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Carbocyclic carbene ligands in palladium-catalyzed C–N coupling reactions

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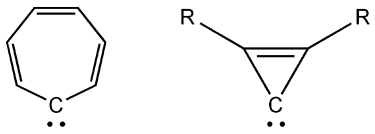
ABSTRACT

Palladium complexes bearing a cycloheptatrienylidene ligand are powerful precatalysts for C–N coupling reactions. Their catalytic performance is directly compared to analogous 2,3-diphenylcyclopropenylidene complexes. The crystal structure of *cis*-dibromo(cycloheptatrienylidene)(triphenylphosphane)palladium(II) is presented.

1. Introduction

Hartwig's and Buchwald's palladium-catalyzed aromatic amination has become a powerful tool for the synthesis of a great variety of products, ranging from laboratory to technical scale [1,2]. The palladium metal centers are supported and controlled by strong donor ligands. The most common ligand concepts comprise a wide range of phosphanes, including phosphapalladacycles, and *N*-heterocyclic carbenes (NHC) [3]. It is noteworthy and probably intrinsic for these systems that ligand-free catalysis is intensely discussed for C–C coupling, but not yet for C–N coupling reactions [4].



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In the course of our research with and beyond NHCs in organometallic chemistry and catalysis, we recently discovered that a simple carbocyclic carbene **I**, cycloheptatrienylidene (CHT), is comparable and even superior as a supporting ligand in catalysis in comparison to well-established NHC systems [5]. This observation was unforeseen and seems even more astonishing if one takes into account that transition metal complexes of both NHCs and carbocyclic carbenes have the same origin [6], though the latter have been treated as laboratory curiosities over decades [7,8]. In this context the recently reported isolation of a stable diaminocyclopropenylidene derivative and its corresponding lithium adduct by Bertrand et al. [9] as well as a chiral analogue [10] deserves to be mentioned. These precursors readily afford a range of metal carbene complexes [11] and will certainly stimulate growth in this area. We first described the catalytic application of this ligand class for the Heck and Suzuki coupling. Expanding our efforts to explore and optimize this new class of catalysts, we also included the analogous palladium complexes bearing the smallest possible carbocyclic carbene ligand cyclopropenylidene **II** [12,13]. The three-membered ring systems yielded inferior catalytic activities in C–C coupling, especially for deactivated chloro arenes. Hence, we focused further work on the seven-membered ring system and now report on a new application of the CHT ligand, as well as on a comparison with the 2,3-diphenylcyclopropenylidene ligand [14].

2. Discussion

A series of dinuclear halo-bridged carbocyclic carbene palladium(II) complexes **1** [5a], **2**, **5** [6c,12,14] and the mononuclear compounds **3a** [5a], **3b**, **4**, **6** [6,12,13] bearing a carbocyclic carbene and a phosphane ligand (Fig. 1) were used for investigations into the catalytic activity for Hartwig–Buchwald amination.

It was not surprising that the synthesis of the cyclopropenylidene Pd(II) complex **5** also works straightforwardly with

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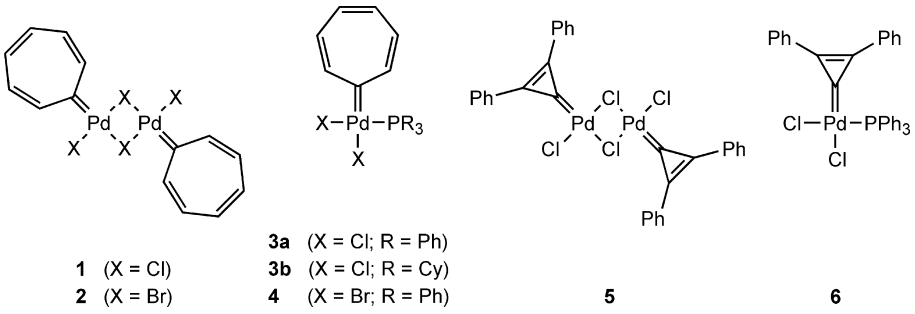


Fig. 1. Palladium precatalysts supported by carbocyclic carbene ligands.

molecularly defined soluble palladium sources like bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] as reported by Wass et al. [14] instead of palladium black. We exploited this minor variation for the synthesis of the seven-membered ring complexes, thus obtaining almost quantitative yields for bis[dibromo(cycloheptatrienylidene)palladium(II)] (**2**). Nevertheless, the bad atom economy ($M(Pd(dba)_2)$ = 575.0 g/mol vs. M(Pd) = 106.4 g/mol), high price and the air-sensitivity of this precursor must be seen critical.

