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Six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl) guanidines: Synthesis, reactivity studies and structural aspects

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ABSTRACT

Six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl)guanidines, [(ArNH)$_2$C=NAr] (*sym* = symmetrical; Ar = 4-MeC$_6$H$_4$; LH$_2^{4\text{-tolyl}}$) of the types [(*C*,*N*)Pd(μ-OC(O)R)]$_2$ (**1** and **2**), [(*C*,*N*)Pd(μ-Br)]$_2$ (**3**), *cis*-[(*C*,*N*)PdLBr] (**4**–**7**), and [(*C*,*N*)Pd(acac)] (**8**) were prepared in high yield by established methods with a view aimed at understanding the influence of the 4-tolyl substituent of the guanidine moiety upon the solution behaviour of **1**–**8**. The composition of **1**–**8** was confirmed by elemental analysis, IR, and NMR spectroscopy, and mass spectrometry. The molecular structures of **1**–**6** were determined by single-crystal X-ray diffraction. Palladacycles **1**–**3** exist as a dimer in *transoid* conformation in the solid state while **4**–**6** exist as a monomer with *cis* configuration around the palladium atom as the Lewis base is placed *cis* to the Pd–C bond due to antisymbiosis. The NMR spectra of **1**–**8** revealed the presence of a single isomer in solution and this spectral feature is ascribed to the rapid inversion of the six-membered "[*C*,*N*]Pd" ring due to the presence of sterically less hindered and more symmetrical 4-tolyl substituent in the =NAr unit of the guanidine moiety.

1. Introduction

Six-membered [*C*,*N*] cyclopalladated imines are one of the interesting classes of palladacyclic compounds due to their (i) intriguing structural and reactivity pattern such as bridge-splitting reaction (bsr), (ii) regioselective aspects of C–H activation, and (iii) role as precatalysts for C–C coupling reactions, and photophysical properties [1–10]. We have recently reported syntheses, reactivity studies, structural aspects, and solution behaviour of five- and six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-triarylguanidines, [(ArNH)$_2$C=NAr] (*sym* = symmetrical; Ar = 2–RC$_6$H$_4$; R = OMe (LH$_2^{2\text{-anisyl}}$) [11] and Me (LH$_2^{2\text{-tolyl}}$) [12]). The number and nature of solution species of six-membered [*C*,*N*] cyclopalladated LH$_2^{2\text{-anisyl}}$ and LH$_2^{2\text{-tolyl}}$ varied depending upon the steric bulk and donor capability of *ortho* substituent of the aryl ring in the =NAr unit of the guanidine moiety. Herein, we extend our investigation on the synthesis, reactivity studies, structural aspects, and solution behaviour of six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl)guanidines, [(ArNH)$_2$C=NAr] (Ar = 4-MeC$_6$H$_4$; LH$_2^{4\text{-tolyl}}$) and the results emerged from our endeavour are presented in this manuscript.

2. Results and discussion

2.1. Carboxylato bridged dimeric palladacycles (*1* and *2*)

The reaction of Pd(OC(O)R)$_2$ (R = CF$_3$ and ^{t}Bu) with LH$_2^{4\text{-tolyl}}$ in 1:1 mol ratio in toluene at 70 °C for 6 h afforded **1** and **2** as greenish yellow, and pale yellow crystals in 84% and 92% yields, respectively as shown in Scheme 1.

The molecular structures of **1** and **2** are depicted in Fig. 1. Selected bond distances and bond angles are listed in Tables 1 and 2, respectively. Palladacycles **1** and **2** exist as a dimer wherein two palladium atoms are bridged by a pair of *syn*–*syn* bidentate carboxylato moiety. Palladacycle **1** revealed a pseudo C_2 symmetry while **2** displayed a crystallographic C_2 symmetry that passes vertically across the centre of the Pd···Pd vector to afford a *transoid* in–in conformation. In this conformation, the imine nitrogen bound to the palladium atom of one six-membered "[*C*,*N*]Pd" ring is located *trans* to the identical atom of the other six-membered "[*C*,*N*]Pd" ring and the ring NH proton of one six-membered "[*C*,*N*]Pd" ring points toward the identical atom of the second six-membered "[*C*,*N*]Pd" ring.

The palladium atom in **1** and **2** is surrounded by the oxygen atom of two separate carboxylato moieties, an imine nitrogen atom, and the aryl carbon atom. Further, the palladium atom revealed a distorted square planar geometry as inferred from the dihedral

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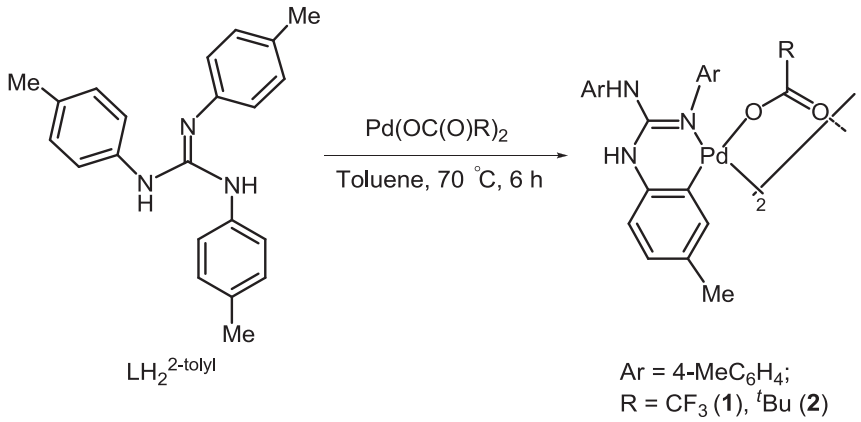


Scheme 1.

angle between two mean planes defined by N–Pd–C and O–Pd–O units (5.63(22) and 2.92(6)° (**1**); 4.84(6)° (**2**)). The six-membered "[*C*,*N*]Pd" ring exhibited a pseudo boat conformation. The bond parameters around the palladium atom in **1** and **2** are comparable with those reported for the related six-membered [*C*,*N*] cyclopalladated imines [8,11–13].

