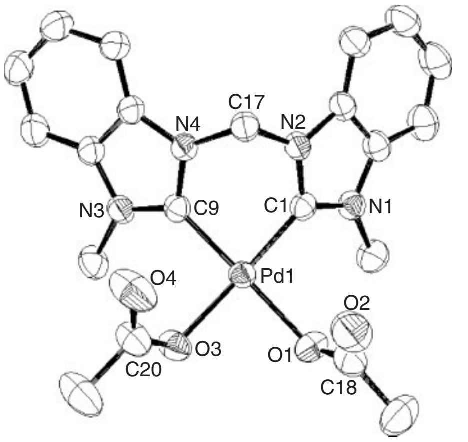


Fig. 2. Molecular structure of $[Pd(OAc)_2(diNHC)]$ (**2**) showing 50% probability ellipsoids with the crystallographic numbering scheme; solvent molecules and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Pd1-C1 1.972(3), Pd1-C9 1.958(2), Pd1-O1 2.0685(19), Pd1-O3 2.0668(19), N1-C1 1.343(3), N2-C1 1.354(3), N2-C17 1.449(3), N4-C17 1.450(3), N4-C9 1.354(3), N3-C9 1.341(3); C9-Pd1-C1 85.32(10), N1-C1-N2 106.4(2), N2-C17-N4 108.86(19), N3-C9-N4 106.4(2); PdC_2O_2/carbene dihedral angles 39.15 and 42.96.

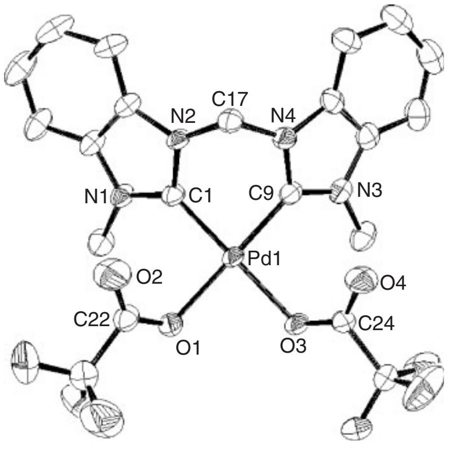


Fig. 3. Molecular structure of $[Pd(O_2CCF_3)_2(diNHC)]$ (**3**) showing 50% probability ellipsoids with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Pd1-C1 1.956(3), Pd1-C9 1.951(3), Pd1-O1 2.0614(19), Pd1-O3 2.0721(18), N1-C1 1.339(3), N2-C1 1.355(3), N2-C17 1.446(3), N4-C17 1.451(3), N4-C9 1.362(3), N3-C9 1.333(3); C9-Pd1-C1 85.42(11), N1-C1-N2 107.1(2), N2-C17-N4 108.8(2), N3-C9-N4 106.5(2); PdC_2O_2/carbene dihedral angles 41.49 and 42.49.

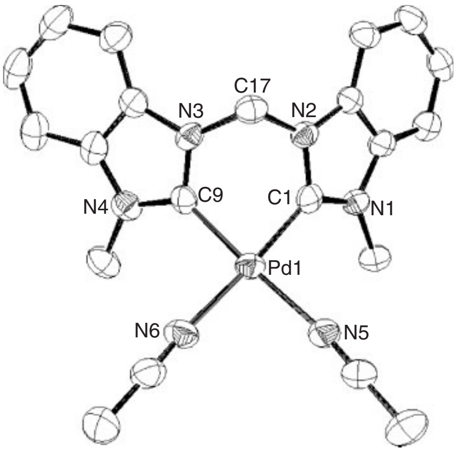


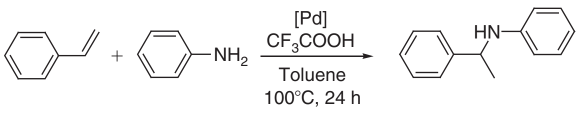
Fig. 4. Molecular structure of $[Pd(diNHC)(NCCH_3)_2](SO_3CF_3)_2$ (**4**) showing 50% probability ellipsoids with the crystallographic numbering scheme; a solvent molecule, counter anions and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Pd1-C1 1.971(6), Pd1-C9 1.958(5), Pd1-N5 2.076(5), Pd1-N6 2.066(5), N1-C1 1.317(7), N2-C1 1.370(3), N2-C17 1.452(7), N3-C17 1.456(7), N4-C9 1.337(7), N3-C9 1.356(7); C9-Pd1-C1 83.5(2), N1-C1-N2 107.3(5), N2-C17-N3 109.0(5), N3-C9-N4 107.1(5); PdC_2N_2/carbene dihedral angles 46.39 and 46.94.

