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Synthesis of dinuclear palladium complexes having two parallel isocyanide ligands, and their application as catalysts to pyrrole formation from *tert*-butylisocyanide and alkynes

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ABSTRACT

Novel dinuclear palladium complexes having two isocyanide ligands were synthesized by using a binucleating ligand, *N*,*N*′-bis[2-(diphenylphsphino)phenyl]formamidinate (dpfam). The structure of [Pd_2(μ-dpfam)(*tert*-BuNC)$_2$]Cl was confirmed by X-ray analysis, showing that the Pd–Pd bond length of 2.5824(3) Å falls well within the range of those for known dipalladium complexes having the edge-sharing structure and two isocyanides coordinate to palladium in almost parallel and in close proximity. The dinuclear complex [Pd_2(μ-dpfam)(*tert*-BuNC)$_2$]PF_6 served as catalyst for pyrrole formation from *tert*-butylisocyanide and various alkynes.

1. Introduction

Catalysis using dinuclear transition metal complexes has recently received considerable attention [1]. Cooperation of two metal centers can improve the selectivity and efficiency of catalyzation, and can promote reactions that are not possible using a single metal center. Bis(diphenylphosphino)methane (dppm), or its analogues, is one of the most useful binucleating ligands [2], particularly for palladium and platinum complexes [3]. Although those complexes are known to adopt several geometries [2a], as illustrated in Chart 1A, their application as catalysts has been rarely reported. In our previous papers [4,5], we focused on the importance of cis orientation of two reactant ligands (Y in Chart 1B) for catalysis [4,6,7], and reported synthesis of the corresponding A-frame complexes having a new binucleating ligand, *N*,*N*′-bis[2-(diphenylphsphino)phenyl]formamidinate (dpfam) [4] and their application to catalysis [5]. We report here synthesis of dinuclear palladium complexes having the edge-sharing structure, which have two parallel isocyanide ligands, and their application as catalysts to pyrrole formation.

2. Results and discussion

2.1. Synthesis of dinuclear palladium complexes

The reaction of dpfamH with $PdCl_2$(tmeda), $Pd_2(dba)_3 \cdot CHCl_3$, and excess *tert*-butylisocyanide in dichloromethane at room temperature resulted in the formation of the dinuclear palladium complex [Pd_2(*t*-BuNC)$_2$(μ-dpfam)]Cl (**1a**) (Scheme 1). Treatment of **1a** with excess NH_4PF_6 gave [Pd_2(*t*-BuNC)$_2$(μ-dpfam)]PF_6 (**1b**) in 81% yield. Crystallization of **1** by slow diffusion of diethyl ether into a solution of 1,2-dichloroethane afforded a red crystal suitable for X-ray analysis. The molecular structure of **1a** is shown in Fig. 1. The Pd–Pd bond length of 2.5824(3) Å is shorter than those of the corresponding A-frame complexes [4] and falls well within the range of those for known dipalladium complexes having the edge-sharing structure [2a]. Although the two palladium planes are slightly twisted (N(1)–Pd(1)–Pd(2)–N(2) 21.19(12)°, C(38)–Pd(1)–Pd(2)–C(43) 30.26(19)°), two isocyanides coordinate to palladium in almost parallel and in close proximity. A number of Pd–Pd bonded complexes having isocyanide ligands have been reported [8–11]. In most of unbridged complexes, the dihedral angles between two coordination planes are much larger than that of **1a**, and isocyanide ligands are distant each other [8]. In dipalladium complexes bridged by binucleating ligands such as dppm, the dihedral angles are smaller, however, two isocyanides coordinate to palladium centers in trans orientation (Chart 1A) [9]. There are only a few reports on dipalladium complexes having parallel isocyanide ligands [10].

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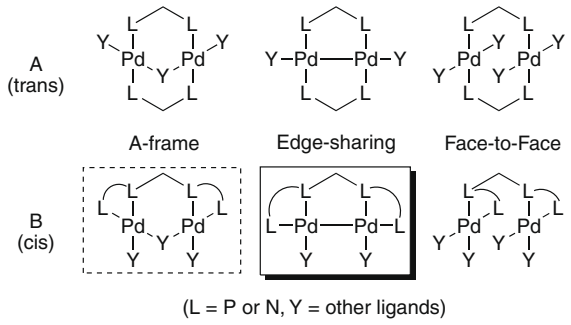
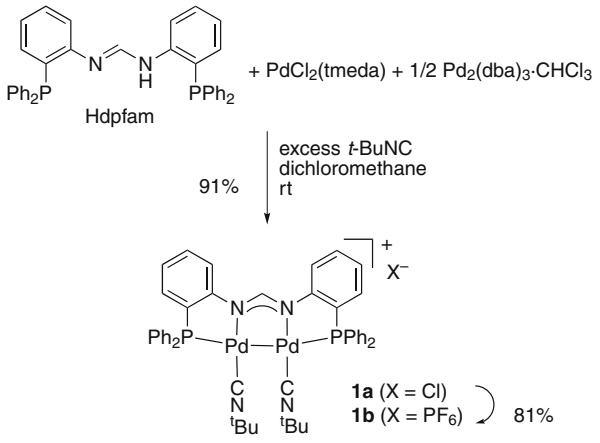


Chart 1.