The degree of n–π conjugation involving the lone pair of the ring and exocyclic amino nitrogen atoms with C=N π* orbital of the guanidine unit can be estimated from the values of Δ_{CN} and Δ_{CN}', respectively. The Δ_{CN} value is the difference between the C=N double bond and the adjacent *endocyclic* C–N single bond distances, whereas the Δ_{CN}' value is the difference between the C=N double bond and the adjacent *exocyclic* C–N single bond distances [11]. The values of Δ_{CN} (0.047(8), and 0.036(8) Å (**1**); 0.061(6) Å (**2**)) are comparable or smaller than the values of Δ_{CN}' (0.050(8), and 0.071(8) Å (**1**); 0.069(6) Å (**2**)) and these values in turn are comparable or smaller than the values of Δ_{CN} and Δ_{CN}' observed for free guanidine, $LH_2^{4\text{-tolyl}}$ ($\Delta_{CN}' = 0.106(4)$ Å; $\Delta_{CN} = 0.077(4)$ Å) [14]. Thus, n–π conjugation involving the lone pair of the ring amino nitrogen atom with C=N π* orbital of the guanidine unit in **1** and **2** is comparable or greater than that observed with the exocyclic amino nitrogen atom. Both the amino nitrogen atoms in **1** and **2** are planar.

The ^{1}H and ^{13}C NMR spectra of **1** and **2** revealed the presence of a single isomer in solution. In principle, acetato bridged six-membered [*C*,*N*] cyclopalladated 2-benzylpyridine [15] and $LH_2^{4\text{-tolyl}}$ such as **1** and **2** can exist as a mixture of *transoid* in–in, *transoid* in–out, and *transoid* out–out conformers in solution. Further, [Pd{κ^2(*C*,*N*)–C_6H_3Me-3(NHC(NHAr)(=NAr))-2}(μ-OAc)]$_2$ (Ar = 2-MeC_6H_4; **I**), which was present in *transoid* in–in conformer in the solid state was shown to equilibrate with a small quantity of κ^2-*O*,*O*′-OAc monomeric [*C*,*N*] cyclopalladated $LH_2^{2\text{-tolyl}}$ in solution due to the presence of sterically hindered 2-tolyl substituent in the =NAr unit of the guanidine moiety [12]. It appears that the rate of six-membered "[*C*,*N*]Pd" ring inversion among three conformers mentioned above is faster than the NMR time scale due to the presence of sterically less hindered 4-tolyl substituent in the =NAr unit of the guanidine moiety of **1** and **2**. Hence, the NMR spectra of **1** and **2** apparently indicated the presence of only one isomer in solution.

2.2. Bromo bridged dimeric palladacycle (*3*)

Palladacycle **1** was subjected to a metathetical reaction with LiBr in aq. ethanol at 80 °C to afford **3** as yellow crystals in 94% yield as illustrated in Scheme 2. The molecular structure of **3** is practically identical to that found in [Pd{κ^2(*C*,*N*)–C_6H_3Me-3(NHC(NHAr)(=NAr))-2}(μ-Br)]$_2$ (Ar = 2-MeC_6H_4; **II** [12]) with the following exception (see the Supplementary material for the molecular structure of **3**). The $[Pd(\mu\text{-}Br)_2Pd]^{2+}$ unit in **3** revealed a planar rhomboid conformation (Pd(1)–Br(1)–Pd(1): 95.42(1)°; Br(1)–Pd(1)–Br(1): 84.57(1)°) in contrast to the folded conformation of the same unit observed in **II** [12]. The aforementioned difference is ascribed to the presence of sterically less hindered 4-tolyl substituent in the =NAr unit of the guanidine moiety of **3**. The degree of n–π conjugation involving the lonepair of the endocyclic and the exocyclic amino nitrogen atoms with C=N π* orbital in **3** are comparable as reflected from the values of Δ_{CN} = 0.051(6) Å and Δ_{CN}' = 0.053(6) Å. Both the amino nitrogen atoms in **3** are planar.

2.3. Monomeric palladacycles (*4*–*8*)

Palladacycle **1** was subjected to the bsr with 2,6-lutidine and PTA in CH_2Cl_2 at ambient temperature to afford **4**, and **5** in 96% and 94% yields, respectively. Similarly, **3** was subjected to the bsr with 2,6-lutidine, and PTA in CH_2Cl_2 at ambient temperature to afford **6**, and **7** in 97% and 86% yields, respectively (see Scheme 3). Palladacycle **3** was treated with Na(acac) (acac = acetylacetonate) in CH_2Cl_2 at ambient temperature to afford a bis-chelated palladacycle, **8** in 97% yield as illustrated in Scheme 4.

The molecular structures of **4** and **5** are depicted in Fig. 2. Selected bond distances and bond angles are listed in Table 3. The molecular structure of **6** is practically identical to that found in [Pd{κ^2(*C*,*N*)–C_6H_3Me-3(NHC(NHAr)(=NAr))-2}Br(2,6-$Me_2C_6H_3$N)] (Ar = 2-MeC_6H_4 (**III**); see the Supplementary material for the molecular structure of **6**). Two molecules crystallized in an asymmetric unit in the case of **4** and the structural features are described here only for molecule 1. The palladium atom is surrounded by the imine nitrogen, the aryl carbon, nitrogen or phosphorus atom of the Lewis base, and oxygen atom of the TFA (**4** and **5**) or bromide (**6**). The palladium atom revealed a slightly distorted square planar geometry. The angle between NPdC and OPdE planes (*E* = N or P) in **4**–**6** are 2.79(28), 8.08(9), 11.37(17)°, respectively. The Lewis base is coordinated to the palladium atom in *cis* relation with respect to the Pd–C bond due to antisymbiosis [16]. The molecular structures of six-membered [*C*,*N*] cyclopalladated imines of the type [(*C*,*N*)PdX(phosphine)] are known to contain the phosphine in *cis* orientation with respect to the Pd–C bond [5,7,11,12] due to antisymbiosis. The six-membered "[*C*,*N*]Pd" ring in **4**–**6** adopts a pseudo boat conformation.