As we extended our catalytic studies to the bromo derivatives **2** and **4**, we were interested if any significant structural differences would occur. Hence, we employed a comparison of the solid-state structure of complex **4** (Fig. 2) [15] to that of **3a** already reported previously [5a]. Both compounds crystallize in *cis*-configuration with nearly identical bond angles and a similar carbene bond length lying in the range typical for NHC–Pd complexes (Table 1). A considerable *trans*-influence of the CHT ligand indicated by a longer Pd–Br2 bond length (0.017 Å) compared to Pd–Br1 in **4** is a further hint for the strong σ-donor and poor π-acceptor character of this carbene ligand. Moreover, almost identical C–C bond lengths (1.39 ± 0.02 Å) in the seven-membered ring suggest extensive 6π delocalization including the carbene p_z-orbital in the bromo derivative, too.

Table 1
Selected bond lengths (Å) and bond angles (°) of the CHT palladium complexes **3a** and **4**

	3a	4
Pd–C1	1.968(2)	1.983(3)
Pd–X1	2.3697(6)	2.4895(5)
Pd–X2	2.3884(7)	2.5064(4)
Pd–P	2.2483(6)	2.2575(9)
X1–Pd–X2	91.83(2)	92.38(2)
X1–Pd–P	175.89(2)	175.15(3)
X1–Pd–C1	85.14(7)	84.78(11)
X2–Pd–P	92.27(2)	92.42(3)
X2–Pd–C1	174.55(6)	174.63(9)
P–Pd–C1	90.76(7)	90.38(11)

For compound **3a** X = Cl, for compound **4** X = Br.

However, we note that a similar stabilization for the three-membered ring system (2π–e^--aromaticity), as proposed *inter alia* by Wass et al. [14], was recently ruled out by an experimental

