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Research paper

Synthesis of palladium complexes with anionic N,NR- or neutral NH,NR-theophylline-derived NHC ligands

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ABSTRACT

Four C8-halogenated theophyllines (**1**–**4**) featuring N7-methyl or N7-allyl and C8-chloro or C8-bromo substituents have been prepared. The halogenotheophyllines react with $[Pd(PPh_3)_4]$ in an oxidative addition to give complexes of type *trans*-[Pd(theophyllinato)X$(PPh_3)_2$] (*trans*-[**5**]–*trans*-[**8**]). The protonation of the unsubstituted theophyllinato ring-nitrogen atom to give the *p*NHC complexes was achieved either by performing the oxidative addition of **1** in the presence of NH_4BF_4 to give complex *trans*-[**9**]BF_4 or by *N*-protonation of the coordinated theophyllinato ligand in *trans*-[**6**]–*trans*-[**8**] with $HBF_4{\cdot}Et_2O$ to give complexes *trans*-[**10**]BF_4–*trans*-[**12**]BF_4. The molecular structures of *trans*-[**5**], *trans*-[**7**], *trans*-[**9**]BF_4, *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 were determined by X-ray diffraction showing significant differences of comparable metric parameters in the theophylline-derived five-membered diaminoheterocycles. No interaction of the *N*-allyl substituents with the metal center was observed.

1. Introduction

N-Heterocyclic carbenes (NHCs) have evolved into an important class of ligands over the last two decades [1], due to the numerous application of their complexes in catalysis [2], pharmaceutics [3], luminescent materials [4] or as building blocks for metallosupramolecular assemblies [5,6]. Most of the known NHC ligands feature an NR,NR substitution pattern of the five-membered heterocycle, which prevents a further functionalization of the NHC ligand after complex formation. Such modifications of an NHC ligand, however, are possible in complexes bearing protic NHC ligands (*p*NHCs) [7]. Reactions at coordinated *p*NHC ligands have allowed the template-controlled formation of NHC-containing macrcrocycles [8]. In addition, the NH group of a *p*NHC ligand can serve as recognition unit for substrate binding via hydrogen bonds during a catalytic reaction [9]. Today, the number of complexes possessing *p*NHC ligands is still low compared to the number of complexes with the ubiquitous NR,NR-NHC ligands, although a number of protocols for the synthesis of *p*NHC complexes exist [7]. Among these are the template-controlled cyclization of *β*-functionalized isocyanides [8,10], the reaction of C2-lithiated azoles with metal ions followed by *N*-protonation [11], the removal of a protection group (PG) from a coordinated NR,NPG-NHC ligand [12] or the metal mediated tautomerization of neutral *N*-coordinated azoles [13].

Recently, a new synthetic approach to complexes with *p*NHC ligands has been developed based on the oxidative addition of the C2-R bond of azoles to transition metals followed by *N*-protonation [7]. While the oxidative addition of the C2—H bond of an *N*-alkylated azole has not been observed so far, functionalization of one of the azole ring-nitrogen atoms with an amine [14] or phosphine [15] donor group facilitates the reaction. It is assumed that the *N*-tethered donor pre-coordinates to the metal center bringing the C2-H bond of the azole in close proximity to the metal, which then oxidatively adds yielding an azolato complex. The initially formed hydrido complex is normally not stable and reductively eliminates a proton which protonates the unsubstituted ring-nitrogen atom of the azolato ligand, leading to complex **A** with a *p*NHC ligand (Fig. 1). Contrary to the oxidative addition of the C2-H bond, the oxidative addition of the C2-X (X = Cl, Br, I) bond of *N*-alkylated azoles proceeds readily and in the absence of an *N*-tethered donor group, leading after protonation of the initially formed azolato ligand, to complexes with NR,NH-NHC ligands **B** (Fig. 1) [16]. Even complexes bearing NH,NH-NHCs [17] or mesoionic *p*NHC ligands [18] could be obtained using this method. Recently, we also described the synthesis of platinum complexes bearing adenine- (**C**) or caffeine-derived (**D**) *p*NHC ligands (Fig. 1) [19].

In this contribution we describe the oxidative addition of a series of C8-halogeno-N7-alkyltheophyllines to $[Pd(PPh_3)_4]$ in order to evaluate the influence of different C8-halogens present and regarding a potential involvement of the *N*-alkyl (alkyl = allyl) function on the reaction

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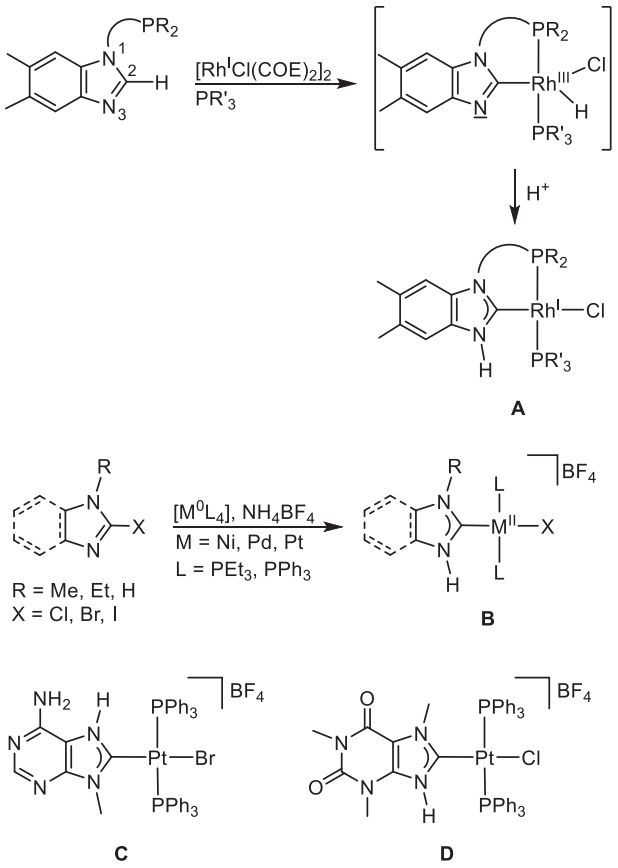


Fig. 1. Synthesis of complexes possessing *p*NHC ligands by oxidative addition of C2-H (**A**, top) or C2-halogen (**B**, middle) bonds to selected transition metals and selected complexes bearing purine-derived *p*NHC ligands (**C** and **D**, bottom).

outcome.

2. Experimental

2.1. General procedures and materials

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. The solvents were freshly distilled by standard procedures prior to use. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AVANCE I or AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm using the residual protonated solvent as an internal standard. Coupling constants are expressed in Hertz. Mass spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific) spectrometer. 8-Chlorotheophylline, 8-bromotheophylline and [Pd(PPh$_3$)$_4$] were purchased from commercial sources and used as received. 8-Chloro- and 8-bromocaffeine were synthesized following a published procedure [20].

2.2. Synthesis of N7-allyl-8-halogenotheophyllines *3–4*

An appropriate 8-halogenotheophylline (X = Cl or Br, 1.50 mmol) was dissolved in dry DMF (15 mL) and an excess of potassium carbonate (1.0 g, 7.2 mmol) was added. The resulting suspension was treated with allyl bromide (0.15 mL, 1.74 mmol) and the reaction mixture was stirred for 16 h at ambient temperature. Subsequently, water (20 mL) was added and the suspension was stored at 4 °C for 12 h. A colorless precipitate formed, which was isolated by filtration and was washed with cold water (20 mL) and diethyl ether (5 mL) giving compounds **3** and **4** as colorless solids.

2.2.1. N7-Allyl-8-chlorotheophylline (*3*)

Yield: 0.326 g (1.28 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.04–5.92 (m, 1H, H13), 5.22 (d, ^{3}J = 10.4 Hz, 1H, H14a), 4.99 (d, ^{3}J = 17.2 Hz, 1H, H14b), 4.93 (d, ^{3}J = 4.9 Hz, 2H, H12), 3.40 (s, 3H, *H*11), 3.22 (s, 3H, *H*10). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.5 (C6), 150.6 (C2), 146.6 (C4), 137.6 (C8), 131.7 (C13), 117.4 (C14), 107.1 (C5), 47.4 (C12), 29.4 (C11), 27.5 (C10). HRMS (ESI, positive ions): *m/z* 255.0644 (calcd for [**3** + H]$^{+}$ 255.0649).