The Pd–C distance in **4**–**6** (1.982(5) Å (**4**), 1.978(3) Å (**5**), and 1.983(3) Å (**6**)), the Pd–N distances in **4** and **6** (Pd–$N_{guanidine}$: 2.016(4) Å (**4**), 2.038(2) Å (**6**); Pd–$N_{lutidine}$ = 2.060(4) Å (**4**), 2.049(2) Å (**6**)) are comparable with the corresponding distances observed around the palladium atom in **III** (Pd–C = 1.985(2) Å; Pd–$N_{guanidine}$ = 2.034(1) Å;

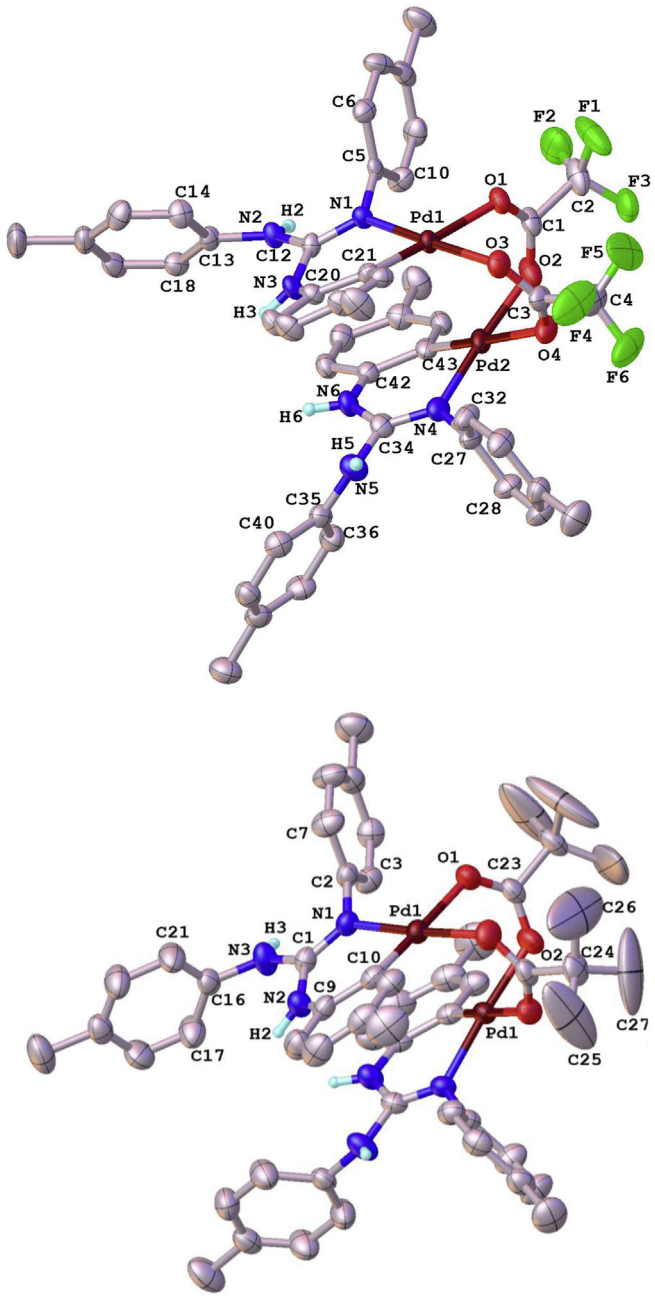


Fig. 1. Molecular structures of **1** (top) and **2** (bottom) at the 50% probability level. Only hydrogen atoms of the amino moieties are shown for clarity.

Pd–$N_{lutidine}$ = 2.048(1) Å) [12]. The Pd–$N_{guanidine}$ distance of 2.100(2) Å in **5** is longer than the corresponding distance observed in **4**, and **6** due to greater *trans* influence of PTA in the former palladacycle than 2,6-lutidine in the latter two. The value of Δ_{CN} = 0.039(5) Å in **6** is slightly smaller than the corresponding value known for **III** (Δ_{CN} = 0.052(2) Å) [12] indicating a better n–π conjugation in the former. The Δ_{CN}' value of 0.043(4) Å in **6** is comparable with the corresponding value known for **II** (Δ_{CN}' = 0.050(2) Å). Both the amino nitrogen atoms in **4**–**6** are planar.

The ^{1}H and ^{13}C NMR spectra of **4** and **6** revealed the presence of only one isomer in solution. Six-membered [*C*,*N*] cyclopalladated 2-benzylbenzothiazole and $LH_2^{2\text{-tolyl}}$ of the type [(*C*,*N*)PdX(2,6-$Me_2C_6H_3N$)] were shown to exist as a mixture of two boat conformers [12,17] and these conformers interconvert via the six-membered "[*C*,*N*]Pd" ring inversion. When the rate of six-membered "[*C*,*N*]Pd" ring inversion is comparable with the NMR timescale, two conformers can be detected and this situation persists particularly when the palladium atom is present in sterically more hindered environment [12,17]. When the palladium is present in sterically less hindered environment as has been observed in the six-membered [*C*,*N*] cyclopalladated 2-neopentylpyridine of the type [(*C*,*N*)PdCl(3,5-$Me_2C_6H_3N$)] [18], the six-membered "[*C*,*N*]Pd" ring inversion occurs faster than the NMR time scale. Though palladacycles **4** and **6** possess sterically hindered 2,6-lutidine, the six-membered [*C*,*N*] ring inversion appears to occur faster than the NMR timescale due to the presence of sterically less hindered 4-tolyl substituent in the =NAr unit of the guanidine moiety.

Table 1
Selected bond distances (Å) and bond angles (°) for **1**.

Pd(1)–C(21)	1.955(5)	Pd(1)···Pd(2)	3.0054(5)
Pd(1)–O(3)	2.090(3)	C(21)–Pd(1)–N(1)	89.3(2)
Pd(1)–N(1)	2.003(4)	N(1)–Pd(1)–O(3)	178.2(1)
Pd(1)–O(1)	2.167(3)	C(21)–Pd(1)–O(3)	91.9(2)
Pd(2)–C(43)	1.947(5)	C(21)–Pd(1)–O(1)	172.8(2)
Pd(2)–N(4)	2.017(4)	N(1)–Pd(1)–O(1)	95.2(1)
Pd(2)–O(2)	2.110(4)	C(21)–Pd(1)–N(1)	89.3(2)
Pd(2)–O(4)	2.170(4)	C(43)–Pd(2)–N(4)	90.2(2)
N(1)–C(12)	1.311(6)	C(43)–Pd(2)–O(2)	92.7(2)
N(2)–C(12)	1.358(6)	N(4)–Pd(2)–O(2)	176.3(2)
N(3)–C(12)	1.361(6)	C(43)–Pd(2)–O(4)	175.4(2)
N(3)–C(20)	1.404(6)	N(4)–Pd(2)–O(4)	94.0(2)
N(4)–C(34)	1.308(6)	C(12)–N(2)–C(13)	123.5(4)
N(5)–C(34)	1.379(7)	C(12)–N(3)–C(20)	126.1(4)
N(6)–C(34)	1.344(6)	C(34)–N(5)–C(35)	123.0(4)
N(6)–C(42)	1.408(6)	C(34)–N(6)–C(42)	127.2(4)