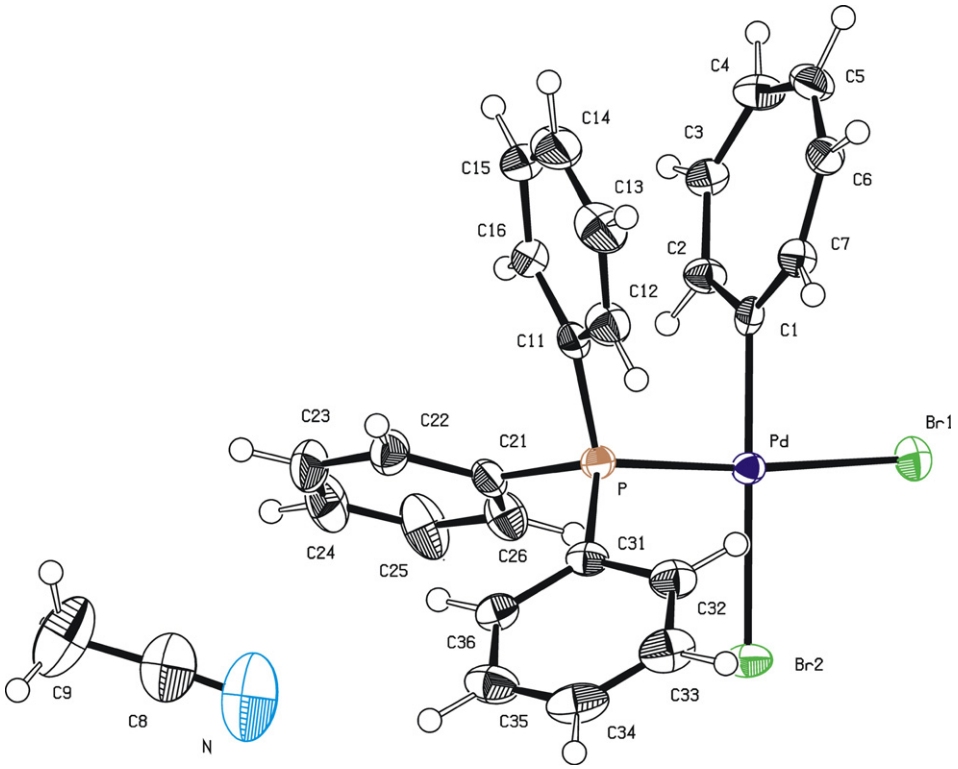


Fig. 2. ORTEP style plot of compound **4** · ACN in the solid state; thermal ellipsoids set at 50% probability.

charge-density approach for free as well as coordinated cyclopropenylidene carbenes by Scherer et al. [16]. Clearly a higher π-acceptor capability relative to *N*-heterocyclic carbenes was shown. Work is underway to further elucidate the σ-donor/π-acceptor properties of the CHT ligand.

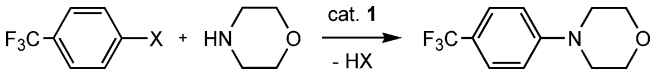
For a catalytic evaluation, we followed established standard protocols [1] to facilitate the comparison of the results obtained. We extended phosphane screening with compound **1** (Table 2) as this *in situ*-method provides an efficient and valuable probe for identifying which catalytic systems may warrant further study. The halo-bridged complexes **1**, **2**, **5** are known to undergo easy cleavage by phosphanes, thus yielding the relevant precatalysts. In the coupling of the activated bromo substrate *p*-bromo benzotrifluoride with morpholine at elevated temperatures, our CHT complex is active with a variety of phosphanes employed (Table 2, entries 2–7). For the corresponding chloro substrate distinct differences were observed. Appreciable yields could only be obtained with the more basic alkylphosphanes PCy_3 and P^tBu_3 (Table 2, entries 13 and 14). In addition, the phosphane with the largest cone angle, $PMes_3$, was not compatible with the CHT ligand and yielded the same poor results as the phosphane-free runs (Table 2, entries 1, 5, 8 and 12) suggesting the crucial role of a second suitable donor ligand attached to the palladium metal center. Comparing GC-based conversions and yields in terms of catalyst selectivity for several runs, more than 30% higher conversion than yield was observed due to side reactions (Table 2, e.g. entries 6 and 13). However, employing only conversion as a measure for catalyst activity is in a way misleading and the importance of yield-based discussion should be emphasized [13]. Finally in this screening experiment for each run (except Table 2, entry 1) with the CHT system superior results could be realized in comparison with the preliminary data published by Wass et al. for the 2,3-diphenylcyclopropenylidene system [14].

Having in mind the strong influence of the participating phosphane, further investigations as to the effects of aryl halide deactivation, catalyst loading, temperature, base, etc., were carried out with various catalytic systems (Table 3). Similar yields were observed for application of an *in situ*-mixture in comparison to the isolated precatalyst suggesting the same active species is present in both reactions (Table 2, entry 3 *vs*. Table 3, entry 1). The amination of chloro-arenes is possible with precatalyst **3b**; however, the efficiency is strongly governed by the degree of substrate activation (Table 3, entries 5–7). On the one hand, this highlights the limitations of catalyst **3b**. On the other hand, it emphasizes the important role of P^tBu_3 in this particular catalytic system. A significant loss of activity was also observed by decreasing the catalyst concentration from 2% to 0.5% (Table 3, entries 9, 11 and 12). The use of the stronger base KO^{t}Bu instead of NaO^{t}Bu resulted in slightly higher yields (Table 3, entries 1 and 9). A carbene-free palladium source was employed to confirm the importance of the carbocyclic carbene ligand (Table 3, entry 22). As previously reported, an excess of phosphane is shown to be rather detrimental to the system (Table 3, entry 23) [17].

