Pd(II) Complexes of *N*-Allyl Substituted *N*-Heterocyclic Carbenes

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

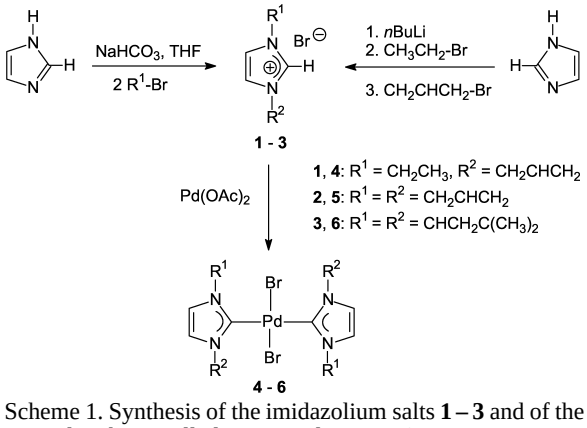
The unsymmetrically substituted imidazolium salt 1-ethyl-3-allyl-imidazolium bromide **1** was synthesized by treatment of imidazole with one equivalent each of *n*-butyl lithium and ethyl bromide followed by treatment with one equivalent of allyl bromide. The symmetrically substituted derivatives 1,3-diallyl-imidazolium bromide **2** and 1,3-bis(3-methyl-2-butenyl)-imidazolium bromide **3** were obtained from imidazole and two equivalents of allyl bromide or 4-bromo-2-methyl-2-butenyl bromide, respectively, in the presence of sodium hydrogencarbonate as a base. The imidazolium bromides **1 – 3** react with $Pd(OAc)_2$ to afford the palladium(II) dicarbene complexes *trans*-$[PdBr_2(L)_2]$ (L = 1-ethyl-3-allyl-imidazolin-2-ylidene, **4**; L = 1,3-diallyl-imidazolin-2-ylidene, **5**; L = 1,3-di(3-methyl-2-butenyl)imidazolin-2-ylidene, **6**) by *in situ* deprotonation of the imidazolium salts. The X-ray structure analyses of **4 – 6** show all three complexes to be mononuclear with palladium(II) coordinated in a square-planar fashion by two carbene and two bromo ligands.

Key words: Carbene Ligand, Allyl Substituents, Palladium(II), Crystal Structure

Introduction

Complexes of *N*-heterocyclic carbenes (NHC's) have attracted much interest recently due to their applications in coordination chemistry and catalysis [1]. A number of synthetic procedures for the generation of such complexes have been developed. These include the direct reaction of an imidazolin-2-ylidene [2] with a transition metal complex [3], the reaction of an imidazolium salt with a metal complex containing basic ligands under in situ deprotonation [4, 5], the deprotonation of imidazolium salts with bases and trapping of the free carbene with metal complexes [6], the transmetallation with silver carbene complexes [7] or the oxidative addition of imidazolium salts to zero valent transition metals [8]. In addition, complexes with benzannulated *N*-heterocyclic carbene ligands can be obtained from dibenzotetraazafulvalenes [9], benzimidazolium salts [10] or β-functionalized phenyl isocyanides [11].

Little is known about imidazolin-2-ylidenes with *N*-allyl substituents. The preparation of such ligands appears problematic as the deprotonation of *N,N'*-diallylimidazolium halides can proceed under deprotonation of the imidazolium C2 carbon atom or the *N,N'*-allyl substituents. The situation is even more complicated for *N,N'*-diallylbenzimidazolium halides as the benzimidazolin-2-ylidene obtained after C2 deprotonation dimerizes and undergoes further reactions [12]. Complexes of *N*-heterocyclic carbenes with *N*-allyl substituents have been prepared *via* the metal template directed cyclization of β-functionalized phenyl isocyanides and subsequent alkylation of the NH-stablized ylidene complex [11, 13].



Scheme 1. Synthesis of the imidazolium salts **1 – 3** and of the *trans*-dicarbene palladium complexes **4 – 6**.