In conclusion, four classes of six-membered [*C*,*N*] cyclopalladated $LH_2^{4\text{-tolyl}}$ were isolated in good yield and characterised by elemental analysis, IR and NMR spectroscopy and the molecular structures of six of them were determined by single-crystal X-ray diffraction. The subtle differences observed in the structures of six-membered [*C*,*N*] cyclopalladated $LH_2^{4\text{-tolyl}}$ with those of $LH_2^{2\text{-tolyl}}$ were highlighted. The new palladacycles revealed the presence of a single isomer in solution and this is attributed to the rapid inversion of the six-membered "[*C*,*N*]Pd" ring due to the presence of a less bulky and more symmetrical 4-tolyl substituent in the = NAr unit of the guanidine moiety.

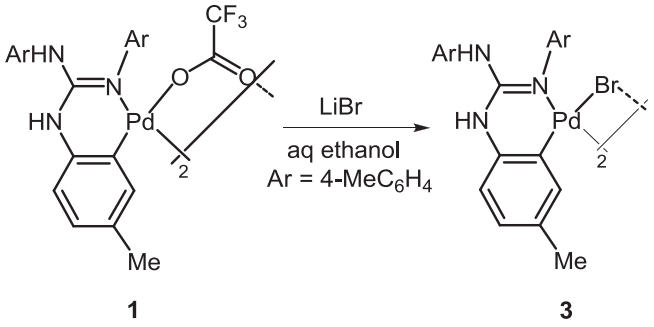
3. Experimental section

3.1. General considerations

$LH_2^{4\text{-tolyl}}$ was prepared according to the literature procedure [14]. Other chemicals were procured from commercial sources and used as received. The instrumental details pertinent to IR, NMR spectroscopy, mass spectrometry, and elemental analysis are as reported in our previous publication [19]. For few samples, $^{31}P\{^{1}H\}$

Table 2
Selected bond distances (Å) and bond angles (°) for **2**.

Pd(1)–O(1)	2.137(2)	O(1)–Pd(1)–N(1)	93.1(1)
Pd(1)–O(2)	2.045(2)	O(1)–Pd(1)–C(10)	175.0(1)
Pd(1)–N(1)	2.014(2)	O(2)–Pd(1)–N(1)	176.6(1)
Pd(1)–C(10)	1.959(3)	O(2)–Pd(1)–C(10)	91.1(1)
N(1)–C(1)	1.296(4)	Pd(1)–C(10)–C(9)	122.4(2)
N(2)–C(1)	1.357(4)	N(2)–C(9)–C(10)	122.7(3)
N(3)–C(1)	1.365(4)	C(1)–N(2)–C(9)	127.1(3)
N(2)–C(9)	1.403(4)	N(1)–C(1)–N(2)	121.9(3)
Pd(1)···Pd(1)	2.9214(9)	N(2)–C(1)–N(3)	114.8(3)
		N(1)–C(1)–N(3)	121.9(3)
O(1)–Pd(1)–O(2)	85.5(1)		



1 3

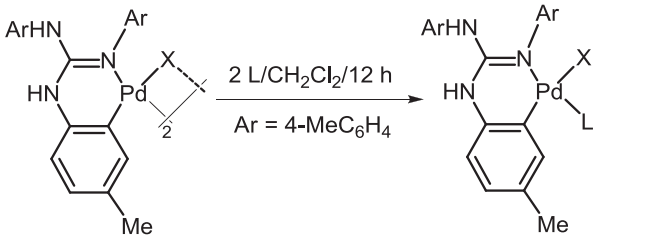
Scheme 2.

and ^{19}F NMR spectra were recorded on a Bruker AMX 400 MHz NMR spectrometer operating at field strengths of 85.8, and 282.4 MHz, respectively. The $\delta(^{31}P)$ and $\delta(^{19}F)$ values are reported relative to 85% H_3PO_4 (external standard) and $CFCl_3$, respectively and are proton decoupled.

3.2. Synthesis and characterization

3.2.1. Palladacycle *1*

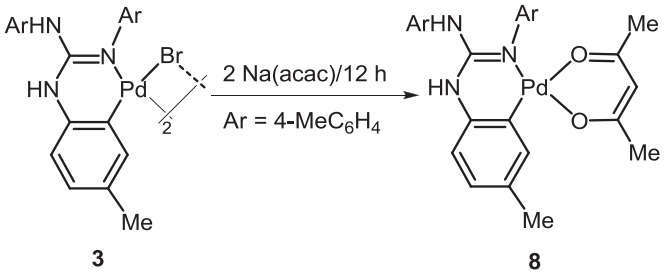
A 50 mL Schlenk flask was charged with $LH_2^{4\text{-tolyl}}$ (248 mg, 0.753 mmol) and $Pd(OC(O)CF_3)_2$ (250 mg, 0.752 mmol) in toluene (20 mL). The contents in the flask were stirred and heated simultaneously at 70 °C for 6 h under the atmosphere of nitrogen. Subsequently, the reaction mixture was cooled and filtered through a Whatman filter paper. The filtrate was diluted with chloroform (10 mL) and set aside at ambient temperature for several hours to afford **1** as greenish yellow crystals in 84% yield (376 mg, 0.633 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3414 (w); ν_a(OCO) 1685 (vs); ν(C=N) 1633 (s); ν_s(OCO) 1512 (m); $\nu(CF_3)$ 1206 (vs); 1147 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.22, 2.37, 2.42 (each s, 3 × 3 H, CH_3), 5.66 (s, 1 H, N*H*), 6.29 (d, J_{HH} = 7.5 Hz, 1 H, Ar*H*), 6.38 (br, 2 H, Ar*H*), 6.72 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 6.90 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*), 6.95 (s, 1 H, Ar*H* or N*H*), 7.11 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.29 (s, 2 H, Ar*H* or N*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.78, 20.90, 20.94 (CH_3), 112.80 (Ar*C*/ArCH), 115.16 (q, $^1J_{CF}$ = 287.9 Hz, CF_3), 118.28, 124.62, 125.54, 126.16, 129.83, 130.69, 131.22, 132.84, 133.56, 135.55, 136.02, 136.92, 141.30, 144.40 (Ar*C*/ArCH, and *C*=N), 163.54 (q, $^2J_{CF}$ = 37.5 Hz, OC(O)). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ − 75.0. Anal. Calcd for $C_{48}H_{44}N_6O_4F_6Pd_2 \cdot C_7H_8$ (Mw: 1095.75 + 92.14): C, 55.61; H, 4.41; N, 7.07%. Found: C, 55.64; H, 4.41; N, 7.04. Greenish yellow crystals of **1**·3S(O)Me_2 suitable for X-ray diffraction were grown from $Me_2S(O)$ at ambient temperature over a period of several days.