The role of the halogen attached to the palladium by parallel screening of the halo-bridged complexes **1** and **2** and the mononuclear complexes **3a** and **4** was investigated, too. Both **1** and **2**, in combination with P^tBu_3, are able to aminate deactivated chloro-arenes in excellent yields (Table 3, entries 18 and 19). In comparison to its chloro derivative, compound **4** with *p*-bromo anisole gave significantly higher yields (Table 3, entries 2 and 8). Moreover, better performance at moderate temperatures could be observed (Table 3, entries 14 and 15), though for the coupling of deactivated chloro-arenes, i.e. *p*-chloro anisole at room temperature (Table 3, entry 21), our CHT-system requires further optimization to be competitive with other highly active catalysts [18].

In agreement with our phosphane screening experiments (Table 2), the CHT system was shown to be superior to the 2,3-cyclopropenylidene system when employed as isolated mixed carbene phosphane complexes (Table 3, entries 1–4) or when generated by the *in situ*-method (Table 3, entries 18 and 20). High reactivity with a variety of other amines (2,4,6-trimethylaniline, *N*-methylaniline, *o*-toluidine, diphenylamine) was also observed (not shown). However, quantification using ^{1}H NMR as suggested by Wass et al. [14] for these substrates, particularly for the diphenylamine, turned out to be capricious, as such GC-FID quantification was employed [1].

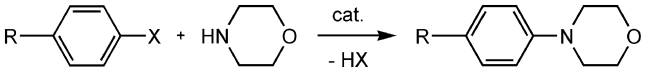
Table 2
Phosphane screening



Entry[a]	Phosphane	X	Conversion[b] (yield)[c]%
1	None	Br	35 (19)
2	P(*p*-F–Ph)$_3$	Br	100 (69)
3	PPh_3	Br	100 (70)
4	P(*o*-Tol)$_3$	Br	100 (90)
5	$PMes_3$	Br	37 (20)
6	PCy_3	Br	100 (68)
7	P^tBu_3	Br	100 (100)
8	None	Cl	5 (1)
9	P(*p*-F–Ph)$_3$	Cl	1 (1)
10	PPh_3	Cl	1 (1)
11	P(*o*-Tol)$_3$	Cl	10 (5)
12	$PMes_3$	Cl	8 (3)
13	PCy_3	Cl	100 (64)
14	P^tBu_3	Cl	100 (98)

[a] Conditions: 1.0 mmol of aryl halide, 1.2 mmol of morpholine, 1.4 mmol of NaO^{t}Bu, 2.0 mol% of Pd, 1.0 equiv. of phosphane, 8 ml toluene, 100 °C, 18 h.
[b] GC conversion based on aryl halide with *n*-eicosane as the internal standard.
[c] GC yield with *n*-eicosane as the internal standard.