We report here on the preparation of three *N*1,*N*3-diallyl substituted imidazolium bromides and their re-

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actions with $Pd(OAc)_2$ giving the dicarbene complexes *trans*-$[PdBr_2L_2]$ (L = *N*-allyl-imidazolin-2-ylidene) (Scheme 1).

Results and Discussion

N-allyl substituted imidazolium salts can be prepared from imidazole. Deprotonation with *n*BuLi followed by reaction with ethyl bromide and subsequent reaction with allyl bromide at elevated temperature gives the unsymmetrically substituted derivative **1** (Scheme 1). The introduction of two identical allyl substituents (compounds **2** and **3**, Scheme 1) can be achieved in the one step reaction of imidazole with two equivalents of allyl bromides in the presence of $NaHCO_3$ as a base. The allylated imidazolium bromides **1 – 3** are air-stable solids which are hygroscopic. The ^{1}H NMR spectra of **1 – 3** show the resonance for the NC*H*N proton as a singlet with a characteristic downfield shift around $\delta = 9.3 - 9.4$ ppm. The hydrogen atoms at the C=C double bond appear as multiplets owing to $^3J_{HH}$ and $^2J_{HH}$ coupling.

Deprotonation of the 1,3-disubstituted imidazolium bromides **1 – 3** with palladium(II) acetate in THF yields the air-stable *trans*-dicarbene complexes **4 – 6** (Scheme 1). The preparation of the palladium complexes was performed at room temperature to avoid side reactions. The *in situ* deprotonation prevents unwanted reactions of the free carbene. After deprotonation, ligand **1** is potentially bidentate [13], while ligands **2** and **3** could acts as tridentate ligands by olefine coordination. However, no coordination of the olefins was observed under the reaction conditions. In contrast to complexes with two *N*1,*N*3-allylated benzannulated *N*-heterocyclic carbene ligands, which are only soluble in DMF and DMSO [12], complexes **1 – 3** are soluble in THF which allows the recording of ^{1}H and ^{13}C NMR spectra.

Complex **4** was obtained as a yellow powder which can be recrystallized from CH_2Cl_2/*n*-hexane. The resonances for the allyl protons are only slightly shifted in **4** compared to those of the imidazolium salt **1** indicating, that the olefine does not participate in coordination. This was confirmed by an X-ray structure determination. This analysis reveals a square-planar coordination geometry around the palladium atom with a *trans*-configuration of the ligands (Fig. 1). The imidazolin-2-ylidene plane is oriented almost perpendicular to the PdC_2Br_2 plane (angle between planes 75.2°). The Pd-$C_{carbene}$ bond length of 2.026(2) Å (Table 1) is slightly longer than the equivalent distances in palladium(II) complexes with two imidazolin-2-ylidene ligands in *cis*-configuration [4].

Table 1. Selected interatomic distances [Å] and angles [°] for **4**, **5** and **6**·C_6H_{14}.

	4	**5**	**6**·C_6H_{14}
Pd-Br	2.4333(3)	2.4355(9)	2.4291(6)
Pd-C2	2.026(2)	2.028(5)	2.019(4)
N1-C2	1.348(3)	1.348(6)	1.346(3)
N1-C5 (C3)	1.385(3)	1.382(6)	1.385(4)
N1-C6 (C4)	1.466(3)	1.465(6)	1.470(3)
N3-C2	1.346(3)	1.329(6)	
N3-C4	1.387(3)	1.374(6)	
N3-C9	1.457(3)	1.469(7)	
C4-C5	1.335(4)	1.327(7)	
C3-C3*			1.349(6)
C7-C8	1.309(4)	1.281(8)	
C10-C11		1.301(10)	
C5-C6			1.324(4)
Br-Pd-Br	180	180	180
$C_{carbene}$-Pd-$C_{carbene}$	180	180	180
N-$C_{carbene}$-N	104.6(2)	105.1(4)	104.7(3)