2.2.2. N7-Allyl-8-bromotheophylline (*4*)

Yield: 0.381 g (1.27 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.03–5.89 (m, 1H, H13), 5.21 (d, ^{3}J = 10.5 Hz, 1H, H14a), 4.96 (d, ^{3}J = 17.6 Hz, 1H, H14b), 4.92–4.87 (m, 2H, H12), 3.39 (s, 3H, *H*11), 3.20 (s, 3H, *H*10). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.4 (C6), 150.5 (C2), 147.6 (C4), 131.8 (C13), 127.8 (C8), 117.4 (C14), 107.9 (C5), 48.4 (C12), 29.4 (C11), 27.5 (C10). HRMS (ESI, positive ions): *m/z* 320.9957 (calcd for [**4** + Na]$^{+}$ 320.9963), 299.0138 (calcd for [**4** + H]$^{+}$ 299.0144).

2.3. Synthesis of trans-*[5]*

Essentially equimolar amounts of 8-chlorocaffeine **1** (8.9 mg, 0.039 mmol) and [Pd(PPh$_3$)$_4$] (40 mg, 0.035 mmol) were dissolved in toluene (10 mL). The mixture was heated under reflux for 6 d. After removal of the solvent *in vacuo* the residue was washed twice with hexane (5 mL each) and diethyl ether (5 mL each). Drying *in vacuo* gave *trans*-[**5**] as colorless solid. Crystals of *trans*-[**5**]·CH$_2$Cl$_2$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of *trans*-[**5**]. Yield: 17 mg (0.02 mmol, 57%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.65–7.56 (m, 12H, Ph-H$_{ortho}$), 7.44–7.38 (m, 6H, Ph-H$_{para}$), 7.36–7.27 (m, 12H, Ph-H$_{meta}$), 3.28 (s, 3H, *H*10), 3.17 (s, 6H, *H*11, H12). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ 162.8 (t, $^{2}J_{CP}$ = 4.9 Hz, C8), 153.7 (C2), 151.5 (C6), 151.4 (C4), 134.8 (v-t, $^{2/4}J_{CP}$ = 6.4 Hz, Ph-C$_{ortho}$), 131.0 (Ph-C$_{para}$), 130.6 (v-t, $^{1/3}J_{CP}$ = 24.0 Hz, Ph-C$_{ipso}$), 128.6 (v-t, $^{3/5}J_{CP}$ = 5.2 Hz, Ph-C$_{meta}$), 110.1 (C5), 34.4 (C12), 29.4 (C11), 27.5 (C10). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 21.0 (s). HRMS (ESI, positive ions): *m/z* 861.1352 (calcd for [[**5**]+H]$^{+}$ 861.1355).

2.4. Synthesis of trans-*[6]*

Equimolar amounts of 8-bromocaffeine **2** (27 mg, 0.1 mmol) and [Pd(PPh$_3$)$_4$] (115 mg, 0.1 mmol) were dissolved in toluene (10 mL) and stirred at ambient temperature for 2 d. After removal of the solvent *in vacuo* the yellow residue was washed with hexane (15 mL) and diethyl ether (15 mL) and dried *in vacuo*. Yellowish crystals of *trans*-[**6**]·CH$_2$Cl$_2$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of *trans*-[**6**]. Yield: 61.8 mg (0.068 mmol, 68%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.70–7.57 (m, 12H, Ph-H$_{ortho}$), 7.46–7.38 (m, 6H, Ph-H$_{para}$), 7.37–7.28 (m, 12H, Ph-H$_{meta}$), 3.33 (s, 3H, *H*10), 3.19 (s, 6H, *H*11, H12). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ 163.9 (t, $^{2}J_{CP}$ = 4.1 Hz, C8), 153.7 (C2), 151.4 (C6), 151.3 (C4), 134.8 (v-t, $^{2/4}J_{CP}$ = 6.4 Hz, Ph-C$_{ortho}$), 130.92 (Ph-C$_{para}$), 130.87 (v-t, $^{1/3}J_{CP}$ = 24.3 Hz, Ph-C$_{ipso}$), 128.6 (v-t, $^{3/5}J_{CP}$ = 5.2 Hz, Ph-C$_{meta}$), 110.2 (C5), 34.3 (C12), 29.5 (C11), 27.6 (C10). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 20.9 (s). HRMS (ESI, positive ions): *m/z* 905.0842 (calcd for [[**6**]+H]$^{+}$ 905.0848).

2.5. Synthesis of trans-*[7]*

The synthesis of *trans*-[**7**] was performed as described for *trans*-[**5**] by treatment of **3** (8.9 mg, 0.035 mmol) with [Pd(PPh$_3$)$_4$] (40 mg, 0.035 mmol). Yield: 16.8 mg (0.019 mmol, 54%). Colorless crystals of *trans*-[**7**]·CH$_2$Cl$_2$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of *trans*-[**7**]. ^{1}H NMR (400 MHz,

CD_2Cl_2): δ 7.65–7.55 (m, 12H, Ph-H_{ortho}), 7.45–7.38 (m, 6H, Ph-H_{para}), 7.37–7.27 (m, 12H, Ph-H_{meta}), 5.74–5.62 (m, 1H, H13), 5.18 (d, $^3J_{trans}$ = 17.2 Hz, 1H, H14a), 4.84 (d, $^3J_{cis}$ = 10.1 Hz, 1H, H14b), 4.36 (d, ^3J = 6.4 Hz, 2H, H12), 3.20 (s, 3H, *H*10), 3.12 (s, 3H, *H*11). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 161.9 (t, $^2J_{CP}$ = 4.4 Hz, C8), 153.5 (C2), 151.6 (C4), 151.4 (C6), 134.9 (v-t, $^{2/4}J_{CP}$ = 6.4 Hz, Ph-C_{ortho}), 134.5 (C13), 131.0 (Ph-C_{para}), 130.6 (v-t, $^{1/3}J_{CP}$ = 24.1 Hz, Ph-C_{ipso}), 128.6 (v-t, $^{3/5}J_{CP}$ = 5.2 Hz, Ph-C_{meta}), 118.4 (C14), 109.5 (C5), 51.3 (C12), 29.5 (C11), 27.6 (C10). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 21.7 (s). HRMS (ESI, positive ions): *m/z* 887.1499 (calcd for $[[\mathbf{7}]+H]^+$ 887.1512).

2.6. Synthesis of trans-[8]

The synthesis of *trans*-[**8**] was performed as described for *trans*-[**6**] by treatment of **4** (29.9 mg, 0.10 mmol) with $[Pd(PPh_3)_4]$ (115 mg, 0.10 mmol). Compound *trans*-[**8**] was obtained as bright yellow solid. Yield: 65.3 mg (0.070 mmol, 70%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.65–7.58 (m, 12H, Ph-H_{ortho}), 7.44–7.38 (m, 6H, Ph-H_{para}), 7.35–7.29 (m, 12H, Ph-H_{meta}), 5.79–5.66 (m, 1H, H13), 5.25 (dd, $^3J_{trans}$ = 17.2 Hz, ^2J = 1.3 Hz, 1H, H14a), 4.90 (dd, $^3J_{cis}$ = 10.1 Hz, ^2J = 1.3 Hz, 1H, H14b), 4.39 (d, ^3J = 6.5 Hz, 2H, H12), 3.20 (s, 3H, *H*10), 3.13 (s, 3H, *H*11). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 163.1 (t, $^2J_{CP}$ = 3.4 Hz, C8), 153.5 (C2), 151.6 (C4), 151.4 (C6), 135.0 (v-t, $^{2/4}J_{CP}$ = 6.3 Hz, Ph-C_{ortho}), 134.5 (C13), 131.0 (v-t, $^{1/3}J_{CP}$ = 24.6 Hz, Ph-C_{ipso}), 130.9 (Ph-C_{para}), 128.5 (v-t, $^{3/5}J_{CP}$ = 5.2 Hz, Ph-C_{meta}), 118.5 (C14), 109.6 (C5), 51.3 (C12), 29.4 (C11), 27.6 (C10). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 21.3 (s). HRMS (ESI, positive ions): *m/z* 931.1005 (calcd for $[[\mathbf{8}]+H]^+$ 931.1005), 849.1755 (calcd for $[[\mathbf{8}]-Br]^+$ 849.1756).