Scheme 1.

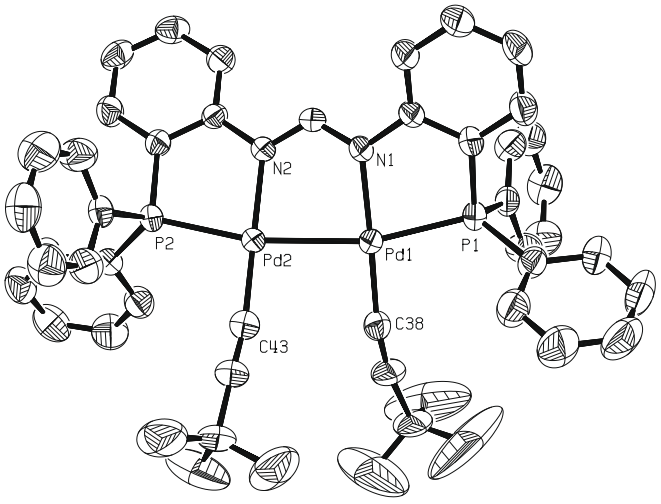


Fig. 1. Molecular structure of the cation of **1a**, showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd(1)–Pd(2) 2.5824(3), Pd(1)–P(1) 2.3417(10), Pd(2)–P(2) 2.3140(10), Pd(1)–N(1) 2.061(2), Pd(2)–N(2) 2.064(2), Pd(2)–Pd(1)–P(1) 165.64(2), Pd(1)–Pd(2)–P(2) 167.86(2), C(38)–Pd(1)–Pd(2)–C(43) 30.26(19), N(1)–Pd(1)–Pd(2)–N(2) 21.19(12).

2.2. Catalytic pyrrole formation

Since the dinuclear palladium complexes having two parallel isocyanide ligands were expected to be effective as catalysts in the reactions oligomerizing more than two isocyanides, we next investigated the application of the complexes **1** to a pyrrole forming reaction, in which 2-amino-5-cyanopyrroles are formed from three molecules of *tert*-butylisocyanide and one molecule of alkynes (Eq. (1)). Although the nickel-catalyzed version of this pyrrole forming reaction was reported by Jautelat and Ley in 1970 [12,13], the yield was moderate and no further studies have been done. Expectedly, the reaction of *tert*-butylisocyanide with phenylacetylene using **1b** as catalyst in 1,2-dichloroethane (DCE) at 80 °C afforded pyrroles **3a** and **3b** in high yield, while complex **1a** did not serve as catalyst (Eq. (1), Table 1, entries 1 and 2). When the reaction was conducted at higher and lower temperature or in other solvents such as THF, toluene, and acetonitrile, pyrroles **3** were obtained in lower yields (entries 3–8). Although ordinary mononuclear palladium complexes such as $Pd(PPh_3)_4$ and $Pd(OAc)_2$ could be used as a catalyst, the yield of **3** was moderate (entries 10–13). In the reaction using $Pd(OAc)_2$, a significant amount of 5-imino-3-pyrrolin-2-one **4** was formed (entry 13). The use of proportionate amounts of reactants decreased the yield of **3** (entries 9 and 12). Higher concentration of *tert*-butylisocyanide probably prevents coordination of phenylacetylene to palladium. When a solution of *tert*-butylisocyanide in DCE was added dropwise over 5 h using a syringe pump, pyrroles **3** were obtained in a satisfactory yield (Eq. (2)).

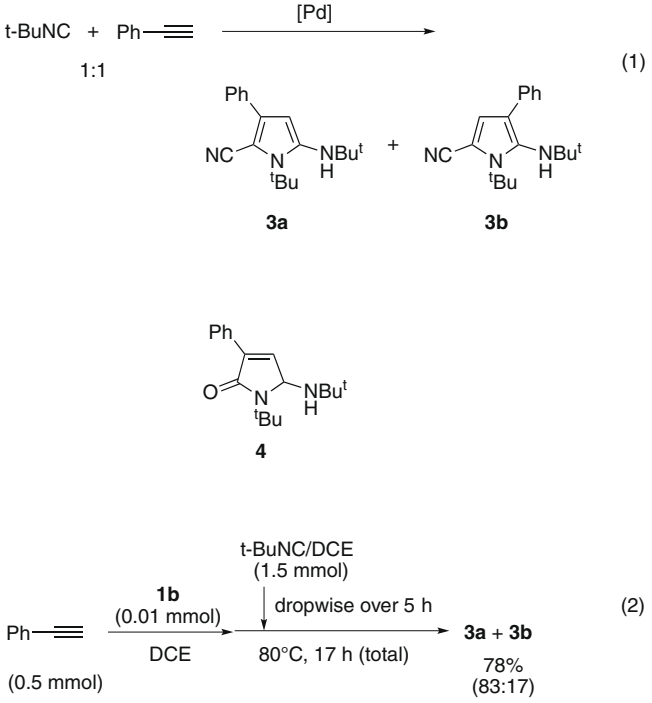


Table 1
Palladium-catalyzed pyrrole forming reaction from phenylacetylene and *tert*-butylisocyanide.[a]