	X
1	$OC(O)CF_3$
3	Br

	X	L
4	$OC(O)CF_3$	2,6-$Me_2C_5H_3N$
5	$OC(O)CF_3$	PTA
6	Br	2,6-$Me_2C_5H_3N$
7	Br	PTA

Scheme 3.



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Scheme 4.

3.2.2. Palladacycle *2*

Palladacycle **2** was prepared from $LH_2^{4\text{-tolyl}}$ (107 mg, 0.325 mmol) and $Pd(OC(O)^tBu)_2$ (100 mg, 0.324 mmol) in toluene (20 mL) and purified by a procedure analogous to that described previously for

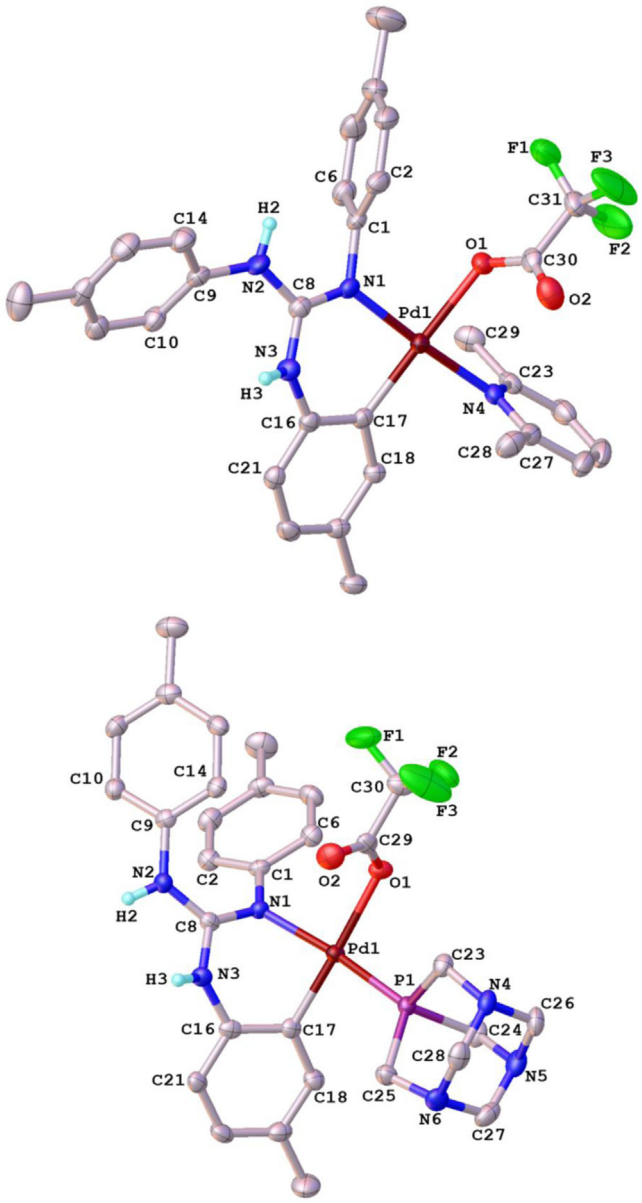

Fig. 2. Molecular structures of **4** (top) and **5** (bottom) at the 50% probability level. Only hydrogen atoms of the amino moieties are shown for clarity.

Table 3
Selected bond distances (Å) and bond angles (°) for **4** and **5**.

	4	5
Pd(1)–C(17)	1.982(5)	1.978(3)
Pd(1)–N(1)	2.016(4)	2.100(2)
Pd(1)–N(4)/Pd(1)–P(1)	2.060(4)	2.2397(8)
Pd(1)–O(1)	2.139(3)	2.181(2)
N(1)–C(8)	1.311(6)	1.317(4)
N(2)–C(8)	1.371(6)	1.361(4)
N(3)–C(8)	1.348(6)	1.367(4)
N(3)–C(16)	1.413(6)	1.417(4)
C(17)–Pd(1)–N(1)	90.4(2)	84.9(1)
C(17)–Pd(1)–N(4)/C(17)–Pd(1)–P(1)	93.53(9)	91.04(9)
N(1)–Pd(1)–N(4)/N(1)–Pd(1)–P(1)	91.04(9)	171.23(6)
C(17)–Pd(1)–O(1)	171.23(6)	177.3(1)
N(1)–Pd(1)–O(1)	90.22(6)	93.53(9)
N(4)–Pd(1)–O(1)/P(1)–Pd(1)–O(1)	126.2(2)	90.22(6)
C(8)–N(2)–C(9)	122.0(2)	126.2(2)
C(8)–N(3)–C(16)	125.7(3)	122.0(2)
N(1)–C(8)–N(2)	113.9(2)	125.7(3)
N(1)–C(8)–N(3)	120.4(3)	120.4(3)
N(2)–C(8)–N(3)	117.4(4)	113.9(2)

1. Yield: 92% (160 mg, 0.149 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3387 (m); ν_a(OCO) 1628 (s); ν(C=N) 1604 (vs); ν_s(OCO) 1458 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.78 (s, 9 H, C(CH_3)$_3$), 2.18, 2.37, 2.38 (each s, 3 × 3 H, CH_3), 5.66 (s, 1 H, Ar*H*), 6.12 (br, 1 H, N*H*), 6.35 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 6.38 (s, 1 H, Ar*H*), 6.71 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 6.78 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 6.90 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 7.05 (d, J_{HH} = 8.2 Hz, 2 H, Ar*H*), 7.40 (s, 1 H, N*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.9, 21.1 (*C*H_3), 28.0 (C(*C*H_3)$_3$), 39.6 (*C*(CH$_3$)$_3$), 112.1, 122.4, 124.3, 124.7, 126.6, 129.5, 130.6, 130.7, 133.9, 134.1, 134.7, 136.4, 137.1, 142.5, 144.6 (Ar*C*/Ar*C*H, and *C*=N), 185.2 (O*C*(O)). Anal. Calcd for $C_{54}H_{62}N_6O_4Pd_2$ (Mw: 1071.96): C, 60.51; H, 5.83; N, 7.84%. Found: C, 60.55; H, 5.69; N, 7.83.