markedly shorter (1.9535 Å). This observation indicates that the donor ability of acetato and acetonitrile ligands is comparable regardless of the overall charge of the resulting complex. The trifluoroacetato ligands in **3**, however, are expected to be less basic, thus leading to a more Lewis acidic metal centre, which in turn results in shorter and supposedly stronger Pd-C bonds. The bite angles for the two carboxylato complexes **2** and **3** amounting to 85.32° and 85.42° are very similar. The angle for the complex-cation **4** is with 83.5°, surprisingly smaller.

For both complexes **2** and **3**, the two carboxylato ligands coordinate in a monodentate fashion with their pendant oxygen atoms found in *syn* conformation. However, this does not indicate the preference of *syn* over *anti* conformation, because both have been observed in related complexes previously.[10] Further structural parameters are unexceptional and do not require further comments.

Preliminary Catalytic Test for the Hydroamination Reaction

In a preliminary study, the catalytic activity of the title complexes **2**–**4** has been tested in the challenging intermolecular hydroamination reaction of styrene with aniline in the presence of CF_3CO_2H as activator (Scheme 2).



Scheme 2. Pd-catalyzed hydroamination of styrene with aniline.

Disappointingly, only complex **3** showed low activity giving the desired addition product in 15% yield after 24 h at 2 mol-% catalyst loading and under non-optimized conditions. Complexes **2** and **4**, however, showed no activity at all, although very different observations were made for these two complexes.

Table 1. Selected crystallographic data for salt A and complexes 2–4

	A·2H_2O	**2**·CH_2Cl_2·H_2O	**3**	**4**·2CH_3CN
Formula	$C_{17}H_{22}Br_2N_4O_2$	$C_{22}H_{26}Cl_2N_4O_5Pd$	$C_{21}H_{16}F_6N_4O_4Pd$	$C_{25}H_{25}F_6N_7O_6PdS_2$
Formula weight	474.21	603.77	608.78	804.04
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	C2/c	Pccn	P-1	P2(1)/n
a [Å]	20.822(5)	15.7032(17)	9.3832(5)	8.6202(6)
b [Å]	8.2040(18)	17.4546(19)	11.1193(6)	13.4411(10)
c [Å]	13.855(4)	18.665(2)	11.7971(6)	27.9130(18)
α [°]	90	90	68.4750(10)	90
β [°]	126.080(8)	90	81.2280(10)	97.264(2)
γ [°]	90	90	78.6820(10)	90
V [Å^3]	1912.8(8)	5116.0(10)	1118.36	3208.2(4)
Z	4	8	2	4
D_c [g cm^{-3}]	1.647	1.568	1.808	1.665
μ [mm^{-1}]	4.256	0.974	0.917	0.794
θ range [°]	2.76 to 27.47	1.74 to 27.50	1.86 to 27.50	1.68 to 25.00
Max., min. transmission	0.4832 and 0.3820	0.7999 and 0.6968	0.8823 and 0.7833	0.9320 and 0.7418
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0268$, $wR_2 = 0.0661$	$R_1 = 0.0355$, $wR_2 = 0.0861$	$R_1 = 0.0359$, $wR_2 = 0.0891$	$R_1 = 0.0636$, $wR_2 = 0.1431$
R indices (all data)	$R_1 = 0.0335$, $wR_2 = 0.0675$	$R_1 = 0.0477$, $wR_2 = 0.0916$	$R_1 = 0.0389$, $wR_2 = 0.0907$	$R_1 = 0.0821$, $wR_2 = 0.1520$
Goodness-of-fit on F^2	0.973	1.055	1.084	1.117
Large diff. peak and hole [e Å^{-3}]	0.658 and −0.371	0.588 and −0.452	0.834 and −0.421	0.852 and −0.855

Complex **2** did not show any sign of decomposition, whereas complex **4** led to a black mixture upon heating to 100°C most likely due to the formation of palladium black. The same observation was made in the absence of co-acid. This leads to the assumption that the acetato ligands in **2** are too stabilizing, whereas the acetonitrile ligands in **4** are too labile despite having similar donor strengths (*vide supra*). As mentioned above, the trifluoroacetato ligands in **3** give rise to the most Lewis acidic metal centre and, at the same time, seem to have the best properties in terms of donor strength and lability in this series.