Entry	Catalyst	Solvent	Temperature (°C)	Yield[b] (%)	Ratio[c] (**3a**:**3b**)
1	**1a**	DCE	80	0	–
2	**1b**	DCE	80	92	78:28
3	**1b**	THF	80	68	53:47
4	**1b**	Toluene	80	48	58:42
5	**1b**	Acetonitrile	80	32	75:25
6	**1b**	DMF	80	0	–
7	**1b**	DCE	60	53	77:23
8	**1b**	DCE	100	76	80:20
9[d]	**1b**	DCE	80	13	69:31
10	$[Pd_2(PhCN)_2(PPh_3)_2](BF_4)_2$	DCE	80	0	–
11	$Pd(PPh_3)_4$	DCE	80	59	73:27
12[d]	$Pd(PPh_3)_4$	DCE	80	26	65:35
13	$Pd(OAc)_2$[e]	DCE	80	24	100:0

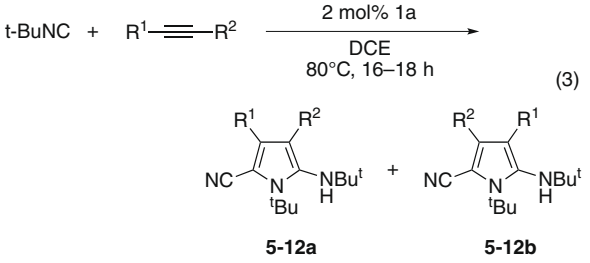
[a] A mixture of pheylacetylene (0.5 mmol), *tert*-butylisocyanide (0.5 mmol), catalyst (0.01 mmol, 2 mol%) in solvent (2 ml) were stirred for 16–18 h.
[b] GC yields based on *tert*-butylisocyanide.
[c] Determined by GC.
[d] 1.5 mmol of *tert*-butylisocyanide was used.
[e] 4 mol% of palladium acetate was used.

Table 2
Palladium-catalyzed pyrrole forming reaction from various alkynes and *tert*-butylisocyanide.[a]

Entry	R^1	R^2	Product	Yield[b] (%)	Ratio[c] (**a**:**b**)
1	*n*-Bu	H	**5**	90	79:21
2	*n*-Hex	H	**6**	74	72:28
3	CO_2Me	H	**7**	24	>95:<5
4	CH_2OMe	H	**8**	46	>95:<5
5	Ph	CO_2Me	**9**	73	49:51
6	Me	CO_2Me	**10**	42	>95:<5
7	Et	Et	**11**	24	–
8	*n*-Pr	*n*-Pr	**12**	13	–

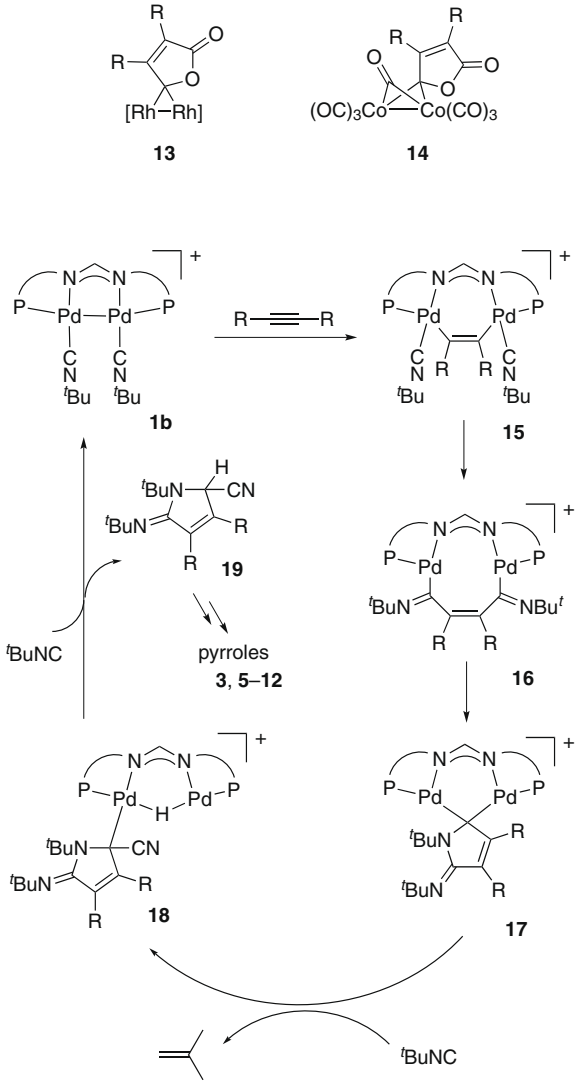
[a] A mixture of an alkyne (0.5 mmol), *tert*-butylisocyanide (0.5 mmol), **1b** (0.01 mmol, 2 mol%) in DCE (2 ml) were stirred at 80 °C for 16–18 h.
[b] Isolated yields based on *tert*-butylisocyanide.
[c] Determined by GC.