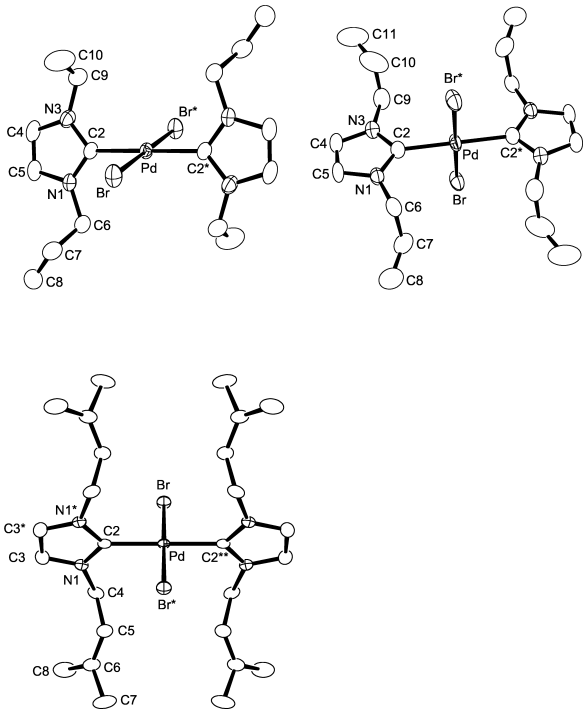

Fig. 1. Molecular structures of **4 – 6**.

Complex **5** was prepared as described for **4** as an air-stable yellow solid. The protons at the terminal CH_2 groups of the allyl groups appear in the ^{1}H NMR spectrum as doublet of doublets of triplets owing to $^2J_{HH}$, $^3J_{HH}$ and $^4J_{HH}$ couplings with the typ-

ical *trans* (17.4 Hz) and *cis* (10.2 Hz) $^3J_{HH}$ coupling constants. The molecular structure of **5** is depicted in Fig. 1. Again a square-planar complex in the *trans*-configuration is obtained. The steric demand of the *N*1,*N*3-substituents in **5** is slightly larger than in **4**. This leads to an even larger angle of the imidazol-2-ylidene plane relative to the PdC_2Br_2 plane (angle between planes 84.9°). However, the Pd-$C_{carbene}$ bond length in **5** (2.028(5) Å) is identical within experimental error to the value observed in **4**.

A slightly different protocol was used for the preparation of **6**. Here a THF solution containing the imidazolium salt and $Pd(OAc)_2$ was first sonicated in an ultrasound bath for 5 min and the stirred at room temperature for 2 d. Complex **6** was obtained in good yield as a yellow oil. The ^{13}C NMR spectrum shows two slightly different resonances for the terminal methyl groups of the *N*-substituents. Complex **6** exhibits a square-planar coordination geometry (Fig. 1) with bond lengths and bond angles similar to **4**–**5** (Table 1).

The olefinic groups in **4**–**6** do not coordinate under the reaction conditions employed. It was attempted to enforce this coordination by abstraction of bromide with silver tetrafluoroborate. However, in all cases this leads to insoluble black solids.

Experimental Section

If not noted otherwise, all manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use.

1-Ethyl-3-allyl-imidazolium bromide **1***:* Imidazole (1.36 g, 20 mmol) is dissolved in THF (50 ml) and cooled to −78 °C. To this solution is added *n*-butyl lithium (20 mmol, 8 ml of a 2.5 *M* solution). The reaction mixture is stirred for 1 h at −78 °C and ethyl bromide (2.18 g, 1.49 ml, 20 mmol) is added. Under stirring the solution is allowed to warm up to room temperature over 12 h. Half of the solvent is removed under reduced pressure and dichloromethane (20 ml) is added. The solution is washed with water and the organic phase is dried over $MgSO_4$. The solvent is removed leaving 1-ethylimidazole as a brown oil. The oil is dissolved in THF (30 ml) and allyl bromide (9.68 g, 6.96 ml, 80 mmol) is added. The reaction mixture is heated under reflux for 20 h. Subsequently the solvent is removed and **1** is obtained as a brown oil. Yield 1.14 g (5.25 mmol, 26%). – ^1H NMR (200.1 MHz, $[D_6]$DMSO, ppm): $\delta = 9.31$ (s, 1 H, NC*H*N), 7.87 (m, 1 H, NC*H*CHN), 7.76 (m, 1 H, NCHC*H*N), 6.03 (m, 1 H, NCH_2CHCH_2), 5.32 (m, 2 H, NCH_2CHCH_2), 4.86 (d, 2 H, NCH_2CHCH_2), 4.21 (q, 2 H, NCH_2CH_3), 1.42 (t, 3 H, NCH_2CH_3). – ^{13}C NMR (100.6 MHz, $[D_6]$DMSO, ppm): $\delta = 136.21$ (*N*CN), 132.13 (NCH_2CHCH_2), 122.77 (NC*H*C*H*N), 120.64 (NCH_2CHCH_2), 51.13 (NCH_2CHCH_2), 44.63 (NCH_2CH_3), 15.47 (NCH_2CH_3). – $C_8H_{13}N_2Br$ (217.11): calcd. C 44.26, H 6.04, N 12.90; found C 43.82, H 6.46, N 12.71.