Table 3
Catalysis data



Entry[a]	Cat.	mol% Pd	*T*/°C	Base	R	X	Yield[b]/%
1	**3a**	2.0	100	NaO^{t}Bu	F_3C	Br	70
2	**3a**	2.0	100	NaO^{t}Bu	MeO	Br	31
3 [14]	**6**	2	100	NaO^{t}Bu	F_3C	Br	63
4 [14]	**6**	2	100	NaO^{t}Bu	MeO	Br	23
5	**3b**	2.0	100	NaO^{t}Bu	F_3C	Cl	66
6	**3b**	2.0	100	NaO^{t}Bu	H	Cl	41
7	**3b**	2.0	100	NaO^{t}Bu	MeO	Cl	12
8	**4**	2.0	100	NaO^{t}Bu	MeO	Br	62
9	**3a**	2.0	100	KO^{t}Bu	F_3C	Br	77
10	**4**	2.0	100	KO^{t}Bu	F_3C	Br	81
11	**3a**	1.0	100	KO^{t}Bu	F_3C	Br	78
12	**3a**	0.5	100	KO^{t}Bu	F_3C	Br	37
13	**3a**	2.0	75	KO^{t}Bu	F_3C	Br	79
14	**3a**	2.0	50	KO^{t}Bu	F_3C	Br	50
15	**4**	2.0	50	KO^{t}Bu	F_3C	Br	81
16	**1**[c]	2.0	50	KO^{t}Bu	F_3C	Br	100
17	**5**[c]	2.0	50	KO^{t}Bu	F_3C	Br	100
18	**1**[c]	2.0	100	NaO^{t}Bu	MeO	Cl	100
19	**2**[c]	2.0	100	NaO^{t}Bu	MeO	Cl	94
20	**5**[c]	2.0	100	NaO^{t}Bu	MeO	Cl	86
21	**2**[c]	2.0	r.t.	KO^{t}Bu	MeO	Cl	11
22	$Pd(PhCN)_2Cl_2$[c]	2.0	100	NaO^{t}Bu	MeO	Cl	50
23	$Pd(PhCN)_2Cl_2$[d]	2.0	100	NaO^{t}Bu	MeO	Cl	31

[a] Conditions: 1.0 mmol of aryl halide, 1.2 mmol of morpholine, 1.4 mmol of base, 8 ml toluene, 18 h.
[b] GC yield with *n*-eicosane as the internal standard.
[c] *In situ* with 1.0 equiv. P^tBu_3.
[d] *In situ* with 2.0 equiv. P^tBu_3.

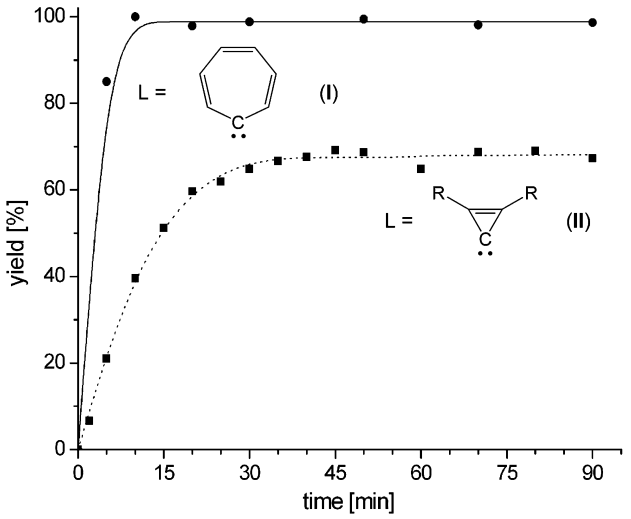


Fig. 3. Yield *vs.* time plot at room temperature for the coupling of *p*-bromo benzotrifluoride (1.0 mmol) with morpholine (1.2 mmol) catalyzed by **1** (–•–) and **5** (–■–) *in situ* with 1.0 equiv. P^tBu_3 (other conditions: 2 mol% Pd, 1.4 mmol NaO^tBu, 8 ml toluene; GC yield with *n*-eicosane as the internal standard).

As already shown, carbocyclic carbene palladium precatalysts do not suffer from an induction period [5,12–14]. We could confirm these findings also for C–N coupling catalysis, even at room temperature (Fig. 3). It was surprising to observe even for the strongly activated substrate *p*-bromo benzotrifluoride that the CHT system is superior over the 2,3-diphenylcyclopropenylidene system: the CHT system gave quantitative yields already after ca. 10 min, while the three-membered carbocyclic carbene had its limit at 70% maximum.

3. Conclusion

Our carbocyclic carbene palladium complexes show high activity in Hartwig–Buchwald amination reactions. In each particular screening experiment, the CHT-supported palladium precatalysts in combination with a phosphane ligand formed catalytically more active species than the analogous 2,3-diphenylcyclopropenylidene systems. Both isolated mononuclear complexes *cis*-(CHT)(PPh_3)PdX_2 (X = Cl, Br) exhibit very similar structural features in the solid state. However, the catalytic activity of the bromo derivative is significantly higher. Work is underway to investigate electronically and sterically modified CHT ligands, and to elucidate the role of the carbocyclic carbene ligand in the catalytic cycle.