Table 2 summarizes the results of reaction of *tert*-butylisocyanide with various alkynes. The reactions with aliphatic terminal alkynes also gave corresponding pyrroles **5** and **6** with moderate regioselectivity (entries 1 and 2). In the reaction with methyl propiolate, one regioisomer **7a** was selectively obtained, although the yield was low (entry 3). Methoxy group at a propargylic position also controlled the regioselectivity, giving single isomer **8a** in better yield (entry 4). Internal alkynes also reacted with *tert*-butylisocyanide to afford highly substituted pyrroles. The reaction of methyl phenylpropiolate gave **9** in high yield and the reaction of methyl tetrolate proceeded regioselectively, affording **10a** (entries 5 and 6). Although unactivated internal alkynes were less reactive, pyrroles **11** and **12** were obtained by using **1b** as a catalyst. In contrast, the corresponding reactions using $Ni(OAc)_2$ or $Pd(PPh_3)_4$ as catalysts gave no products.



2.3. Mechanistic considerations

To gain insight into the mechanism of the pyrrole formation by **1b**, some stoichiometric reactions of **1b** with pheylacetylene or 3-hexyne in the presence or absence of *tert*-butylisocyanide were performed under several reaction conditions. Unfortunately, all reaction gave mixtures of unidentified several complexes. Although details of the reaction mechanism are unclear at the present time, some considerations have been made based on the mechanisms for the synthesis of 2(5*H*)-furanones from alkynes, carbon monoxide and water [14]. Joh et al. reported the furanone formation catalyzed by rhodium carbonyl clusters, for which they proposed the mechanism via multinuclear rhodium furanone complex **13** [14c]. Proposal of the intermediate **13** was based on the isolated dicobalt franone complex **14** formed from $Co_2(CO)_8$ and alkynes [15]. Although the authors conclusively proposed a different mechanism via a mononuclear anionic complex for the reaction in their next paper [14d], the present pyrrole formation could proceed via a dipalladium complex similar to **13** and **14** because two palladium atoms are held



Scheme 2.

in adjacent positions by dpfam. A plausible pathway via dipalladium intermediates is shown in Scheme 2. Initially, alkynes would insert to the Pd–Pd bond of **1b** [16], and then isocyanides would insert to the resulted Pd–C bond on **15**. Intramolecular cyclization of **16** would afford iminopyrrolinyl complex **17**. Complex **18** could be formed by cyanation of **17** with a cyanide ligand generated by C–N bond cleavage [17] of third *tert*-butylisocyanide on palladium. Pyrroles **3** and **5**–**12** would be obtained by reductive elimination [18] of **19** from **18** and isomerization of **19**.

Other reaction pathways via mononuclear intermediates are also possible [14b,d,e]. At the present time, we cannot determine which pathway is more suitable for the pyrrole formation using **1b** as a catalyst.

3. Conclusion

The dinuclear palladium complexes **1** having the edge-sharing structure were prepared from Pd(0) and Pd(II) precursors, dpfamH, and excess of *tert*-butylisocyanide. Two isocyanides in **1** coordinate to palladium in almost parallel and in close proximity. The complex **1b** was effective as a catalyst in pyrrole formation from three molecules of *tert*-butylisocyanide and one molecule of alkyne. The

reaction using **1b** gave products in better yields than that using $Pd(PPh_3)_4$. Furthermore, unactivated internal alkynes reacted with *tert*-butylisocyanide by using **1b**, affording poly-substituted pyrroles. The reaction of internal alkynes using $Ni(OAc)_2$ or $Pd(PPh_3)_4$ did not give any products. Although the precise mechanism of the present pyrrole formation has remained unclear, two adjacent palladium atoms in **1b** seems to effectively cooperate each other. Other catalysis using **1** and synthesis of different types of edge-sharing dinuclear complexes are under investigation.

4. Experimental

All reactions were carried out under a nitrogen atmosphere. Alkynes and *tert*-butylisocyanide were purchased from Aldrich or TCI and used without further purification. DCE was distilled from CaH_2 under a nitrogen atmosphere.

NMR spectra were recorded by using a Bruker DPX-400 or Bruker DRX-500 spectrometer. ^1H NMR chemical shifts were measured relative to tetramethylsilane in $CDCl_3$. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. IR spectra were recorded by using a JEOL FT/IR-350.

4.1. Synthesis of $[Pd_2(tert\text{-}BuNC)_2(\mu\text{-}dpfam)]Cl$ (**1a**)

To a solution of dpfamH (0.225 g, 0.40 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (0.207 g, 0.20 mmol) in dichloromethane (16 mL) were added *tert*-butylisocyanide (0.452 mL, 4.0 mmol) and then $PdCl_2$(tmeda) (0.117 g, 0.40 mmol). After the mixture was stirred at room temperature for 20 h, Excess *tert*-butylisocyanide and dichloromethane were removed under reduced pressure. The residue was redissolved in dichloromethane (4 mL). Ether (40 mL) was added to the solution. Resulted red precipitates was collected by filtration, washed with ether, and dried. Yield: 0.36 g, 91%. ^1H NMR (400 MHz, $CDCl_3$) δ9.35 (s, 1H), 7.58–7.33 (m, 24H), 7.24–7.15 (m, 2H), 7.12–7.02 (m, 2H), 1.41 (s, 18H); ^{31}P {^1H} NMR (400 MHz, $CDCl_3$) δ 18.49. Anal. Calc. for $C_{47}H_{47}ClN_4P_2Pd_2$: C, 57.71; H, 4.84; N 5.73; Cl, 3.62. Found: C, 57.08; H, 5.09; N, 5.25; Cl, 3.36%.