1,3-Diallyl-imidazolium bromide **2***:* A mixture of 1.36 g (20 mmol) of imidazole and 5.04 g (60 mmol) of sodium hydrogencarbonate in acetonitrile (90 ml) is treated with allyl bromide (9.68 g, 6.96 ml, 80 mmol). The reaction mixture is heated under reflux for 12 h and filtered. Removal of all solvents gives **2** as a brown oil. Yield: 3.65 g (15.9 mmol, 80%). – ^1H NMR (200.1 MHz, $[D_6]$DMSO, ppm): $\delta = 9.41$ (s, 1 H, NC*H*N), 7.81 (d, 2 H, NC*H*C*H*N), 5.89 (m, 2 H, NCH_2CHCH_2), 5.23 (m, 4 H, NCH_2CHCH_2), 4.87 (d, 4 H, NCH_2CHCH_2). – ^{13}C NMR (100.6 MHz, $[D_6]$DMSO, ppm): $\delta = 137.10$ (*N*CN), 132.66 (NCH_2CHCH_2), 123.55 (NC*H*C*H*N), 121.20 (NCH_2CHCH_2), 51.77 (NCH_2CHCH_2). – $C_9H_{13}N_2Br$ (229.12): calcd. C 47.18, H 5.72, N 12.23; found C 46.68, H 5.50, N 12.15.

1,3-Bis(3-methyl-2-butenyl)-imidazolium bromide **3***:* Compound **3** was synthesized as described for **2** from 0.37 g (5.5 mmol) of imidazole, 1 g (12 mmol) of sodium hydrogencarbonate and 1.3 ml (1.639 g, 11 mmol) of 4-bromo-2-methyl-2-butene in acetonitrile (12 ml). Yield 1.34 g (4.7 mmol, 86%) of a brown oil. – ^1H NMR (200 MHz, $[D_6]$DMSO, ppm): $\delta = 9.32$ (s, 1 H, NC*H*N), 7.75 (s, 2 H, NC*H*C*H*N), 5.38 (m, 2 H, $NCH_2CHC(CH_3)_2$), 4.82 (m, 4 H, $NCH_2CHC(CH_3)_2$), 1.74 (s, broad, 12 H, $NCH_2CHC(CH_3)_2$). – ^{13}C NMR (50.3 MHz, $[D_6]$DMSO, ppm): $\delta = 136.53$ (*N*CN), 131.85 ($NCH_2CHC(CH_3)_2$), 118.73 (NC*H*C*H*N), 113.83 ($NCH_2CHC(CH_3)_2$), 42.99 ($NCH_2CHC(CH_3)_2$), 21.78, 14.64 ($NCH_2CHC(CH_3)_2$). – Satisfactory microanalytical data were not obtained owing to the hygroscopic behaviour of **3**.