2.7. Synthesis of trans-[9]BF_4

A sample of 8-chlorocaffeine **1** (8.9 mg, 0.039 mmol), $[Pd(PPh_3)_4]$ (40 mg, 0.035 mmol) and an excess of NH_4BF_4 (10.5 mg, 0.10 mmol) were dissolved in toluene (10 mL) and heated under reflux for 6 d. After removal of the solvent *in vacuo* the residue was washed with hexane (5 mL) and diethyl ether (5 mL). The residue was then dissolved in dichloromethane (40 mL) and insoluble material was removed by filtration. Removal of the solvent gave *trans*-[**9**]BF_4 as a colorless solid. Crystals of *trans*-[**9**]$BF_4{\cdot}2CH_2Cl_2$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of *trans*-[**9**]BF_4. Yield: 28.0 mg (0.030 mmol, 86%). ^1H NMR (400.0 MHz, CD_2Cl_2): δ 11.00 (s, 1H, H9), 7.78–7.70 (m, 12H, Ph-H_{ortho}), 7.49–7.38 (m, 18H, Ph-H_{meta}, Ph-H_{para}), 3.76 (s, 3H, H12), 3.24 (s, 3H, *H*11), 3.07 (s, 3H, *H*10). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 167.3 (t, $^2J_{CP}$ = 10.1 Hz, C8), 153.0 (C2), 149.5 (C6), 142.0 (C4), 134.7 (v-t, $^{2/4}J_{CP}$ = 6.4 Hz, Ph-C_{ortho}), 131.8 (Ph-C_{para}), 129.3 (v-t, $^{3/5}J_{CP}$ = 5.4 Hz, Ph-C_{meta}), 129.2 (v-t, $^{1/3}J_{CP}$ = 25.5 Hz, Ph-C_{ipso}), 108.3 (C5), 32.7 (C12), 29.8 (C11), 27.9 (C10). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 20.9 (s). HRMS (ESI, positive ions): *m/z* 861.1353 (calcd for $[\mathbf{9}]^+$ 861.1355).

2.8. Synthesis of trans-[10]BF_4

A sample of *trans*-[**7**] (8.9 mg, 0.01 mmol) was dissolved in THF (20 mL) and $HBF_4{\cdot}Et_2O$ (0.2 mL of a 1.6 g·mL^{-1} solution) was added slowly to this solution. A yellow precipitate formed, which was separated by filtration and washed twice with ice cold diethyl ether (5 mL each). The residue was dried *in vacuo* to give *trans*-[**10**]BF_4 as a yellow solid. Yield: 8.8 mg (0.009 mmol, 90%). ^1H NMR (400 MHz, CD_2Cl_2/DMSO-d_6): δ 12.91 (s, 1H, NH), 7.68–7.61 (m, 12H, Ph-H_{ortho}), 7.53–7.47 (m, 6H, Ph-H_{para}), 7.46–7.38 (m, 12H, Ph-H_{meta}), 5.74–5.61 (m, 1H, H13), 5.07 (d, $^3J_{trans}$ = 17.0 Hz, 1H, H14a), 4.80 (d, $^3J_{cis}$ = 10.2 Hz, 1H, H14b), 4.55 (d, 2H, ^3J = 6.5 Hz, H12), 3.23 (s, 3H, *H*11), 3.03 (s, 3H, *H*10). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2/DMSO-d_6): δ 163.6 (t, $^2J_{CP}$ = 9.7 Hz, C8), 151.5 (C2), 148.4 (C6), 141.4 (C4), 133.7 (v-t, $^{2/4}J_{CP}$ = 6.2 Hz, Ph-C_{ortho}), 131.1 (Ph-C_{para}), 129.8 (C13), 128.3 (v-t, $^{3/5}J_{CP}$ = 5.3 Hz, Ph-C_{meta}), 128.1 (v-t, $^{1/3}J_{CP}$ = 25.4 Hz, Ph-C_{ipso}), 121.1 (C14), 107.1 (C5), 52.8 (C12), 30.3 (C11), 27.6 (C10). $^{31}P\{^1H\}$ (162 MHz, CD_2Cl_2/DMSO-d_6): δ 21.0 (s). HRMS (ESI, positive ions): *m/z* 887.1501 (calcd for [10] 887.1512).

2.9. Synthesis of trans-[11]BF_4

Samples of 8-bromocaffeine **2** (27.0 mg, 0.1 mmol) and $[Pd(PPh_3)_4]$ (115 mg, 0.1 mmol) were dissolved in toluene (10 mL) and stirred at ambient temperature for 1 d. Then $HBF_4{\cdot}Et_2O$ (0.2 mL of a 1.6 g·mL^{-1} solution) was added and stirring was continued for 2 h. After removal of the solvent *in vacuo* the yellowish residue was washed with hexane (15 mL) and diethyl ether (15 mL). Then the residue was then dissolved in MeCN (20 mL) and insoluble materials were separated by filtration. Removal of the solvent *in vacuo* gave *trans*-[**11**]BF_4 as colorless solid. Crystals of *trans*-[**11**]BF_4 were obtained by slow diffusion of diethyl ether into a saturated MeCN solution of [**11**]BF_4. Yield: 87 mg (0.088 mmol, 88%). ^1H NMR (400.0 MHz, CD_3CN/DMSO-d_6): δ 13.12 (s, 1H, NH), 7.72–7.62 (m, 12H, Ph-H_{ortho}), 7.52–7.39 (m, 18H, Ph-H_{meta}, Ph-H_{para}), 3.56 (s, 3H, H12), 3.16 (s, 3H, *H*11), 3.08 (s, 3H, *H*10). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN/DMSO-d_6): δ 165.1 (t, $^2J_{CP}$ = 9.4 Hz, C8), 152.2 (C2), 149.1 (C6), 141.4 (C4), 134.2 (v-t, $^{2/4}J_{CP}$ = 6.4 Hz, Ph-C_{ortho}), 131.5 (Ph-C_{para}), 129.1 (v-t, $^{1/3}J_{CP}$ = 25.6 Hz, Ph-C_{ipso}), 128.7 (v-t, $^{3/5}J_{CP}$ = 5.3 Hz, Ph-C_{meta}), 108.2 (C5), 36.6 (C12), 30.7 (C11), 27.6 (C10). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN/DMSO-d_6): δ 20.4 (s). HRMS (ESI, positive ions): *m/z* 905.0856 (calcd for $[\mathbf{11}]^+$ 905.0848), 861.1368 (calcd for $\{[\mathbf{11}]-Br+Cl\}^+$ 861.1355).

2.10. Synthesis of trans-[12]BF_4

Samples of compound **4** (29.9 mg, 0.1 mmol) and $[Pd(PPh_3)_4]$ (115 mg, 0.1 mmol) were dissolved in toluene (10 mL) and stirred in toluene for 2 d. Then $HBF_4{\cdot}Et_2O$ (0.2 mL of a 1.6 g·mL^{-1} solution) was slowly added leading to the formation of a yellow precipitate. After 2 h of stirring at ambient temperature the solvent was removed *in vacuo* and the yellow residue was washed with hexane (20 mL) and diethyl ether (20 mL) to give *trans*-[**12**]BF_4 as a yellow solid. Crystals of *trans*-[**12**]BF_4 were obtained by slow diffusion of diethyl ether into a saturated MeCN solution of *trans*-[**12**]BF_4. Yield: 91.5 mg (0.09 mmol, 90%). ^1H NMR (400 MHz, CD_3CN/DMSO-d_6): δ 12.69 (s, 1H, NH), 7.72–7.63 (m, 12H, Ph-H_{ortho}), 7.54–7.48 (m, 6H, Ph-H_{para}), 7.48–7.40 (m, 12H, Ph-H_{meta}), 5.74–5.60 (m, 1H, H13), 5.17–5.09 (m, 1H, H14a), 4.83–4.77 (m, 1H, H14b), 4.61 (d, 2H, ^3J = 6.4 Hz, H12), 3.19 (s, 3H, *H*11), 3.01 (s, 3H, *H*10). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN/DMSO-d_6): δ 165.5 (t, $^2J_{CP}$ = 9.3 Hz, C8), 153.1 (C2), 150.1 (C6), 142.9 (C4), 135.5 (v-t, $^{2/4}J_{CP}$ = 6.3 Hz, Ph-C_{ortho}), 132.6 (Ph-C_{para}), 131.7 (C13), 130.2 (v-t, $^{1/3}J_{CP}$ = 25.6 Hz, Ph-C_{ipso}), 129.8 (v-t, $^{3/5}J_{CP}$ = 5.3 Hz, Ph-C_{meta}), 121.9 (C14), 108.7 (C5), 54.4 (C12), 31.8 (C11), 28.7 (C10). $^{31}P\{^1H\}$ (162 MHz, CD_3CN/DMSO-d_6): δ 20.4 (s). HRMS (ESI, positive ions): *m/z* 931.1003 (calcd for $[\mathbf{12}]^+$ 931.1005), 887.1512 (calcd for $[[\mathbf{12}]-Br+Cl]^+$ 887.1512).