Recrystallization by slow diffusion of diethyl ether into a solution of DCE gave a red crystal (**1a** · $ClCH_2CH_2Cl \cdot 1.5H_2O$). Data collection was carried out on a Rigaku CCD mercury system fitted with a monochromatic Mo Ka radiation source (l = 0.71069 Å) at room temperature. Eighteen preliminary data frames were measured at 0.5° increments of w, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of w. The intensity images were integrated using the CRYSTAL CLEAR program package, and the empirical absorption correction was applied for the data. The structures were solved by a direct method (SIR-92). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique. All hydrogen atoms were placed in idealized positions, and were included but not refined. All calculations were performed using the CRYSTAL STRUCTURE software package of Rigaku Corporation. Crystal data and refinement details are summarized in Table 3.

Table 3
Crystal data and refinement details for **1a**.

	1a · $ClCH_2CH_2Cl \cdot 1.5H_2O$
Formula	$C_{49}H_{54}Cl_3N_4O_{1.5}P_2Pd_2$
Formula weight	1104.10
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
a (Å)	13.920(3)
b (Å)	25.632(5)
c (Å)	14.937(3)
β (°)	104.873(2)
Z	4
V (Å^3)	5150.8(16)
D_{calcd} (g cm^{-3})	1.424
$F(100)$	2244.00
μ (Mo Kα) (cm^{-1})	9.553
No. of data collected	39707
No. of unique data [$R_{(int)}$]	11465 (0.041)
R_1 [$I > 2\sigma(I)$]	0.0471
wR_2	0.0662
Goodness-of-fit indicator	1.011

4.2. Synthesis of $[Pd_2(tert\text{-}BuNC)_2(\mu\text{-}dpfam)]PF_6$ (**1b**)

To a solution of **1a** (97.8 mg, 0.10 mmol) in dichloromethane (2.0 mL) and THF (4.0 mL) was added NH_4PF_6 (163 mg, 1.0 mmol). After stirring for 2 h, solvents were removed under reduced pressure, and then the residue was dissolved in dichloromethane (4 mL). White precipitates were removed by filtration and washed with dichloromethane several times. After the volume of the combined filtrate was reduced to 1 mL under reduced pressure, ether (10 mL) was added to the solution. Resulted red precipitates were collected by filtration, washed with ether, and dried. Yield: 88 mg, 81%. ^1H NMR (400 MHz, $CDCl_3$) δ9.36 (s, 1H), 7.58–7.34 (m, 24H), 7.24–7.16 (m, 2H), 7.11–7.00 (m, 2H), 1.39 (s, 18H); ^{31}P {^1H} NMR (400 MHz, $CDCl_3$) δ 17.15, −143.78. Anal. Calc. for $C_{47}H_{47}F_6N_4P_3Pd_2$: C, 51.90; H, 4.36; N 5.15. Found: C, 51.20; H, 4.32; N, 5.15%.

4.3. General procedure for the reaction of tert-butylisocyanide and alkynes

To a solution of **1b** (10.9 mg, 0.01 mmol) and *tert*-butylisocyanide (57 ml, 0.5 mmol) in DCE (2.0 mL) was added an alkyne (0.5 mmol) under a nitrogen atmosphere in a pressure vial. After heating at 80 °C for 16–18 h, the mixture was cooled to room temperature and filtered through a short plug of silica gel using ether as an eluent. Volatiles were evaporated and the residue was purified by silica gel column chromatography to give pyrroles.

4.4. 1-tert-Butyl-5-(tert-butylamino)-3-phenyl-1H-pyrrole-2-carbonitrile (**3a**) [12]

^1H NMR (400 Hz, $CDCl_3$): δ 7.62 (m, 2H), 7.39 (m, 2H), 7.30 (m, 1H), 5.78 (s, 1H), 3.88 (s, 1H), 1.83 (s, 9H), 1.34 (s, 9H).

4.5. 1-tert-Butyl-5-(tert-butylamino)-4-phenyl-1H-pyrrole-2-carbonitrile (**3b**) [12]

^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.18 (m, 5H), 6.94 (s, 1H), 2.88 (s, 1H), 1.87 (s, 9H), 0.82 (s, 9H).

4.6. 1-tert-Butyl-5-(tert-butylamino)-3-butyl-1H-pyrrole-2-carbonitrile (**5a**) [12]

^1H NMR (400 MHz, $CDCl_3$): δ 5.47 (s, 1H), 3.26 (s, 1H), 2.51 (t, J = 7.8 Hz, 2H), 1.75 (s, 9H), 1.55 (m, 2H), 1.38 (m, 2H), 1.30 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H).