4. Experimental

General comments: All manipulations were performed under an inert atmosphere of argon using standard Schlenk and dry-box techniques. Dry, oxygen-free solvents were employed. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 400 spectrometer (frequencies: ^1H 399.8 MHz, ^{13}C 100.5 MHz, ^{31}P 161.8 MHz) at room temperature and referenced to the residual ^1H and ^{13}C signals of the solvents or 85% H_3PO_4 as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Elemental analyses were carried out by the Microanalytical Laboratory at TU München. Mass spectra were performed on a Finnigan MAT 90 spectrometer using the FAB technique (Mass Spectrometry Laboratory, TU München). Catalysis was performed with a Heidolph Synthesis 1 Liquid system. GC spectra were measured on a Varian gas chromatograph CP-3800 (column: FactorFour VF-5 ms) equipped with a FID detector. Compounds **1**, **3a**, **5** and **6** were prepared according to the literature [5a,12].

4.1. Synthesis

4.1.1. Bis[dibromo(cycloheptatrienylidene)palladium(II)] (**2**)

This compound has been prepared by combination, with slight modifications, of two procedures reported previously [5a,14].

$Pd(dba)_2$ (244 mg, 0.424 mmol) and dibromocycloheptatriene (104 mg, 0.416 mmol) were suspended in 10 ml THF at −78 °C. The mixture was allowed to reach room temperature and was stirred over night. The precipitate formed was filtered off, thoroughly washed with diethyl ether and dried in vacuo. Compound **2** was obtained as bright orange microcrystalline powder containing 0.5 equiv. of diethyl ether. Yield: 151 mg (97%).

^1H NMR (ACN-d_3)[1]: δ [ppm] = 9.54 (d, ^3J = 10 Hz, 2H, CHT), 8.34 (dd, ^3J = 3.6/6.4 Hz, 2H, CHT), 8.05 (m, 2H, CHT), 3.42 (q, ^3J = 6.9 Hz, 1H, O–CH_2–CH_3), 1.12 (t, ^3J = 6.8 Hz, 1.5H, O–CH_2–CH_3).

^{13}C NMR (ACN-d_3)[1]: δ [ppm] = 217.5 (carbene C), 162.7 (CHT), 147.7 (CHT), 139.8 (CHT), 66.1 (O–CH_2–CH_3), 15.5 (O–CH_2–CH_3).

Elemental analysis calcd for $C_{14}H_{12}Br_4Pd_2 \cdot 0.5C_4H_{10}O$ (M = 749.76 g/mol): C, 25.63; H, 2.29; Pd, 28.39. Found: C, 25.16; H, 2.21; Pd, 28.2%.

4.1.2. cis-Dichloro(cycloheptatrienylidene)(tricyclohexylphosphane) palladium(II) (**3b**)

This compound has been prepared by a procedure reported previously [5a].

Elemental analysis calcd for $C_{25}H_{39}Cl_2PPd$ (M = 547.88 g/mol): C, 54.81; H, 7.17; Pd, 19.42. Found: C, 54.50; H, 7.40; Pd, 19.4%.

^1H NMR (ACN-d_3): δ [ppm] = 9.49 (d, ^3J = 10 Hz, 2H, CHT), 8.40 (m, 2H, CHT), 8.13 (m, 2H, CHT), 2.1–1.1 (m, 33H, PCy_3).

$^{31}P\{^1H\}$ NMR (ACN-d_3): δ [ppm] = 51.6 (s).

MS(FAB): *m/z* (%): 513 (16, $[M-Cl]^+$).

4.1.3. cis-Dibromo(cycloheptatrienylidene)(triphenylphosphane)-palladium(II) (**4**)

This compound has been prepared by a procedure reported previously [5a].

Elemental analysis calcd for $C_{25}H_{21}Br_2PPd$ (M = 618.64 g/mol): C, 48.54; H, 3.42; Pd, 17.20. Found: C, 50.06; H, 3.80; Pd, 16.9%.