2.11. X-ray crystallography

Diffraction data for *trans*-[**5**]$\cdot CH_2Cl_2$ and *trans*-[**9**]$BF_4{\cdot}2CH_2Cl_2$ were collected at T = 153(2) K with a Bruker AXS APEX I CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo*Kα* radiation (λ = 0.71073 Å). Diffraction data for *trans*-[**7**]$\cdot CH_2Cl_2$, *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 were collected with a Bruker APEX II CCD Diffractometer equipped with a microsource using Mo*Kα* radiation (λ = 0.71073 Å) at T = 153(2) K (*trans*-[**7**]$\cdot CH_2Cl_2$) or T = 100(2) K (*trans*-[**11**]BF_4 and *trans*-[**12**]BF_4). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXT [21a] package using direct methods and were refined with SHELXL [21b] against all $|F^2|$ using first isotropic and

later anisotropic thermal parameters (for exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models on calculated positions if not noted otherwise.

2.11.1. Crystal data for trans-[5]·CH_2Cl_2

Formula $C_{45}H_{41}N_4Cl_3O_2P_2Pd$, M = 944.51 g·mol^{-1}, colorless prism, 0.12 × 0.09 × 0.05 mm^3, a = 14.2664(7), b = 10.7009(5), c = 28.3413(13) Å, β = 91.3750(10)°, V = 4325.4(4) Å^3, ρ_{calc} = 1.450 g·cm^{-3}, μ = 0.731 mm^{-1}, monoclinic, space group $P2_1/c$, Z = 4, semiempirical absorption correction (0.827 ≤ T ≤ 0.954), ω- and φ-scans, 41742 measured intensities (2.9° ≤ 2Θ ≤ 55.0°), 9932 independent (R_{int} = 0.0261) and 9126 observed intensities ($I \geq 2\sigma(I)$), refinement of 516 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0798, wR = 0.1749, R_{all} = 0.0849, wR_{all} = 0.1764. The asymmetric unit contains one molecule of *trans*-[**5**] and one molecule of CH_2Cl_2. One of the phenyl substituents and the CH_2Cl_2 molecule are disordered. No hydrogen atoms were added to the structure model for the disordered CH_2Cl_2 molecule.

2.11.2. Crystal data for trans-[7]·CH_2Cl_2

Formula $C_{47}H_{43}N_4Cl_3O_2P_2Pd$, M = 970.54 g·mol^{-1}, colorless prism, 0.19 × 0.16 × 0.12 mm^3, a = 11.2988(4), b = 12.1975(4), c = 16.3021(6) Å, α = 80.668(2)°, β = 83.396(2)°, γ = 75.886(2)°, V = 2143.35(13) Å^3, ρ_{calc} = 1.504 g·cm^{-3}, μ = 0.739 mm^{-1}, triclinic, space group P-1, Z = 2, semiempirical absorption correction (0.871 ≤ T ≤ 0.916), ω- and φ-scans, 38151 measured intensities (6.1° ≤ 2Θ ≤ 62.8°), 13159 independent (R_{int} = 0.0300) and 11750 observed intensities ($I \geq 2\sigma(I)$), refinement of 513 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0456, wR = 0.1189, R_{all} = 0.0514, wR_{all} = 0.1243. The asymmetric unit contains one molecule of *trans*-[**7**] and one molecule of CH_2Cl_2. One of the phenyl substituents and the CH_2Cl_2 molecule are disordered. No hydrogen atoms were added to the structure model for the disordered phenyl group and the CH_2Cl_2 molecule.

2.11.3. Crystal data for trans-[9]BF_4·2CH_2Cl_2

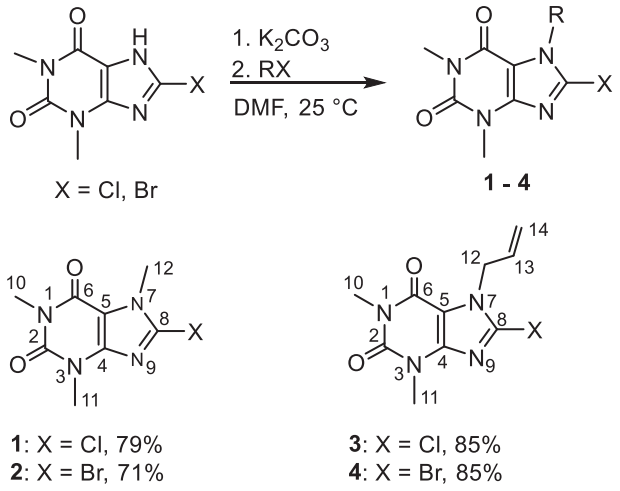
Formula $C_{46}H_{44}N_4BCl_5F_4O_2P_2Pd$, M = 1117.25 g·mol^{-1}, colorless prism, 0.29 × 0.14 × 0.11 mm^3, a = 15.9986(8), b = 18.1562(10), c = 17.2072(9) Å, β = 97.3880(10)°, V = 4956.7(5) Å^3, ρ_{calc} = 1.497 g·cm^{-3}, μ = 0.765 mm^{-1}, monoclinic, space group $P2_1/n$, Z = 4, semiempirical absorption correction (0.809 ≤ T ≤ 0.921), ω- and φ-scans, 49266 measured intensities (3.3° ≤ 2Θ ≤ 60.0°), 14438 independent (R_{int} = 0.0307) and 11847 observed intensities ($I \geq 2\sigma(I)$), refinement of 589 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0362, wR = 0.0884, R_{all} = 0.0473, wR_{all} = 0.0947. The asymmetric unit contains one formula unit of *trans*-[**9**]BF_4 and two molecules of CH_2Cl_2.

2.11.4. Crystal data for trans-[11]BF_4

Formula $C_{44}H_{40}N_4BBrF_4O_2P_2Pd$, M = 991.86 g·mol^{-1}, colorless prism, 0.31 × 0.16 × 0.14 mm^3, a = 14.2526(2), b = 10.3371(2), c = 28.7506(5) Å, β = 92.8790(10)°, V = 4230.50(13) Å^3, ρ_{calc} = 1.557 g·cm^{-3}, μ = 1.519 mm^{-1}, monoclinic, space group $P2_1/c$, Z = 4, semiempirical absorption correction (0.664 ≤ T ≤ 0.764), ω- and φ-scans, 78192 measured intensities (3.9° ≤ 2Θ ≤ 64.6°), 13999 independent (R_{int} = 0.0310) and 12366 observed intensities ($I \geq 2\sigma(I)$), refinement of 539 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0313, wR = 0.0805, R_{all} = 0.0379, wR_{all} = 0.0868. The asymmetric unit contains one formula unit of *trans*-[**11**]BF_4.

2.11.5. Crystal data for trans-[12]BF_4

Formula $C_{46}H_{42}N_4BBrF_4O_2P_2Pd$, M = 1017.89 g·mol^{-1}, colorless prism, 0.26 × 0.12 × 0.06 mm^3, a = 14.2481(2), b = 10.57620(10), c = 28.6188(4) Å, β = 93.6260(10)°, V = 4303.96(9) Å^3, ρ_{calc} = 1.571 g·cm^{-3}, μ = 1.495 mm^{-1}, monoclinic, space group $P2_1/c$, Z = 4, semiempirical absorption correction (0.648 ≤ T ≤ 0.746), ω- and φ-scans, 67400 measured intensities (6.2° ≤ 2Θ ≤ 57.6°), 11191 independent (R_{int} = 0.0373) and 9732 observed intensities ($I \geq 2\sigma(I)$), refinement of 556 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0269, wR = 0.0664, R_{all} = 0.0346, wR_{all} = 0.0697. The asymmetric unit contains one formula unit of *trans*-[**12**]BF_4.