4.7. 1-tert-Butyl-5-(tert-butylamino)-4-butyl-1H-pyrrole-2-carbonitrile (**5b**) [12]

^1H NMR (400 MHz, $CDCl_3$): δ 6.74 (s, 1H), 2.35–2.30 (m, 3H), 1.78 (s, 9H), 1.53–1.45 (m, 2H), 1.37–1.28 (m, 2H), 0.92 (t, J = 7.29 Hz, 3H).

*4.8. 1-tert-Butyl-5-(tert-butylamino)-3-hexyl-1H-pyrrole-2-carbonitrile (**6a**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.47 (s, 1H), 3.23 (s, 1H), 2.50 (t, J = 7.8 Hz, 2H), 1.74 (s, 9H), 1.65–1.50 (m, 2H), 1.40–1.21 (m, 15H), 0.94–0.80 (m, 3H); ^{13}C NMR (125 Hz, $CDCl_3$): δ 142.30, 140.06, 118.25, 98.12, 52.20, 32.45, 31.71, 31.31, 30.30, 29.91, 29.85, 29.13, 26.98, 22.67; IR (neat): 3313, 2961, 2928, 2858, 2190, 1653, 1554, 1461, 1367, 1216, 958, 881, 767 cm^{-1}; MS (EI): *m/z* 47 (95), 57 (100), 96 (27), 121 (47), 191 (32), 232 (12), 247 (26), 303 (7); HRMS (ESI) calcd for $C_{19}H_{33}N_3Na$ [*M*+Na]$^+$: 326.2567; found: 326.2566.

*4.9. 1-tert-Butyl-5-(tert-butylamino)-3-hexyl-1H-pyrrole-2-carbonitrile (**6b**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.73 (s, 1H), 2.44–2.53 (m, 2H), 2.27–2.35 (m, 3H), 1.78 (s, 9H), 1.24–1.37 (m, 6H), 1,14 (s, 9H), 0.83–0.94 (m, 3H); ^{13}C NMR (125 Hz, $CDCl_3$): δ 138.58, 122.43, 121.02, 117.91, 98.68, 60.24, 55.12, 32.00, 31.70, 30.63, 30.42, 29.27, 26.75, 22.60, 14.05; IR (neat): 3330, 2960, 2926, 2857, 2202, 1658, 1556, 1458, 1366, 1221, 1154, 1030, 940, 815 cm^{-1}; MS (EI): *m/z* 47 (85), 57 (100), 120 (75), 191 (41), 232 (14), 247 (27), 303 (3); HRMS (ESI) calcd for $C_{19}H_{33}N_3Na$ [*M*+Na]$^+$: 326.2567; found: 326.2567.

*4.10. Methyl 1-tert-butyl-5-(tert-butylamino)-2-cyano-1H-pyrrole-3-carboxylate (**7a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 1H), 3.87 (s, 3H), 3.29 (s, 1H), 1.83 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.28, 141.90, 125.82, 115.71, 115.16, 100.16, 60.78, 52.50, 51.65, 31.27, 29.70; IR (KBr): 3443, 2976, 2208, 1720, 1564, 1506, 1200, 1118 cm^{-1}; MS (EI): *m/z* 41 (71), 57 (100), 133 (53), 165 (86), 174 (22), 189 (14), 206 (24), 221 (39), 277 (9); HRMS (ESI) calcd for $C_{15}H_{23}N_3NaO_2$ [*M*+Na]$^+$: 300.1682; found: 300.1683.

*4.11. 1-tert-Butyl-5-(tert-butylamino)-3-methoxymethyl-1H-pyrrole-2-carbonitrile (**8a**) [12]*

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69 (s, 1H), 4.38 (s, 2H), 3.40 (s, 3H), 3.26 (s, 1H), 1.76 (s, 9H), 1.31 (s, 9H).

*4.12. Methyl 1-tert-butyl-5-(tert-butylamino)-2-cyano-3-phenyl-1H-pyrrole-4-carboxylate (**9a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.43 (m, 5H), 4.11 (s, 1H), 3.59 (s, 3H), 1.86 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.54, 146.68, 138.16, 132.23, 129.41, 127.75, 116.24, 110.59, 100.03, 62.67, 56.87, 50.91, 31.81, 29.47. IR (KBr): 3320, 2974, 2208, 1726, 1689, 1516, 1451, 1368, 1279, 1189, 1127, 1035, 822, 709, 662 cm^{-1}; MS (EI): *m/z* 41 (82), 57 (66), 128 (18), 154 (8), 180 (15), 209 (100), 241 (34), 297 (25). Anal. Calc. for $C_{21}H_{27}N_3O_2$: C, 71.39; H, 7.65; N 11.90. Found: C, 71.29; H, 7.84; N, 11.69%.