3.2.3. Palladacycle **3**

Palladacycle **3** was prepared from **1** (500 mg, 0.420 mmol) and excess of LiBr (198 mg, 2.280 mmol) in ethanol: water (27/3, v/v) mixture following the procedure previously published for the related palladacycle [11]. Yield: 94% (405 mg, 0.393 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3404 (br); ν(C=N) 1625 (vs). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.22, 2.30, 2.34 (each s, 3 × 3 H, CH_3), 6.15 (s, 1 H, N*H*), 6.18 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.34 (s, 1 H, Ar*H*), 6.69 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.90 (d, J_{HH} = 8.0 Hz, 2 H, Ar*H*), 7.13 (br s, 2 H, Ar*H*), 7.17 (d, J_{HH} = 8.3 Hz, 2 H, Ar*H*), 7.27 (br, 3 H, Ar*H* and N*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.9, 21.1, 21.2 (*C*H_3), 113.6, 113.7 124.4, 125.4, 125.6, 127.1, 127.5, 129.7, 130.1, 130.8, 132.0, 133.5, 133.9, 135.4, 135.7, 137.3, 140.1, 143.4, 147.2 (Ar*C*/Ar*C*H, and *C*=N). MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 516 (97) [(*C*,*N*)PdBr + H]$^+$; 475 (77), [(*C*,*N*)Pd + K]$^+$; 329 (100), [$LH_2^{4\text{-tolyl}}$]$^+$. Anal. Calcd for $C_{44}H_{44}N_6Br_2Pd_2$ (Mw: 1029.52): C, 51.33; H, 4.31; N, 8.16%. Found: C, 51.32; H, 4.34; N, 8.12. Greenish yellow crystals of **3**·2$CHCl_3$ suitable for X-ray diffraction were grown from chloroform/toluene mixture at ambient temperature over a period of several days.

3.2.4. Palladacycle **4**

A 25 mL round bottom flask was charged with **1** (100 mg, 0.091 mmol) and CH_2Cl_2 (7 mL) solution of 2,6-lutidine (21 mg, 0.20 mmol). The suspension was stirred for 12 h at room temperature to afford a clear pale yellow solution. The solution was concentrated under vacuum to about 2 mL and layered with methanol to afford **4**·0.5H_2O as pale yellow crystals in 96% (0.115 g, 0.175 mmol) yield. FT–IR (KBr, cm^{-1}): ν(NH) 3399 (w); 3277 (br); ν_a(OCO) 1681 (vs); ν(C=N) 1628 (s); ν_s(OCO) 1470 (m); ν(CF_3) 1198 (vs); 1132 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.98, 2.33, 2.38 (each s, 3 × 3 H, CH_3), 3.23 (s, 6 H, NC_5H_3(*C*H_3)$_2$-2,6), 5.86 (s, 1 H, Ar*H* or N*H*), 6.10 (s, 1 H, Ar*H* or N*H*), 6.28 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.54 (s, 1 H, Ar*H* or N*H*), 6.73 (d, J_{HH} = 7.5 Hz, 1 H, Ar*H*), 6.99 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*), 7.09 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.18 (br, 4 H, Ar*H*), 7.23 (d, J_{HH} = 8.4 Hz, 2 H, Ar*H*), 7.57 (t, J_{HH} = 7.6 Hz, 1 H, NC_5H_3(CH$_3$)$_2$–2,6). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.9, 21.0 (*C*H_3), 27.7 (NC_5H_3(*C*H_3)$_2$-2,6), 114.1 (Ar*C*/Ar*C*H), 116.4 (q, $^1J_{CF}$ = 293.2 Hz, *C*F_3), 120.4, 122.5, 125.4, 125.6, 126.5, 130.1, 130.8, 131.5, 133.7, 134.4, 135.8, 136.2, 137.3, 138.0, 141.9, 146.4, 160.1 (Ar*C*/Ar*C*H, and *C*=N), 160.5 (q, $^3J_{CF}$ = 34.5 Hz, O*C*(O)). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ − 75.1. Anal. Calcd for $C_{31}H_{31}N_4O_2F_3Pd$ (Mw: 655.03): C, 56.84; H, 4.77; N, 8.55%. Found: C, 56.75; H, 4.83; N, 8.39. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/MeOH mixture over a period of several days at ambient condition.

3.2.5. Palladacycle **5**

Palladacycle **5** was prepared from **1** (100 mg, 0.091 mmol) and PTA (30.0 mg, 0.191 mmol) in CH_2Cl_2 (7 mL) and purified by a procedure analogous to that described previously for **4**. Yield of **5**·0.5CH_2Cl_2: 94% (121 mg, 0.858 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3362 (br m); 3322 (br m); ν_a(OCO) 1673 (vs); ν(C=N) 1623 (s); ν_s(OCO) 1459 (m); ν(CF_3) 1200 (s); 1144 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43, 2.47, 2.51 (each s, 3 × 3 H, CH_3), 4.28 (s, 3 × 2 H, CH_2, PTA), 4.57 (s, 3 × 2 H, CH_2, PTA), 6.45 (d, J_{HH} = 8.4 Hz, 1 H, Ar*H*), 6.49 (s, 2 H, Ar*H* and N*H*), 6.93 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.09 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*), 7.15 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.26 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.35 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.40 (s, 1 H, N*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.8, 20.9 (*C*H_3), 51.0 (d, $^1J_{CP}$ = 14.4 Hz, PCH_2N), 73.1 (d, $^3J_{CP}$ = 6.7 Hz, NCH_2N), 115.9 (Ar*C*/Ar*C*), 116.3 (q, $^1J_{CF}$ = 291.9 Hz, *C*F_3), 125.3, 125.6, 125.9, 130.0, 130.7, 132.3 (d, $^3J_{PC}$ = 7.7 Hz), 133.6, 135.4, 136.0, 137.2, 139.8 (d, $^2J_{PC}$ = 23.2 Hz), 141.1, 148.3 (Ar*C*/Ar*C*H, and *C*=N), 161.2 (q, $^3J_{CF}$ = 35.1 Hz, O*C*(O)). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −74.4. ^{31}P NMR ($CDCl_3$, 161.8 MHz): δ − 51.3. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 706 (18), [M + H]$^+$; 482 (100), [$LH_3^{4\text{-tolyl}}$ + OC(O)CF_3 + K]$^+$. Anal. Calcd for $C_{30}H_{34}N_6O_2PF_3Pd$ (Mw: 705.03): C, 51.11; H, 4.86; N, 11.92%. Found: C, 51.05; H, 4.66; N, 11.70. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/MeOH mixture over a period of several days at ambient condition.