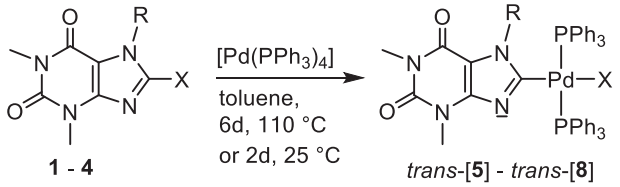


Scheme 1. Synthesis 8-halogenated theophylline derivatives **1**–**4** (the numbering refers to the assignment of the NMR resonances).

3. Results and discussion

The 8-halogenocaffeines **1** and **2** were prepared from the appropriate 8-halogenotheophylline and methyl iodide following a published procedure [20]. The N7-allyl derivatives **3** and **4** were prepared in a similar manner from allyl bromide and the appropriate 8-halogenotheophylline (Scheme 1). Compounds **3** and **4** were characterized by NMR spectroscopy and mass spectrometry. The formation of the theophylline derivatives **3** and **4** was concluded from their NMR spectra exhibiting the typical chemical shifts for the allylic protons and carbon atoms in the expected ranges and multiplicity compared to other reported *N*-allyl-substituted azole derivatives [22].

The 8-chlorotheophylline derivatives **1** and **3** were treated with [Pd(PPh_3)$_4$] in toluene at 110 °C for 6 d to give the azolato complexes *trans*-[**5**] and *trans*-[**7**] in moderate yields of 57% and 54%, respectively. In contrast to the harsh reactions conditions employed for the synthesis of *trans*-[**5**] and *trans*-[**7**], the brominated theophylline derivatives **2** and **4** react with [Pd(PPh_3)$_4$] already at ambient temperature over 2 d to yield azolato complexes *trans*-[**6**] and *trans*-[**8**] in good yields of 68% and 70%, respectively (Scheme 2). Complexes with the two phosphine ligands in *cis*-disposition were not observed [16a]. Complexes *trans*-[**5**] -*trans*-[**8**] were completely characterized by NMR spectroscopy and



Scheme 2. Synthesis of palladium complexes *trans*-[**5**]-*trans*-[**8**].

Table 1
Selected $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR parameters for complexes *trans*-[**5**]-*trans*-[**8**].

Complex[a]	δ(C8) (ppm)	δ(P) (ppm)
trans-[**5**]	162.8 (t, $^2J_{CP}$ = 4.9 Hz)	21.0
trans-[**6**]	163.9 (t, $^2J_{CP}$ = 4.1 Hz)	20.9
trans-[**7**]	161.9 (t, $^2J_{CP}$ = 4.4 Hz)	21.7
trans-[**8**]	163.1 (t, $^2J_{CP}$ = 3.4 Hz)	21.3

[a] NMR spectra were measured in CD_2Cl_2.

mass spectrometry.

Selected $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data of complexes *trans*-[**5**]-*trans*-[**8**] are summarized in Table 1. The $^{13}C\{^1H\}$ NMR spectra of the four complexes feature the resonances for the carbene carbon atom as triplet in a narrow range between δ 161.9 ppm and δ 163.9 ppm. The resonances for the C8 atom in the bromido complexes *trans*-[**6**] and *trans*-[**8**] are located slightly more downfield shifted ($\Delta\delta \approx 1$ ppm) than their chlorido analogues. The $^2J_{CP}$ coupling constants for carbon atom C8 also fall in a narrow range for all four complexes. The observation of triplet resonances for C8 indicates the formation of mononuclear complexes possessing two chemically identical phosphor nuclei occupying *trans*-positions. No dinuclar complexes obtained by attack of the negatively charged azolato ring-nitrogen atom of one complex at a second metal center with substitution of a phosphine ligand, as often observed for the analogous imidazolato and benzimidazolato complexes [16a,b,18b], were observed. The difference in the coordination chemistry of theophyllinato and azolato complexes rests with the difference in nucleophilicity of the unsubstituted ring-nitrogen atom in the theophyllinato ligand compared to the azolato ligands. The anionic purine-base derived ligands feature an electron-withdrawing six-membered ring fused to the diaminoheterocycle thereby reducing the electron density at the unsubstituted ring-nitrogen atom [19]. The $^{31}P\{^1H\}$ NMR spectra of *trans*-[**5**]-*trans*-[**8**] each show only one singlet (Table 1). The resonances for the allylic protons of *trans*-[**7**] and *trans*-[**8**] did not shift significantly when compared to the chemical shifts observed for the parent 8-halogenotheophylline derivatives **3** and **4**. Thus, coordination of the *N*-allyl function in both complexes can be ruled out, since such a coordination would have caused a significant upfield shift of the resonances for the allylic carbon atoms and protons [22].

The formation of mononuclear complexes *trans*-[**5**] and *trans*-[**7**] was confirmed by X-ray diffraction studies with suitable crystals of composition *trans*-[**5**]·CH_2Cl_2 and *trans*-[**7**]·CH_2Cl_2. The molecular structures are depicted in Fig. 2. Both structure analyses confirm the formation of square planar palladium complexes with a *trans*-arrangement of the two PPh_3 groups and a C8-bound theophyllinato ligand oriented essentially perpendicular to the coordination plane of the metal center.

The Pd-C8 bond lengths (*trans*-[**5**]: 2.004(6) Å, *trans*-[**7**]: 1.980(2) Å) as well as the Pd-P bond lengths (*trans*-[**5**]: 2.325(2) and 2.330(2) Å, *trans*-[**7**]: 2.3465(6) and 2.3270(6) Å) in both complexes fall in the range previously observed for related complexes bearing benzimidazole-derived *p*NHC ligands [16a]. The C8-N9 bond lengths involving the unsubstituted ring-nitrogen atom are significantly shorter than the C8-N7 bond lengths in both complexes. This difference is best explained with the formally negative charge residing at the N9 nitrogen atom. A similar effect has been observed for platinum [19] or cobalt [23] complexes bearing anionic C8-bound caffeine-derived azolato ligands. The different number of substituents of the two ring-nitrogen atoms N7 and N9 is also reflected in the C8–N7–C5 (105.5(6) and 106.5(2)° for *trans*-[**5**] and *trans*-[**7**], repectively) and C8–N9–C4 (104.4(5) and 104.4(2)° for *trans*-[**5**] and *trans*-[**7**], respectively) bond angles, where in accord with VSEPR expectations the larger angles are observed for the alkylated ring-nitrogen atom N7. Various complexes bearing *N*-allyl substituted NHCs feature an interaction of the allylic double bond with the metal center [22]. No such interaction was observed in the molecular structure of *trans*-[**7**] in accord with the NMR data.

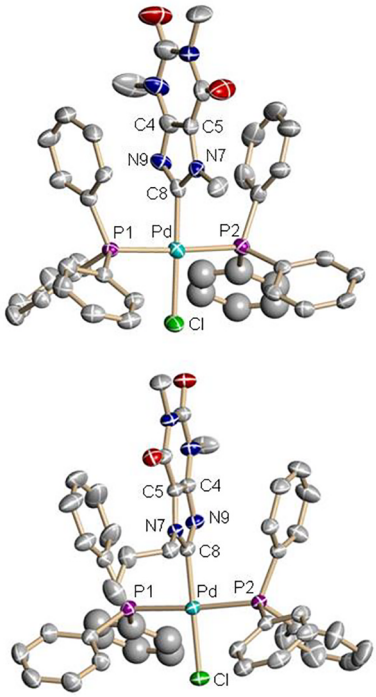
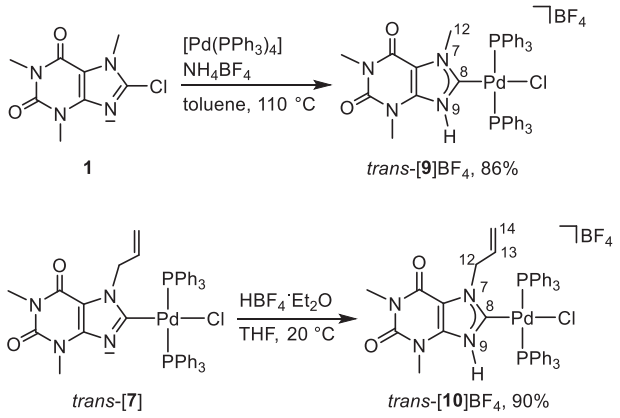


Fig. 2. Molecular structures of *trans*-[**5**] in *trans*-[**5**]·CH_2Cl_2 (top) and of *trans*-[**7**] in *trans*-[**7**]·CH_2Cl_2 (bottom, hydrogen atoms have been omitted for clarity, ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (deg) in *trans*-[**5**] [*trans*-[**7**]]: Pd–Cl 2.367(2) [2.3632(6)], Pd–P1 2.325(2) [2.3465(6)], Pd–P2 2.330(2) [2.3270(6)], Pd–C8 2.004(6) [1.980(2)], N7–C8 1.356(7) [1.362(3)], N9–C8 1.324(7) [1.338(3)]; Cl–Pd–P1 90.48(5) [91.93(2)], Cl–Pd–P2 92.29(6) [91.53(2)], Cl–Pd–C8 179.2(2) [178.89(7)], P1–Pd–P2 176.11(6) [173.69(2)], P1–Pd–C8 88.80(2) [88.56(6)], P2–Pd–C8 88.43(2) [88.07(6)], C8–N7–C5 105.5(6) [106.5(2)], C8–N9–C4 104.4(5) [104.4(2)], N7–C8–N9 113.4(5) [112.1(2)].