*4.13. Methyl 1-tert-butyl-5-(tert-butylamino)-2-cyano-4-phenyl-1H-pyrrole-3-carboxylate (**9b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.34 (m, 2H), 7.32–7.28 (m, 1H), 7.23–7.20 (m, 2H), 3.73 (s, 3H), 2.81 (s, 1H), 1.91 (s, 9H), 0.75 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.29, 139.60, 134.40, 128.02, 127.19, 123.81, 123.79, 115.37, 102.64, 62.60, 55.61, 51.47, 32.14, 30.00; IR (KBr): 3370, 2971, 2210, 1709, 1604, 1510, 1479, 1431, 1362, 1320, 1263, 1181, 1112, 1027, 974, 786, 723, 552 cm^{-1}; MS (EI): *m/z* 41 (89), 57 (85), 127 (10), 155 (16), 180 (14), 209 (24), 241 (100), 281 (10), 297 (32). Anal. Calc. for $C_{21}H_{27}N_3O_2$: C, 71.39; H, 7.65; N, 11.90. Found: C, 71.32; H, 7.77; N, 11.74%.

*4.14. Methyl 1-tert-butyl-5-(tert-butylamino)-2-cyano-3-methyl-1H-pyrrole-4-carboxylate (**10a**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.18 (s,1H), 3.79 (s, 3H), 2.35 (s, 3H), 1.79 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.71, 147.71, 135.18, 116.21, 110.70, 100.25, 62.02, 58.87, 50.83, 31.69, 29.46, 12.49; IR (KBr): 3302, 2975, 2204, 1692, 1548, 1516, 1440, 1368, 1270, 1193, 1110, 1041, 951, 797, 678 cm^{-1}; MS (EI): *m/z* 41 (47), 57 (59), 147 (100), 179 (49), 235 (25), 281 (6). Anal. Calc. for $C_{16}H_{25}N_3O_2$: C, 65.98; H, 8.59; N, 14.43. Found: C, 65.89; H, 8.59; N, 14.27%.

*4.15. 1-tert-Butyl-5-(tert-butylamino)-3,4-diethyl-1H-pyrrole-2-carbonitrile (**11**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (q, J = 7.6 Hz, 2H), 2.40 (q, J = 7.6 Hz, 2H), 2.31 (s, 1H), 1.76 (s, 9H), 1.17 (t, J = 7.6 Hz, 3H), 1.14 (s, 9H), 1.08 (t, J = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.77, 138.25, 120.42, 117.68, 97.52, 59.93, 54.86, 32.09, 30.60, 19.02, 18.05, 15.41, 15.24; IR (KBr): 3329, 2972, 2933, 2874, 2187, 1547, 1444, 1368, 1310, 1264, 1218, 1062, 980, 938, 809 cm^{-1}; MS (EI): *m/z* 41 (87), 57 (79), 148 (56), 163 (100), 219 (27), 275 (4); HRMS (ESI) calcd for $C_{17}H_{29}N_3Na$ [*M*+Na]$^+$: 298.2254; found: 298.2252.

*4.16. 1-tert-Butyl-5-(tert-butylamino)-3,4-dipropyl-1H-pyrrole-2-carbonitrile (**12**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (t, J = 7.6 Hz, 2H), 2.32 (t, J = 7.6Hz, 2H), 2.32 (s, 1H), 1.75 (s, 9H), 1.55 (tt, J = 6.1, 7.4 Hz, 2H), 1.43 (tt, J = 6.1, 7.4 Hz, 2H), 1.13 (s, 9H), 0.93 (t, J = 6.1 Hz, 9H), 0.87 (t, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.93, 137.20, 119.23, 117.70, 98.20, 59.95, 55.08, 32.07, 30.60, 27.70, 23.69, 14.08, 13.88; IR (KBr): 3332, 2963, 2871, 2192, 1659, 1548, 1503, 1445, 1366, 1319, 1228, 957, 778, 695 cm^{-1}; MS (EI): *m/z* 41 (100), 57 (92), 162 (94), 176 (26), 191 (48), 247 (34), 303 (4); HRMS (ESI) calcd for $C_{19}H_{33}N_3$ [*M*+Na]$^+$: 326.2567; found: 326.2566.

*4.17. Synthesis of pyrroles **3** using slow addition of tert-butylisocyanide*

To a solution of **1b** (10.9 mg, 0.01 mmol) in DCE (1.0 mL) was added phenylacetylene (55 ml, 0.50 mmol) under a nitrogen atmosphere in a Schlenk tube with a rubber septum. The flask was placed in an 80 °C oil bath. A solution of *tert*-butylisocyanide (170 ml, 1.5 mmol) in DCE (2.0 mL) was added to the reaction mixture in the flask over 5 h using a syringe pump. After the addition was completed, the reaction mixture was stirred at 80 °C for another 12 h. The mixture was cooled to room temperature and filtered through a short plug of silica gel using ether as an eluent. The yield and the isomer ratio were determined by GC using *n*-dodecane as an internal standard.

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Appendix A. Supplementary material

CCDC 705109 contains the supplementary crystallographic data for **1a** · $ClCH_2CH_2Cl$ · $1.5H_2O$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.039.

References

[1] (a) R.M. Bullock, C.P. Casey, Acc. Chem. Res. 20 (1987) 167;
(b) H. Steimhagen, G. Helmchen, Angew. Chem., Int. Ed. 35 (1996) 2339;
(c) E.K. van den Beuken, B.L. Feringa, Tetrahedron Lett. 54 (1998) 12985;
(d) G.J. Rowlands, Tetrahedron 57 (2001) 1865;
(e) M. Shibasaki, Y. Yamamoto (Eds.), Multimetallic Catalysis in Organic Synthesis, Wiley-VCH, Weinheim, 2004.