3.2.6. Palladacycle **6**

Palladacycle **6** was prepared from **3** (100 mg, 0.097 mmol) and 2,6-lutidine (23.0 mg, 0.215 mmol) in CH_2Cl_2 (7 mL) and purified by a procedure analogous to that described previously for **4**. Yield: 97% (117 mg, 0.188 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3401 (w); 3272 (br m); ν(C=N) 1622 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.97, 2.32, 2.36 (each s, 3 × 3 H, CH_3), 3.14 (s, 6 H, NC_5H_3(*C*H_3)$_2$-2,6), 5.76 (s, 1 H, Ar*H* or N*H*), 6.29 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.38, 6.44 (each s, 2 × 1 H, Ar*H* or N*H*), 6.71 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.94 (d, J_{HH} = 7.5 Hz, 2 H, Ar*H*), 7.08 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.20 (d, J_{HH} = 7.8 Hz, 4 H, Ar*H*), 7.29 (d, J_{HH} = 7.8 Hz, 2 H, C_5H_3N(CH$_3$)$_2$–2,6), 7.52 (t, J_{HH} = 7.6 Hz, 1 H, C_5H_3N(CH$_3$)$_2$–2,6). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.9, 21.0, 21.2 (*C*H_3), 28.3 (NC_5H_3(*C*H_3)$_2$-2,6), 113.6, 122.6, 125.2, 125.5, 125.6, 127.3, 129.7, 130.7, 131.7, 134.0, 135.0, 135.4, 137.1, 137.6, 143.9, 147.4, 159.6 (Ar*C*/Ar*C*H, and *C*=N). MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 623 (53), [M + H]$^+$; 622 (39), [M]$^+$; 554 (26), [M − L + K]$^+$; 352 (100), [$LH_2^{4\text{-tolyl}}$ + Na]$^+$. Anal. Calcd for $C_{29}H_{31}N_4BrPd$ (Mw: 621.91): C, 56.00; H, 5.02; N, 9.01%. Found: C, 55.89; H, 4.70; N, 8.99. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/MeOH mixture over a period of several days at ambient condition.

3.2.7. Palladacycle **7**

Palladacycle **7** was prepared from **3** (100 mg, 0.097 mmol) and PTA (0.032 g, 0.204 mmol) in CH_2Cl_2 (7 mL) and purified by a procedure analogous to that described previously for **4**. Yield: 86% (126 mg, 0.083 mmol). FT–IR (KBr, cm^{-1}): ν(NH) 3390 (m); 3232 (br

Table 4
Crystallographic data for **1**·3S(O)Me_2, **2**, **4**·0.5H_2O, and **5**·CH_2Cl_2.

	1·3S(O)Me_2	**2**	**4**·0.5H_2O	**5**·CH_2Cl_2
Formula	$C_{54}H_{62}F_6N_6O_7Pd_2S_3$	$C_{54}H_{62}N_6O_4Pd_2$	$C_{124}H_{124}F_{12}N_{16}O_9Pd_4$	$C_{61}H_{68}ClF_6N_{12}O_4P_2Pd_2$
fw	1330.08	1071.90	2635.99	1457.46
Temp (K)	100(2)	298(2)	100(2)	100(2)
Wavelength (λ)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$
a (Å)	20.4129(14)	19.011(5)	36.595(4)	26.002(3)
b (Å)	12.9294(8)	15.548(5)	12.6104(13)	10.3808(12)
c (Å)	23.3913(16)	17.710(5)	27.708(3)	24.601(3)
α (°)	90	90	90	90
β (°)	110.388(2)	97.418(5)	113.386(5)	112.176(5)
γ (°)	90	90	90	90
Volume (Å^3)	5786.8(7)	5191(3)	11,736(2)	6149.1(12)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.527	1.372	1.492	1.574
F(000)	2712	2208	5376	2972
μ(Mo Kα) (mm^{-1})	0.804	0.742	0.687	0.757
θ range (°)	1.06–26.37	2.96–26.37	1.21–26.37	1.69–26.37
No. of reflns collected	92,379	22,446	60,985	47,447
No. of reflns used	11,843	5312	11,991	6306
Parameters	710	317	745	398
R_1 [$I > 2\sigma(I)$][a]	0.0555	0.0373	0.0557	0.0425
wR_2 (all reflns)[b]	0.1484	0.0936	0.1486	0.1125
GooF[c]	1.166	1.148	1.112	1.167
Largest diff peak/hole (e·Å^{-3})	1.872/−1.348	0.688/−0.585	3.811/−1.062	1.646/−1.073

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

m); ν(C═N) 1600 (vs). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30, 2.34, 2.36 (each s, 3 × 3 H, C*H*$_3$), 4.30 (s, 3 × 2 H, C*H*$_2$, PTA), 4.44 (s, 3 × 2 H, C*H*$_2$, PTA), 6.31 (s, 2 H, N*H*), 6.40 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.80 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 6.92 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*), 7.04–7.08 (m, 3 H, Ar*H*), 7.15 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*), 7.24 (d, J_{HH} = 8.1 Hz, 2 H, Ar*H*). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ − 49.7. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 673 (15), [M + H]$^+$; 457 (100), [(*C*,*N*)Pd + Na]$^+$. Anal. Calcd for $C_{28}H_{34}N_6PBrPd\cdot CH_2Cl_2$ (Mw: 671.9 + 84.94): C, 46.02; H, 4.79; N, 11.10%. Found: C, 46.15; H, 4.76; N, 11.29.