Next, the N9-protonated derivatives of chloride complexes *trans*-[**5**] and *trans*-[**7**] were prepared. Two different synthetic strategies were employed. Complex *trans*-[**9**]BF_4 was obtained as described for the *trans*-[**5**] except that 8-chlorocaffeine **1** was reacted with an equimolar amount of $[Pd(PPh_3)_4]$ in the presence of an excess of NH_4BF_4 as proton source. This protocol yielded the *p*NHC complex *trans*-[**9**]BF_4 bearing an NH,NMe-theophyllin-8-ylidene ligand in good yield of 86% (Scheme 3, top). However, the oxidative addition of *N*-allyl-8-chlorotheophylline **3** to $[Pd(PPh_3)_4]$ in the presence of NH_4BF_4 did not proceed well and yielded only a small amount of *trans*-[**10**]BF_4. The reasons for the



Scheme 3. Synthesis of *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4.

different behavior of the two theophyllines are not clear as the *N*-substituent should not have a significant influence on the oxidative addition or protonation reaction. In order to obtain *p*NHC complex *trans*-[**10**]BF_4, the previously isolated complex *trans*-[**7**] was treated with the strong acid $HBF_4{\cdot}Et_2O$ to give *trans*-[**10**]BF_4 in good yield of 90% (Scheme 3, bottom). This procedure has previously been employed for the preparation of a related platinum complex bearing a *p*NHC ligand obtained from a coordinated caffeinato ligand [19].

The formation of the compounds *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4 was confirmed by NMR spectroscopy and mass spectrometry. The ^1H NMR spectra of the complexes feature the characteristic N-H resonances at δ 11.00 ppm and δ 12.91 ppm for *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4, respectively. The stronger downfield shift of the N-H resonance in *trans*-[**10**]BF_4 can be attributed to the solvent mixture used (CD_2Cl_2/DMSO-d_6), which allows the formation of N-H···O hydrogen bonds to DMSO which is not possible for *trans*-[**9**]BF_4 measured in CD_2Cl_2. Similar observations have been made for related complexes bearing *p*NHC ligand [16a,c]. The observation of only one resonance in the $^{31}P\{^1H\}$ spectra and of a triplet resonance for the carbon atom C8 in the $^{13}C\{^1H\}$ spectra (δ 167.3 ppm, $^2J_{CP}$ = 10.1 Hz for *trans*-[**9**]BF_4 and at δ 163.6 ppm, $^2J_{CP}$ = 9.7 Hz for *trans*-[**10**]BF_4) indicated the formation of complexes with two *trans*-arranged phosphine ligands. A comparison of the $^{13}C\{^1H\}$ NMR spectra of the two azolato complexes *trans*-[**5**] and *trans*-[**7**] with the *p*NHC complexes *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4 reveals a significant downfield shift of the C8 resonance upon *N*-protonation. This is in accord with previous observation made for complexes bearing benzimidazolato ligands and NH,NR-NHC complexes obtained from *N*-alkylated benzimidazoles [16b]. No coordination of the *N*-allyl substituent was observed in *trans*-[**10**]BF_4 as judged from the chemical shifts of the protons and carbon atoms of the *N*-allyl group, which are rather similar to the values observed for N7-allyl-8-chlorotheophylline **3**.

Crystals of composition *trans*-[**9**]$BF_4{\cdot}2CH_2Cl_2$ were obtained be recrystallization of *trans*-[**9**] from CH_2Cl_2/diethyl ether. The X-ray diffraction analysis with these crystals revealed the expected square-planar molecular structure of cation *trans*-[**9**]$^+$ with the two phosphines in *trans*-configuration (Fig. 3).

A comparison of the metric parameters of *trans*-[**5**] and *trans*-[**9**]$^+$ reveals some changes caused by protonation of ring-nitrogen atom N9. First, the Pd-C8 bond slightly shortens upon N9 protonation in *trans*-[**9**]$^+$ in accord with previous observations [19]. The endocyclic C8-N bond lengths in *trans*-[**9**]$^+$ become more similar compared to the

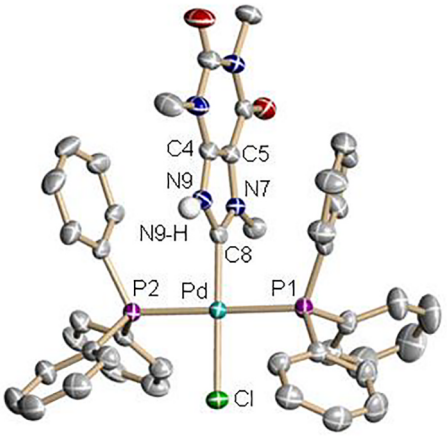
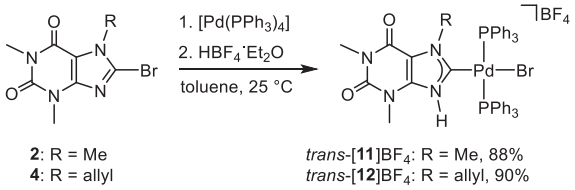


Fig. 3. Molecular structure of *trans*-[**9**]$^+$ in *trans*-[**9**]$BF_4{\cdot}2CH_2Cl_2$ (hydrogen atoms have been omitted for clarity, except for N9-H, ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (deg) in *trans*-[**9**]$^+$: Pd–Cl 2.3309(5), Pd–P1 2.3453(5), Pd–P2 2.3315(5), Pd–C8 1.982(2), N7–C8 1.340(3), N9–C8 1.365(3); Cl–Pd–P1 90.62(9), Cl–Pd–P2 89.82(2), Cl–Pd–C8 178.13(6), P1–Pd–P2 178.81(2), P1–Pd–C8 89.62(6), P2–Pd–C8 89.91(6), C8–N7–C5 109.8(2), C8–N9–C4 109.6(2), N7–C8–N9 106.6(2).



Scheme 4. Synthesis of *p*NHC complexes *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4.

caffeinato complex *trans*-[**5**]. The N9-protonation causes significant changes of the endocyclic bond angles. In accord with previous observations [16b,19], the N7-C8-N9 bond angle shrinks upon N9-protonation by about 6 deg and the endocyclic angles at the ring-nitrogen atoms N7 and N9 become essentially identical in *trans*-[**9**]$^+$ (109.8(2) and 109.6(2)°).

Finally, the N9-protonated analogs of palladium complexes *trans*-[**6**] and *trans*-[**8**] were prepared in a two step protocol similar to the preparation of *trans*-[**10**]BF_4 from *trans*-[**7**]. Thus, the 8-bromotheophylline derivatives **2** and **4** were initially reacted with $[Pd(PPh_3)_4]$ in toluene at room temperature for 2 d. Subsequently, the reaction mixture was treated with $HBF_4{\cdot}Et_2O$ giving complexes *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 in good yields (Scheme 4). While not studied here, we assume that the *p*NHC complexes *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 can be *N*-deprotonated to give the previously isolated stable azolato complexes *trans*-[**6**] and *trans*-[**8**] which were prepared by oxidative addition of 8-bromotheophyllines in the absence of a proton acid (Scheme 2). The reversible *N*-protonation/*N*-deprotonation has been demonstrated multiple times for various azolato/*p*NHC complexes [7,16,17].