Conclusions

In conclusion, we have presented a straightforward and high yielding synthesis of benzannulated dicarbene complexes bearing labile acetato, fluoroacetato, and acetonitrile co-ligands, which are unusually stable in solution and resist ligand disproportionation. All complexes have been fully characterized and their molecular structures established by X-ray single crystal diffraction. A preliminary catalytic study using the hydroamination reaction of styrene with aniline revealed that complex **3** bearing trifluoroacetato ligands showed some activity, whereas the acetato and acetonitrile complexes **2** and **4** were either too stable or too labile under the reaction conditions. Further research in our laboratory is underway to optimize the reaction time and conditions and to find more suitable catalysts with trifluoroacetato ligands for the highly challenging hydroamination reaction.

Experimental

Methods and Materials

All manipulations were carried out in air unless otherwise stated. All solvents were used as received. Dicarbene precursor **A** was synthesized according to a literature report.[14] ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker 300 MHz FT-NMR spectrometers using Me_4Si as an internal and CF_3CO_2H as an external standard at ambient temperature. ESI mass spectra were obtained using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer.

Dibromo-1,1′-methylene-(3,3′-dimethyldibenzimidazolin-2-ylidene)palladium(II) **1**

A mixture of **A** (0.656 g, 1.5 mmol) and $Pd(OAc)_2$ (0.336 g, 1.5 mmol) was dissolved in DMSO (5 mL). The suspension was stirred overnight at 90°C. The solvent was then removed by vacuum distillation. Deionized water was added to the residue and the mixture was stirred overnight and then filtered. The residue was washed with ethanol followed by diethyl ether and dried under vacuum to yield the title compound as an orange amorphous solid. Yield: 0.669 g (1.23 mmol, 82%). ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 8.48 (d, ^3J(H,H) = 7.6 Hz, 2H, Ar-H), 8.23 (d, ^3J(H,H) = 7.4 Hz, 2H, Ar-H), 7.51–7.40 (m, 4H), 7.35 (d, ^2J(H,H) = 14.1 Hz, 1H, C*H*H), 6.78 (d, ^2J(H,H) = 14.1 Hz, 1H, CH*H*), 4.13 (s, 6H, CH_3). MS (ESI, positive ions) *m/z* [%]: 503 (100) [M − Br + MeCN]$^+$.

Di(acetato)-1,1′-methylene-(3,3′-dimethyldibenzimidazolin-2-ylidene)palladium(II) **2**

A mixture of **1** (0.185 g, 0.340 mmol) and AgOAc (0.114 g, 0.680 mmol) was suspended in acetonitrile (10 mL). The reaction mixture was shielded from light and heated under reflux overnight. The resulting yellow suspension was filtered through celite to remove yellow-green solids of AgI and the solvent of the filtrate removed under vacuum. The residue was then suspended in dichloromethane, filtered, and washed with diethyl ether. The title compound was obtained as a white amorphous solid after drying. Single crystals of **2** suitable for X-ray diffraction studies were obtained from a concentrated acetonitrile/dichloromethane solution at ambient temperature. Yield: 116 mg (0.232 mmol, 68%). ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.20 (d, ^3J(H,H) = 7.8 Hz, 2H, Ar-H), 7.67 (d, ^3J(H,H) = 7.8 Hz, 2H, Ar-H), 7.50–7.38 (m, 4H, Ar-H), 7.32 (s, br, 1H, C*H*H), 6.58 (s, br, ^{1}H, CH*H*), 3.99 (s, 6H, NCH_3), 1.78 (s, 6H, O_2CCH_3). ^{13}C{^{1}H} NMR (75.48 MHz, d_6-DMSO): δ 174.4 (s, COO), 169.8 (s, NCN), 133.7, 132.2, 124.0, 123.8, 111.6, 110.8 (s, Ar-C), 56.6 (s, CH_2), 33.6 (s, NCH_3), 23.6 (s, O_2CCH_3). MS (ESI, positive ions) *m/z* [%]: 441 (100) [M − O_2CCH_3]$^+$. Calc. for $C_{21}H_{22}N_4O_4Pd$

(500.84): C, 50.36; H, 4.43; N, 11.19%. Anal. Found: C, 50.54; H, 4.39; N, 10.99%.