trans-Di[1-ethyl-3-allyl-imidazolin-2-ylidene]palladium dibromide **4***:* A sample of 0.304 g (1.4 mmol) of **1** is dissolved in THF (15 ml) and 0.130 g (0.58 mmol) of $Pd(OAc)_2$ is added. The reaction mixture is stirred for 7 d. A yellow suspension is obtained, which is filtered. Removal of the solvent gives **4** as an air-stable yellow solid. Yield: 66 mg (0.123 mmol, 21%). Suitable crystals for an X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a concentrated dichloromethane solution of **4**. ^1H NMR (598.9 MHz, $[D_8]$THF, ppm): $\delta = 7.08$ (d, 2 H, NC*H*CHN), 6.98 (d, 2 H, NCHC*H*N), 6.29 (m, 2 H, NCH_2CHCH_2), 5.36 (m, 2 H, NCH_2CHCHH), 5.21 (m, 2 H, NCH_2CHCHH), 5.12 (m, 4 H, NCH_2CHCH_2), 4.52 (q, 4 H, NCH_2CH_3), 1.57 (t, 6 H, NCH_2CH_3). – ^{13}C NMR (150.6 MHz, $[D_8]$THF, ppm): $\delta = 171.80$ (*N*CN), 135.50 (NCH_2CHCH_2), 121.09, 121.07 (NC*H*C*H*N), 118.15 (NCH_2CHCH_2), 54.12 (NCH_2CHCH_2), 46.39 (NCH_2CH_3),

Table 2. Crystal and data collection details for **4**, **5** and **6**·C_6H_{14}.

	4	**5**	**6**·C_6H_{14}
Crystal habit	yellow plates	colorless plates	colorless plates
Crystal size [mm]	$0.08 \times 0.03 \times 0.01$	$0.06 \times 0.05 \times 0.01$	$0.24 \times 0.11 \times 0.03$
Formula	$C_{16}H_{24}N_4Br_2Pd$	$C_{18}H_{24}N_4Br_2Pd$	$C_{32}H_{54}N_4Br_2Pd$
fw [amu]	538.6	562.63	761.01
T [K]	173(2)	173(2)	123(2)
a [Å]	8.4425(7)	8.551(2)	10.561(3)
b [Å]	9.4788(8)	18.003(4)	12.573(3)
c [Å]	12.4705(11)	7.938(2)	13.506(3)
β [°]	97.721(2)	117.39(3)	92.676(5)
V [Å^3]	988.90(15)	1084.9(4)	1791.3(7)
Space group	$P2_1/n$	$P2_1/c$	$C2/m$
Z	2	2	2
μ [mm^{-1}]	4.983	4.546	2.773
Abs. corr.	empirical	empirical	empirical
	$0.691 \leq T \leq 0.952$	$0.772 \leq T \leq 0.956$	$0.556 \leq T \leq 0.921$
2θ-Range [°]	$5.4 \leq 2\theta \leq 60.0$	$4.5 \leq 2\theta \leq 50.1$	$3.0 \leq 2\theta \leq 60.1$
Unique data	2865	1905	2721
Obsvd. data ($I > 2\sigma(I)$)	2423	1439	2088
R(observed) [%]	2.78, $R_w = 6.43$	3.58, $R_w = 7.27$	4.29, $R_w = 7.79$
R(all) [%]	3.58, $R_w = 6.71$	5.81, $R_w = 7.95$	6.77, $R_w = 8.35$
GOF	1.027	1.029	1.058
No. of variables	107	115	99
Res. el. dens. [e/Å^3]	1.130 / −0.391	0.512 / −0.478	0.934 / −1.271

16.45 (NCH_2CH_3). – $C_{16}H_{24}N_4Br_2Pd$ (538.61): calcd. C 35.68, H 4.49, N 10.40; found C 35.77, H 4.27, N 10.14.