Both compounds were characterized by NMR spectroscopy and mass spectrometry. The ^1H NMR spectra of complexes *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 are rather similar to those of the chlorido complexes *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4. The characteristic N9-H resonances were observed at δ 13.12 ppm and δ 12.69 ppm, respectively. Both, $^{31}P\{^1H\}$ (only one phosphine resonance) and $^{13}C\{^1H\}$ NMR spectroscopy (triplet resonance for C8), confirm the *trans*-configuration of the phosphine ligands in *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4. The resonances of the phosphorous atoms in the azolato complexes *trans*-[**6**] (δ 20.9 ppm) and *trans*-[**8**] (δ 21.3 ppm) do not differ significantly from those observed for the *p*NHC complexes *trans*-[**11**]BF_4 (δ 20.4 ppm) and *trans*-[**12**]BF_4 (δ 20.4 ppm). While the chemical shifts for the C8 carbon atoms in the azolato complexes *trans*-[**6**] and *trans*-[**8**] and the *p*NHC complexes *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 do not differ significantly, the latter ones feature an significantly larger $^2J_{CP}$ coupling constant. In summary, the substitution of the chlorido ligands in *trans*-[**9**]BF_4 and *trans*-[**10**]BF_4 for a bromido ligand in *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 does not lead to a significant change of the NMR spectra in general.

Crystals of *trans*-[**11**]BF_4 and *trans*-[**12**]BF_4 were obtained by slow diffusion of diethyl ether into saturated acetonitrile solutions of the compounds. The molecular structures of the cations *trans*-[**11**]$^+$ and *trans*-[**12**]$^+$ are depicted in Fig. 4.

Both complex cations *trans*-[**11**]$^+$ and *trans*-[**12**]$^+$ exhibit a nearly square-planar coordination geometry with the *p*NHC ligand plane oriented almost perpendicular to the metal coordination plane. Comparable metric parameters in *trans*-[**11**]$^+$ and *trans*-[**12**]$^+$ are rather similar to those of *trans*-[**9**]$^+$. Substitution of the chloro ligand in *trans*-[**9**]$^+$ for a bromo ligand in *trans*-[**11**]$^+$ and *trans*-[**12**]$^+$ does not significantly influence the three other Pd-L bond lengths which fall in the range previous described for complexes bearing NH,NR- [19,24] or NR,NR-NHC ligands [25]. As indicated by the NMR data, no interaction of the *N*-allyl function with the palladium atom was observed.

4. Conclusions

A series of C8-halogeno-N7-alkyltheophyllines have been prepared

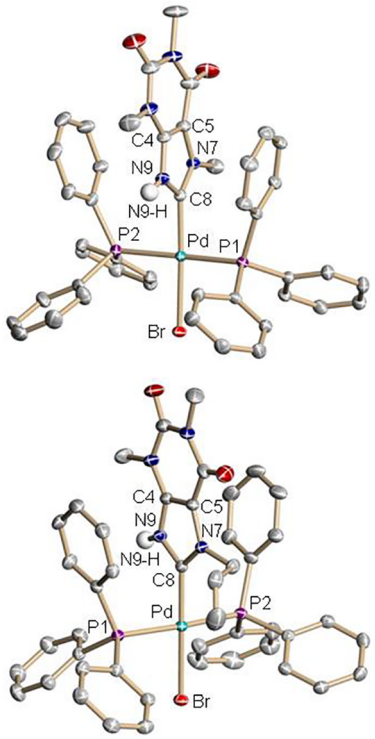


Fig. 4. Molecular structures of *trans*-[**11**]$^+$ in *trans*-[**11**]BF_4 and *trans*-[**12**]$^+$ in *trans*-[**12**]BF_4 (hydrogen atoms have been omitted for clarity, except for N9-H, ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (deg) for *trans*-[**11**]$^+$ [*trans*-[**12**]]: Pd–Br 2.4522(2) [2.4574(2)], Pd–P1 2.3333(5) [2.3528(5)], Pd–P2 2.3345(5) [2.3389(5)], Pd–C8 1.982(2) [1.982(2)], N7–C8 1.340(2) [1.340(2)], N9–C8 1.364(2) [1.365(2)]; Br–Pd–P1 90.228(12) [89.707(13)], Br–Pd–P2 90.139(13) [91.428(13)], Br–Pd–C8 177.39(5) [179.70(6)], P1–Pd–P2 174.03(2) [174.32(2)], P1–Pd–C8 90.45(5) [90.36(5)], P2–Pd–C8 88.93(5) [88.45(5)], C8–N7–C5 109.6(2) [109.3(2)], C8–N9–C4 109.7(2) [109.6(2)], N7–C8–N8 106.5(2) [106.7(2)].

by standard methods. These compounds react in an oxidative addition reaction with [$Pd(PPh_3)_4$] to yield azolato complexes of type *trans*-[Pd(theophyllinato)(X)$(PPh_3)_2$]. The oxidative addition proceeds much faster and under milder condition with the C8-bromo derivatives compared to the C8-chloro derivatives. The coordinated theophyllinato ligand in these complexes has been protonated with $HBF_4{\cdot}Et_2O$ to give *p*NHC complexes of type *trans*-[Pd(*p*NHC)(X)$(PPh_3)_2$]BF_4. Alternatively, the oxidative addition can be performed in the presence of NH_4BF_4 also yielding the *p*NHC complex. The theophyllinato complexes show no tendency to form dinuclear species by attack of the unsubstituted, negatively charged theophyllinato ring-nitrogen atom at another complex molecule under substitution of a PPh_3 ligand, most likely due to the electron withdrawing backbone of the theophyllinato ligand reducing the negative charge at the "naked" nitrogen atom. NMR data as well as the molecular structure determinations on the theophyllinato or *p*NHC complexes bearing an *N*-allyl substituent show no interaction of the allylic C=C double bond with the palladium ion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120055.

References

[1] (a) M.C. Jahnke, F.E. Hahn, Top. Organomet. Chem. 30 (2010) 95–129;
(b) F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122–3172;
(c) D. Martin, M. Melaimi, M. Solveilhavoup, G. Bertrand, Organometallics 30 (2011) 5304–5313;
(d) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature 510 (2014) 485–496.

[2] (a) J.A. Mata, F.E. Hahn, E. Peris, Chem. Sci. 5 (2014) 1723–1732;
(b) M. Poyatos, J.A. Mata, E. Peris, Chem. Rev. 109 (2009) 3677–3707;
(c) S. Díez-Gonzáles, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612–3676;
(d) E. Peris, Chem. Rev. 118 (2018) 9988–10031.

[3] (a) K.M. Hindi, M.J. Panzner, C.A. Tessier, C.L. Cannon, W.J. Youngs, Chem. Rev. 109 (2009) 3859–3884;
(b) W. Liu, R. Gust, Chem. Soc. Rev. 42 (2013) 755–773;
(c) L. Oehninger, R. Rubbiani, I. Ott, Dalton Trans. 42 (2013) 3269–3284.

[4] (a) A.R. Naziruddin, A. Galstyan, A. Iordache, C.G. Daniliuc, C.A. Strassert, L. De Cola, Dalton Trans. 44 (2015) 8467–8477;
(b) N. Sinha, L. Stegemann, T.T.Y. Tan, N.L. Doltsinis, C.A. Strassert, F.E. Hahn, Angew. Chem. Int. Ed. 56 (2017) 2785–2789;
(c) A. Galstyan, A.R. Naziruddin, C. Cebrián, A. Iordache, C.G. Daniliuc, L. De Cola, C.A. Strassert, Eur. J. Inorg. Chem. (2015) 5822–5831;
(d) J. Lin, N.-Y. Chau, J.-L. Liao, W.-Y. Wong, C.-Y. Lu, Z.-T. Sie, C.-H. Chang, M.A. Fox, P.J. Low, G.-H. Lee, Y. Chi, Organometallics 35 (2016) 1813–1824.

[5] (a) M. Schmidtendorf, T. Pape, F.E. Hahn, Angew. Chem. Int. Ed. 51 (2012) 2195-2198; (b) N. Sinha, F. Roelfes, A. Hepp, F.E. Hahn, Chem. Eur. J. 23 (2017) 5939-5942; (c) F.M. Conrady, R. Fröhlich, C. Schulte to Brinke, T. Pape, F.E. Hahn, J. Am. Chem. Soc. 133 (2011) 11496-11499; (d) N. Sinha, F. E. Hahn, Acc. Chem. Res. 50 (2017) 2167-2184.