1,1′-Methylene-(3,3′-dimethyldibenzimidazolin-2-ylidene)di(trifluoroacetato)palladium(II) **3**

Complex **3** was synthesized in analogy to **2** from **1** (0.127 g, 0.234 mmol) and AgO_2CCF_3 (0.103 g, 0.468 mmol) and isolated as a white amorphous solid after drying. Transparent cubic crystals of **3** suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether into a concentrated acetonitrile solution at ambient temperature. Yield: 80 mg (0.132 mmol, 56%). ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.26 (d, ^{3}J(H,H) = 7.7 Hz, 2H, Ar-H), 7.79 (d, ^{3}J(H,H) = 7.7 Hz, 2H, Ar-H), 7.57–7.46 (m, 4H, Ar-H), 7.39 (d, ^{2}J(H,H) = 12.3 Hz, 1H, C*H*H), 6.79 (d, ^{2}J(H,H) = 12.3 Hz, ^{1}H, CH*H*), 4.04 (s, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, d_6-DMSO): δ 161.7 (s, COO), 159.4 (s, NCN), 133.6, 132.6, 124.6, 124.4 (s, Ar-C), 116.4 (q, ^{1}J(C,F) = 290.4 Hz, CF_3), 111.9, 111.3 (s, Ar-C), 57.1 (s, CH_2), 34.0 (s, CH_3). $^{19}F\{^{1}H\}$ NMR (282 MHz, d_6-DMSO): 2.55 (br s, 6F, CF_3). MS (ESI, positive ions) *m/z* [%]: 495 (96) $[M - O_2CCF_3]^+$. Calc. for $PdC_{21}H_{16}N_4O_4F_6$ (608.79): C, 41.43; H, 2.65; N, 9.20%. Anal. Found: C, 40.94; H, 2.69; N, 8.99%.

Bis(acetonitrile)-1,1′-methylene-(3,3′-dimethyldibenzimidazolin-2-ylidene)palladium(II) Ditriflate **4**

Complex **4** was synthesized in analogy to **2**, from **1** (0.197 g, 0.364 mmol) and AgO_3SCF_3 (0.211 g, 0.820 mmol) and isolated as a white solid. Transparent cubic crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether into a concentrated acetonitrile solution at ambient temperature. Yield: 0.136 g (0.200 mmol, 55%). ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.25 (d, ^{3}J(H,H) = 7.7 Hz, 2H, Ar-H), 7.81 (d, ^{3}J(H,H) = 7.9 Hz, 2H, Ar-H), 7.59–7.49 (m, 4H, Ar-H), 7.36 (d, ^{2}J(H,H) = 13.1 Hz, 1H, C*H*H), 6.92 (d, ^{2}J(H,H) = 13.1 Hz, 1H, CH*H*), 4.10 (s, 6H, CH_3), 1.75 (CH_3CN). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, d_6-DMSO): δ 159.1 (s, NCN) 133.8, 132.4, 127.1, 124.8, 124.6 (s, Ar-C), 120.7 (q, ^{1}J(C,F) = 322.8 Hz, CF_3), 112.1, 111.3 (s, Ar-C), 57.0 (s, CH_2), 34.5 (s, CH_3). $^{19}F\{^{1}H\}$ NMR (282 MHz, d_6-DMSO): −1.80 (br s, 6F, CF_3). MS (ESI, positive ions) *m/z* [%]: 531 (44) $[M - O_3SCF_3]^+$.

General Procedure for Pd-catalyzed Hydroamination of Styrene Using Aniline

Complex **3** (0.02 mmol) was weighed into a Schlenk tube. The flask was evacuated and filled with nitrogen. Toluene (0.5 mL), styrene (0.17 mL, 1.5 mmol), and aniline (0.09 mL, 1 mmol) were added stepwise. The mixture was heated and stirred at 100°C for 30 min and CF_3CO_2H (0.015 mL, 0.20 mmol) was added. The mixture was left to stir for 24 h at 100°C. The reaction mixture was adsorbed onto silica gel and eluted with hexane/ethyl acetate (1:0.15).