^1H NMR (ACN-d_3): δ [ppm] = 9.30 (d, ^3J = 10 Hz, 2H, CHT), 8.09 (dd, ^3J = 4.2/6.6 Hz, 2H, CHT), 7.69 (m, 2H, CHT), 7.62 (m, 6H, *o*-Ph), 7.41 (m, 3H, *p*-Ph), 7.31 (m, 6H, *m*-Ph).

$^{31}P\{^1H\}$ NMR (ACN-d_3): δ [ppm] = 29.2 (s).

MS(FAB): *m/z* (%): 538 (100, $[M-Br]^+$).

4.2. C–N coupling

An analogous procedure was followed in each case and is exemplified here for Table 2, entry 2. The reaction vessel was loaded with precatalyst **1** (0.010 mmol), P(*p*-F–Ph)$_3$ (0.020 mmol) and the internal standard *n*-eicosane which were suspended in toluene (8 ml) followed by addition of *p*-bromo benzotrifluoride (1.0 mmol), morpholine (1.2 mmol) and NaO*t*Bu (1.4 mmol). The reaction mixture was heated at 100 °C for 18 h (agitation speed 550 min^{-1}). After this time, the mixture was cooled to room temperature and quenched with water (2 ml). The organic phase was separated and dried over Na_2SO_4. The kinetic runs at room temperature were performed in the same way, only an aliquot of a phosphane-solution with defined concentration in toluene was added

[1] Compound **2** is insoluble in common non-coordinating solvents. Most likely the bromo bridge is cleaved by acetonitrile yielding (ACN)(CHT)$PdBr_2$ (unpublished results).

at the end to start the experiment (t = 0 min). Conversions and yields were determined by GC analysis.

4.3. Single crystal X-ray structure determination of compound 4 · ACN

General: Crystal data and details of the structure determination are presented in Table 4. A suitable single-crystal for the X-ray diffraction study was grown with standard cooling techniques. The selected crystals was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, OXFORD DIFFRACTION, Xcalibur, κ-CCD; sealed tube, Enhance X-ray Source, SPELLMAN, DF3). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection were performed at low temperatures (T = 153 K, OXFORD CRYOSYSTEMS cooling device). The crystal was measured with nine data sets in rotation scan modus ($\Delta\phi/\Delta\omega$ = 2.00°; dx = 50). Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with d_{C-H} = 0.98 Å and iso(H) = 1.5$U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with aromatic d_{C-H} distances of 0.95 Å, and $U_{iso(H)}$ = 1.2$U_{eq(C)}$. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed with the WINGX system, including the programs PLATON, SHELXL-97, and SIR92 [15].

Table 4
Crystallographic data for **4** · ACN

	4 · ACN
Formula	$C_{27}H_{24}Br_2NPPd$
Formula weight	659.66
Color/habit	Yellow/fragment
Crystal dimensions (mm^3)	0.30 × 0.56 × 0.58
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	9.9435(6)
b (Å)	10.6413(6)
c (Å)	12.4012(7)
α (°)	98.629(5)
β (°)	94.270(5)
γ (°)	90.529(5)
V (Å^3)	1293.46(13)
Z	2
T (K)	153
D_{calcd} (g cm^{-3})	1.694
μ (mm^{-1})	3.883
F(000)	648
θ Range (°)	2.74–25.35
Index ranges (h,k,l)	±11, ±12, ±14
Number of reflections collected	23678
Number of independent reflections/R_{int}	4703/0.030
Number of observed reflections ($I > 2\sigma(I)$)	3722
Number of data/restraints/parameters	4703/0/290
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0291/0.0678
R_1/wR_2 (all data)[a]	0.0429/ 0.0769
Goodness-of-fit (on F^2)[a]	1.154
Largest diffraction peak and hole (e Å^{-3})	+0.86/−0.76

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

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Appendix A. Supplementary material

CCDC 680443 contains 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.

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