[6] (a) A. Rit, T. Pape, F.E. Hahn, J. Am. Chem. Soc. 132 (2010) 4572-4573; (b) A. Rit, T. Pape, A. Hepp, F.E. Hahn, Organometallics 30 (2011) 334-347; (c) N. Sinha, F. Roelfes, A. Hepp, C. Mejuto, E. Peris, F.E. Hahn, Organometallics 33 (2014) 6898-6904; (d) C. Mejuto, G. Guisado-Barrios, D. Gusev, E. Peris, Chem. Commun. 51 (2015) 13914-13917; (e) Y. Li, Y.-Y. An, J.-Z. Fan, X.-X. Liu, X. Li, F.E. Hahn, Y.-Y. Wang, Y.-F. Han, Angew. Chem. Int. Ed. 59 (2020) 10073-10080; (f) M.-M. Gan, J.-Q. Liu, L. Zhang, Y.-Y. Wang, F. E. Hahn, Y.-F. Han, Chem. Rev. 118 (2018) 9587-9641.

[7] (a) M.C. Jahnke, F.E. Hahn, Coord. Chem. Rev. 293–294 (2015) 95–115;
(b) M.C. Jahnke, F.E. Hahn, Chem. Lett. 44 (2015) 226–237;
(c) S. Kuwata, F.E. Hahn, Chem. Rev. 118 (2018) 9642–9677.

[8] (a) P.G. Edwards, F.E. Hahn, Dalton Trans. 40 (2011) 10278–10288;
(b) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P.G. Edwards, P.D. Newman, F.E. Hahn, J. Am. Chem. Soc. 131 (2009) 306–317;
(c) A. Flores-Figueroa, T. Pape, K.-O. Feldmann, F.E. Hahn, Chem. Commun. 46 (2010) 324–326;
(d) F.E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, Angew. Chem. Int. Ed. 44 (2005) 3759–3763.

[9] (a) N. Meier, F.E. Hahn, T. Pape, C. Siering, S.R. Waldvogel, Eur. J. Inorg. Chem. (2007) 1210–1214;
(b) S. Kuwata, T. Ikariya, Chem. Commun. 50 (2014) 14290–14300;
(c) F.E. Hahn, ChemCatChem 5 (2013) 419–430.

[10] (a) M. Meier, T.T.Y. Tan, F.E. Hahn, H.V. Huynh, Organometallics 36 (2017) 275–284;
(b) F.E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W.P. Fehlhammer, Chem. Eur. J. 9 (2003) 704–712;
(c) F.E. Hahn, C. Garciá Plumed, M. Münder, T. Lügger, Chem. Eur. J. 10 (2004) 6285–6293;
(d) V. Blase, A. Flores-Figueroa, C. Schulte to Brinke, F.E. Hahn, Organometallics 33 (2014) 4471-4478.

[11] (a) H.G. Raubenheimer, L. Lindeque, S. Cronje, J. Organomet. Chem. 511 (1996) 177–184;
(b) H.G. Raubenheimer, Y. Stander, E.K. Marais, C. Thompson, G.J. Kruger, S. Cronje, M. Deetlefs, J. Organomet. Chem. 590 (1999) 158–168.

[12] (a) X. Wang, H. Chen, X. Li, Organometallics 26 (2007) 4684–4687;
(b) G.E. Dobereiner, C.A. Chamberlin, N.D. Schley, R.H. Crabtree, Organometallics 29 (2010) 5728–5731;
(c) M.C. Jahnke, D. Brackemeyer, T. Pape, F.E. Hahn, Heteroatom Chem. 22 (2011) 476–490.

[13] (a) J. Ruiz, B.F. Perandones, J. Am. Chem. Soc. 129 (2007) 9298–9299;
(b) J. Ruiz, A. Berros, B.F. Perandones, M. Vivanco, Dalton Trans. (2009) 6999–7007;
(c) J. Ruiz, D. Sol, J.F. Van der Maelen, M. Vivanco, Organometallics 36 (2017) 1035–1041.

[14] (a) K. Araki, S. Kuwata, T. Ikariya, Organometallics 27 (2008) 2176–2178;
(b) C. Price, M.R.J. Elsegood, W. Clegg, N.H. Rees, A. Houlton, Angew. Chem. Int. Ed. Engl. 36 (1997) 1762–1764;
(c) C. Price, M.A. Shipman, S.L. Gummerson, A. Houlton, W. Clegg, M.R.J. Elsegood, J. Chem. Soc., Dalton Trans. (2001) 353–354.

[15] (a) V. Miranda-Soto, D.B. Grotjahn, A.G. DiPasquale, A.L. Rheingold, J. Am. Chem.

Soc. 130 (2008) 13200-13201; (b) V. Miranda-Soto, D.B. Grotjahn, A.L. Cooksy, J. A. Golen, C.E. Moore, A.L. Rheingold, Angew. Chem. Int. Ed. 50 (2011) 631-635; (c) S. Cepa, C. Schulte to Brinke, F. Roelfes, F.E. Hahn, Organometallics 34 (2015) 5454-5460; (d) F.E. Hahn, A.R. Naziruddin, A. Hepp, T. Pape, Organometallics 29 (2010) 5283-5288; (e) D. Brackemeyer, C. Schulte to Brinke, F. Roelfes, F.E. Hahn, Dalton Trans. 46 (2017) 4510-4513.

[16] (a) T. Kösterke, T. Pape, F.E. Hahn, J. Am. Chem. Soc. 133 (2011) 2112–2115; (b) T. Kösterke, J. Kösters, E.-U. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz, F.E. Hahn, Chem. Eur. J. 18 (2012) 14594-14598. (c) T. Kösterke, T. Pape, F.E. Hahn, Chem. Commun. 47 (2011) 10773–10775

[17] (a) R. Das, C.G. Daniliuc, F.E. Hahn, Angew. Chem. Int. Ed. 53 (2014) 1163–1166; (b) R. Das, A. Hepp, C.G. Daniliuc, F.E. Hahn, Organometallics 33 (2014) 6975–6987.

[18] (a) H. Jin, T.T.Y. Tan, F.E. Hahn, Angew. Chem. Int. Ed. 54 (2015) 13811–13815; (b) H. Jin, C. Mück-Lichtenfeld, A. Hepp, D.W. Stephan, F.E. Hahn, Chem. Eur. J. 23 (2017) 5943–5947.

[19] D. Brackemeyer, A. Hervé, C. Schulte to Brinke, M.C. Jahnke, F.E. Hahn, J. Am. Chem. Soc. 136 (2014) 7841-7844.

[20] K. Vollmann, C.E. Müller, Heterocycles 57 (2002) 871–879.

[21] (a) G.M. Sheldrick, Acta Crystallogr. A 71 (2015) 3–8; (b) G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3–8.

[22] (a) F.E. Hahn, B. Heidrich, A. Hepp, T. Pape, J. Organomet. Chem. 692 (2007) 4630–4638; (b) F.E. Hahn, B. Heidrich, T. Pape, A. Hepp, M. Martin, E. Sola, L.A. Oro, Inorg. Chim. Acta 359 (2006) 4840–4846; (c) F.E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L.A. Oro, Organometallics 24 (2005) 2203–2209; (d) C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy, M. Albrecht, Organometallics 28 (2009) 5112–5121; (e) R. Corberán, M. Sanaú, E. Peris, Organometallics 26 (2007) 3492–3498.

[23] (a) T. Zheng, H. Sun, F. Lu, K. Harms, X. Li, Inorg. Chem. Commun. 30 (2013) 139–142; (b) T. Zheng, W. Xu, Y. Li, F. Lu, Z. Kristallogr. 228 (2013) 189–190.

[24] H.J. Krentzien, M.J. Clarke, H. Taube, Bioinorg. Chem. 4 (1975) 143–151.

[25] (a) A. Kascatan-Nebioglu, M.J. Panzner, J.C. Garrison, C.A. Tessier, W.J. Youngs, Organometallics 23 (2004) 1928–1931; (b) J. Schütz, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 2995–2999; (c) J.J. Hu, S.-Q. Bai, H.H. Yeh, D.J. Young, Y. Chi, T.S.A. Hor, Dalton Trans. 40 (2011) 4402–4406.