trans-Bis[1,3-diallyl-imidazolin-2-ylidene]palladium dibromide **5***:* Complex **2** is prepared as described for **4** from **2** (280 mg, 1.22 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) in THF (20 ml). Complex **2** is obtained as an air-stable yellow solid. Yield: 217 mg (0.386 mmol, 77%). Suitable crystals for an X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a concentrated dichloromethane solution of **5**. ^{1}H NMR (598.9, [D$_8$]THF, ppm): $\delta = 7.01$ (s, 4 H, NC*H*C*H*N), 6.27 (m, 4 H, NCH_2CHCH_2), 5.34 (ddt, $^2J_{HH} = 1.2$ Hz, $^3J_{HH} = 17.4$ Hz, $^4J_{HH} = 1.2$ Hz, 4 H, NCH_2CHCH_{trans}), 5.22 (ddt, $^2J_{HH} = 1.2$ Hz, $^3J_{HH} = 10.2$ Hz, $^4J_{HH} = 1.2$ Hz, 4 H, NCH_2CHCH_{cis}), 5.12 (dt, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 1.2$ Hz, 8 H, NCH_2CHCH_2). – ^{13}C NMR (150.6 MHz, [D$_8$]THF, ppm): $\delta = 172.30$ (*N*CN), 135.37 (NCH_2CHCH_2), 121.39 (N*CH*C*H*N), 118.25 (NCH_2CHCH_2), 53.91 (NCH_2CHCH_2). – $C_{18}H_{24}N_4Br_2Pd$ (562.63): calcd. C 38.43, H 4.30, N 9.96; found C 38.87, H 4.23, N 9.57.

trans-Di[1,3-bis(3-methyl-2-butenyl)-imidazolin-2-ylidene]palladium dibromide **6***:* A mixture of 0.14 g (0.5 mmol) of **3** and 0.056 g (0.25 mmol) $Pd(OAc)_2$ in THF (20 ml) is sonicated with ultrasound for 5 min. The resulting red solution is then stirred at room temparature for 2 d. Removal of the solvent gave **6** as an air-stable yellow oil. Yield 0.094 g (56%). Suitable crystals for X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a concentrated dichloromethane solution. – ^{1}H NMR (499.8 MHz, [D$_8$]THF, ppm): $\delta = 6.93$ (s, 4 H, NC*H*C*H*N), 5.71 (t, $^3J_{HH} = 6.0$ Hz, 4 H, $NCH_2CH(CH_3)_2$), 5.11 (d, $^3J_{HH} = 6.0$ Hz, 4 H, $NCH_2CH(CH_3)_2$), 1.82 (s, 12 H, $NCH_2CH(CH_3)_2$), 1.77 (s, 12 H, $NCH_2CH(CH_3)_2$). – ^{13}C NMR (125.7 MHz, [D$_8$]THF, ppm): $\delta = 171.83$ (*N*CN), 137.15 ($NCH_2CH(CH_3)_2$), 122.25 ($NCH_2CH(CH_3)_2$), 121.03 (N*CH*C*H*N), 49.47 ($NCH_2CH(CH_3)_2$), 25.22, 17.72 ($NCH_2CH(CH_3)_2$). – $C_{26}H_{40}N_4Br_2Pd$ (674.86): calcd. C 46.27, H 5.97, N 8.30; found C 46.23, H 6.04, N 8.27.

X-ray structure determination of **4** – **6***:* Yellow, air-stable crystals of **4** – **6** were obtained by diffusion of *n*-hexane into dichloromethane solutions. Crystal and data collection details are summarized in Table 2. X-ray intensities were measured with Mo-K_α radiation ($\lambda = 0.71073$ Å) using a Bruker AXS Apex diffractometer equipped with a rotating anode. Structure solution with SHELXS-97 [14] by heavy atom methods and refined with SHELXL-97 [15]. Refinement was carried out with anisotropic displacement parameters for non-hydrogen atoms; hydrogen atoms were added to the structure model on calculated positions. Pd resides on a special position (inversion center) in crystals of **4** and **5** (the asymmetric unit contains 1/2 of the complex). The palladium atom in **6** resides on a special position with 2/m symmetry. The complex is bisected by a twofold axis along C2-Pd-C2** and a mirror plane (incorporating Br-Pd-Br*), the asymmetric unit contains 1/4 of **6**. In addition, the asymmetric unit contains 1/4 molecule of *n*-hexane. Crystallographic data (excluding structure factors) have been deposited with the Cambridge

Crystallographic Data Centre as supplementary publication no. CCDC 251511 (**4**), CCDC 251512 (**5**) and CCDC 251513 (**6**·C_6H_{14}). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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