3.2.8. Palladacycle **8**

A 25 mL round bottom flask was charged with **3** (100 mg, 0.097 mmol) and subsequently dissolved in CH_2Cl_2 (7 mL). Na(acac) (25.0 mg, 0.205 mmol) was added in portion to the above-mentioned solution and the resulting suspension was stirred. The suspension slowly turned into a clear colourless solution after 15 min and subsequently NaBr precipitated out. The solution was filtrated and the filtrate was concentrated under vacuum to about 2 mL, layered with *n*-hexane and stored at ambient temperature over a period of several hours to afford **8** in 97% (0.101 g, 0.094 mmol) yield. FT−IR (KBr, cm^{-1}): ν(NH) 3403 (w); 3340 (w); ν(C═N) 1630 (m); ν(C−O) 1588 (vs). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.56, 1.98 (each s, 2 × 3 H, acacC*H*$_3$), 2.31, 2.33, 2.36 (each s, 3 × 3 H, C*H*$_3$), 5.17 (s, 1 H, acacC*H*), 5.91 (s, 1 H, N*H*), 6.25 (d, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.50 (s, 1 H, N*H*), 6.77 (dd, J_{HH} = 7.8; 3.1 Hz, 1 H, Ar*H*), 6.96 (d, J_{HH} = 8.2 Hz, 2 H, Ar*H*), 7.16 (br, 4 H, Ar*H*), 7.19 (d, J_{HH} = 7.8 Hz, 2 H, Ar*H*), 7.48 (br, 1 H, Ar*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 21.0, 21.1, 21.2 (*C*H$_3$), 27.2, 27.6 (acac*C*H$_3$), 99.6 (acac*C*H), 113.2, 123.5, 125.4, 125.5, 127.7, 129.5, 130.8, 131.2, 134.0, 134.2, 134.7, 135.4, 137.1, 141.6, 146.4 (Ar*C*/Ar*C*H, and *C*═N), 185.7, 187.6 (acac-*C*═O). Anal. Calcd for $C_{27}H_{29}N_3O_2Pd$ (Mw: 533.97): C, 60.73; H, 5.47; N, 7.87%. Found: C, 60.70; H, 5.67; N, 7.82.

3.2.9. X-ray crystallography

Intensity data of suitably sized crystals of **1**·3S(O)Me_2, **4**·0.5H_2O, **5**·CH_2Cl_2, and **6** were collected on a Bruker AXS SMART-APEX diffractometer with a CCD area detector, graphite monochromator. The frames were collected by ω, φ, and 2θ rotation at 10 s per frame with SMART [20]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS [21]. Intensity data of suitably sized crystals of **2**, and **3**·2$CHCl_3$ were collected on an Oxford Xcalibur S diffractometer (4-circle κ goniometer, Sapphire-3 CCD detector, ω scans, graphite monochromator, and a single wavelength enhanced X-ray source with MoK α radiation) [22]. Pre-experiment, data collection, data reduction, and absorption corrections were performed with the CrysAlisPro software suite [23]. The structures were solved by direct methods using SIR 92 [24], which revealed the atomic positions, and refined using the SHELX-97 program package [25] and SHELXL97 (within the WinGX program package) [26]. Non-hydrogen atoms were refined anisotropically. C−H/N−H hydrogen atoms were placed in geometrically calculated positions by using a riding model. The molecular structures were created with Olex2 program [27]. Details of data collections, structure solutions and refinements are presented in Table 4.

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Appendix A. Supplementary material

CCDC 921726–921731 (**1**–**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix B. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.05.030. These data include MOL files and InChiKeys of the most important compounds described in this article.

References

[1] R.M. Ceder, J. Granell, J. Sales, J. Organomet. Chem. 307 (1986) C44.
[2] J. Albert, R.M. Ceder, M. Gómez, J. Granell, J. Sales, Organometallics 11 (1992) 1536.
[3] M. Gómez, J. Granell, M. Martinez, J. Chem. Soc., Dalton Trans. (1998) 37.
[4] J. Albert, J. Granell, Trends Organomet. Chem. 3 (1999) 99.
[5] J. Albert, J.M. Cadena, A. González, J. Granell, X. Solans, M. Font-Bardia, Chem. Commun. (2003) 528.
[6] D. Vázquez-García, A. Fernández, M. Lopez-Torres, A. Rodríguez, N. Gómez-Blanco, C. Viader, J.M. Vila, J.J. Fernandez, Organometallics 29 (2010) 3303.
[7] C.-L. Chen, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Organometallics 24 (2005) 1075.
[8] J.M. Chitanda, D.E. Prokopchuk, J.W. Quail, S.R. Foley, Dalton Trans. (2008) 6023.
[9] S. Lentijo, J.A. Miguel, P. Espinet, Dalton Trans. 40 (2011) 7602.
[10] S. Lentijo, J.A. Miguel, P. Espinet, Organometallics 30 (2011) 1059.
[11] K. Gopi, N. Thirupathi, M. Nethaji, Organometallics 30 (2011) 572.
[12] K. Gopi, P. Saxena, N. Thirupathi, M. Nethaji, Polyhedron 52 (2013) 1041.
[13] J.M. Chitanda, S.-C. Wu, J.W. Quail, S.R. Foley, Inorg. Chim. Acta 379 (2011) 122.
[14] K. Gopi, B. Rathi, N. Thirupathi, J. Chem. Sci. 122 (2010) 157.
[15] K. Hiraki, Y. Fuchita, K. Takechi, Inorg. Chem. 20 (1981) 4316.
[16] R.G. Pearson, Inorg. Chem. 12 (1973) 712.
[17] Y. Fuchita, K. Yoshinaga, H. Kusaba, M. Mori, K. Hiraki, K. Takehara, Inorg. Chim. Acta 239 (1995) 125.
[18] Y. Fuchita, K. Hiraki, T. Uchiyama, J. Chem. Soc., Dalton Trans. (1983) 897.
[19] P. Elumalai, N. Thirupathi, M. Nethaji, Inorg. Chem. 52 (2013) 1883.
[20] SMART, Bruker Molecular Analysis Research Tool, Bruker Analytical X-ray Systems, Madison, WI, 2000. version 5.0.
[21] SAINT-NT, Bruker Analytical X-ray Systems, Madison, WI, 2001. version 6.04.
[22] ENHANCE, Oxford Xcalibur Single Crystal Diffractometer, Oxford Diffraction Ltd., Oxford, UK, 2006. version 1.171.34.40.
[23] CrysAlisPro, Oxford Diffraction Ltd., Oxford, UK, 2006. version 1.171.34.40.
[24] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[25] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[26] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[27] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Cryst. 42 (2009) 339.