X-Ray Diffraction Studies

X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using $Mo_{K\alpha}$ radiation at 223 K with the *SMART* suite of programs.[18] Data were processed and corrected for Lorentz and polarization effects with *SAINT*,[19] and for absorption effect with *SADABS*.[20] Structural solution and refinement were carried out with the *SHELXTL* suite of programs.[21] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Table 1. CCDC 723157 (**A**·$2H_2O$), 723158 (**2**·CH_2Cl_2·H_2O), 723159 (**3**), and 723160 (**4**·$2CH_3CN$) 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.

Acknowledgements

The authors thank the National University of Singapore for financial support (Grant no. R 143–000–327–133) and especially Ms Geok Kheng Tan and Professor Lip Lin Koh for determining the X-ray molecular structures.

References

[1] F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. doi:10.1002/ANIE.200703883

[2] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768. doi:10.1002/ANIE.200601663

[3] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931. doi:10.1002/(SICI)1521-3765(19990604)5:6<1931::AID-CHEM1931>3.0.CO;2-M

[4] F. E. Hahn, L. Wittenbecher, D. Le Van, D. R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541. doi:10.1002/(SICI)1521-3773(20000204)39:3<541::AID-ANIE541>3.0.CO;2-B

[5] F. E. Hahn, T. von Fehren, T. Lügger, *Inorg. Chim. Acta* **2005**, *358*, 4137. doi:10.1016/J.ICA.2004.11.053

[6] F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem. Int. Ed.* **2005**, *44*, 3759. doi:10.1002/ANIE.200462690

[7] F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704. doi:10.1002/CHEM.200390079

[8] F. E. Hahn, C. G. Plumed, M. Münder, T. Lügger, *Chem. Eur. J.* **2004**, *10*, 6285. doi:10.1002/CHEM.200400576

[9] Y. Han, H. V. Huynh, L. L. Koh, *J. Organomet. Chem.* **2007**, *692*, 3606. doi:10.1016/J.JORGANCHEM.2007.04.037

[10] H. V. Huynh, T. C. Neo, G. K. Tan, *Organometallics* **2006**, *25*, 1298. doi:10.1021/OM0510369

[11] H. V. Huynh, J. H. H. Ho, T. C. Neo, L. L. Koh, *J. Organomet. Chem.* **2005**, *690*, 3854. doi:10.1016/J.JORGANCHEM.2005.04.053

[12] A. Marson, A. B. van Oort, W. P. Mul, *Eur. J. Inorg. Chem.* **2002**, 3028. doi:10.1002/1099-0682(200211)2002:11<3028::AID-EJIC3028>3.0.CO;2-8

[13] C. Bianchini, A. Meli, W. Oberhauser, *Organometallics* **2003**, *22*, 4281. doi:10.1021/OM030132B

[14] T. Scherg, S. K. Schneider, G. D. Frey, J. Schwarz, E. Herdtweck, W. A. Herrmann, *Synlett* **2006**, 2894.

[15] (a) The preparation of complex **1** by a different route with a lower yield of 58% has recently been reported: A. Biffis, C. Tubaro, G. Buscemi, M. Basato, *Adv. Synth. Catal.* **2008**, *350*, 189. doi:10.1002/ADSC.200700271
(b) The diiodo analogue of **1** has also been reported: F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241. doi:10.1016/S0022-328X(99)00219-3

[16] H. V. Huynh, D. LeVan, F. E. Hahn, T. S. A. Hor, *J. Organomet. Chem.* **2004**, *689*, 1766. doi:10.1016/J.JORGANCHEM.2004.02.033

[17] H. V. Huynh, R. Jothibasu, *Eur. J. Inorg. Chem.* **2009**, 1926. doi:10.1002/EJIC.200801149

[18] *SMART version 5.628* **2001** (Bruker AXS Inc.: Madison, Wisconsin, USA).

[19] *SAINT+ version 6.22a* **2001** (Bruker AXS Inc.: Madison, Wisconsin, USA).

[20] G. W. Sheldrick, *SADABS version 2.10* **2001** (University of Göttingen).

[21] *SHELXTL version 6.14* **2000** Bruker AXS Inc.: Madison, Wisconsin, USA.