[2] (a) A.L. Balch, Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983;
(b) R.J. Puddephatt, Chem. Soc. Rev. 12 (1983) 99;
(c) B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 191;
(d) R.J. Puddephatt, L. Manojlovic-Muir, K.W. Muir, Polyhedron 9 (1990) 2767;
(e) G.K. Anderson, Adv. Organomet. Chem. 35 (1993) 1.

[3] (a) For recent examples, see D. Evrard, M. Drouin, Y. Mugnier, P.D. Harvey, Inorg. Chim. Acta 350 (2003) 442;
(b) R.U. Kirss, D.A. Forsyth, M.A. Plante, J. Organomet. Chem. 688 (2003) 206;
(c) C.B. Pamplin, S.J. Rettig, B.O. Patrick, B.R. James, Inorg. Chem. 42 (2003) 4117;
(d) G. Besenyei, L. Párkányi, G. Szalontai, S. Holly, I. Pápai, G. Keresztury, A. Nagy, Dalton Trans. (2004) 2041;
(e) G. Szalontai, G. Besenyei, Inorg. Chim. Acta 357 (2004) 4413;
(f) J.H.K. Yip, J. Wu, K.-Y. Wong, K.P. Ho, L.L. Koh, J.J. Vittel, Eur. J. Inorg. Chem. (2004) 1056;
(g) T. Braun, A. Steffen, V. Schorlemer, B. Neumann, H.-G. Stammler, Dalton Trans. (2005) 3331;
(h) D. Evrard, S. Clément, D. Lucas, B. Hanquet, M. Knorr, C. Strohmann, A. Decken, Y. Mugnier, P.D. Harvey, Inorg. Chem. 45 (2006) 1305;
(i) D. Evrard, K. Groison, A. Decken, Y. Mugnier, P.D. Harvey, Inorg. Chim. Acta 359 (2006) 2608.

[4] N. Tsukada, O. Tamura, Y. Inoue, Organometallics 21 (2002) 2521.

[5] (a) N. Tsukada, T. Mitsuboshi, H. Setoguchi, Y. Inoue, J. Am. Chem. Soc. 125 (2003) 12102;
(b) N. Tsukada, K. Murata, Y. Inoue, Tetrahedron Lett. 46 (2005) 7515;
(c) N. Tsukada, H. Setoguchi, T. Mitsuboshi, Y. Inoue, Chem. Lett. 35 (2006) 1164.

[6] (a) N.D. Jones, B.R. James, Adv. Synth. Catal. 344 (2002) 1126;
(b) S.J.L. Foo, N.D. Jones, B.O. Patrick, B.R. James, Chem. Commun. (2003) 988;
(c) N.D. Jones, S.J.L. Foo, B.O. Patrick, B.R. James, Inorg. Chem. 43 (2004) 4056;
(d) J.N.L. Dennett, M. Bierenstiel, M.J. Ferguson, R. McDonald, M. Cowie, Inorg. Chem. 45 (2006) 3705.

[7] (a) P. Nair, G.K. Anderson, N.P. Rath, Inorg. Chem. Commun. 5 (2002) 653;
(b) P. Nair, G.K. Anderson, N.P. Rath, Organometallics 22 (2003) 1494;
(c) P. Nair, G.K. Anderson, N.P. Rath, Inorg. Chem. Commun. 6 (2003) 1307.

[8] (a) N.M. Rutherford, M.M. Olmstead, A.L. Balch, Inorg. Chem. 23 (1984) 2833;
(b) Y. Yamamoto, H. Yamazaki, Bull. Chem. Soc. Jpn. 58 (1985) 1843;
(c) T. Tanase, K. Kawahara, H. Ukaji, K. Kobayashi, H. Yamazaki, Y. Yamamoto, Inorg. Chem. 32 (1993) 3682;
(d) T. Tanase, H. Ukaji, Y. Yamamoto, J. Chem. Soc., Dalton Trans. (1996) 3059;
(e) Y. Yamamoto, F. Arima, J. Chem. Soc., Dalton Trans. (1996) 1815;
(f) T. Tanase, J. Matsuo, T. Onaka, R.A. Begum, M. Hamaguchi, S. Yano, Y. Yamamoto, J. Organomet. Chem. 592 (1999) 103;
(g) J. Vicente, J.-A. Abad, A.D. Frankland, J. López-Serrano, P.G. Jones, Organometallics 21 (2002) 272.

[9] (a) Y. Yamamoto, H. Yamazaki, Organometallics 12 (1993) 933;;
(b) M. Rashidi, J.J. Vittal, R.J. Puddephatt, J. Chem. Soc., Dalton Trans. (1994) 1283;
(c) J.-F. Bérubé, K. Gagnon, D. Fortin, A. Decken, P.D. Harvey, Inorg. Chem. 45 (2006) 2812.

[10] (a) D. Perreault, M. Drouin, A. Michel, P.D. Harvey, Inorg. Chem. 31 (1992) 2740;
(b) P.D. Harvey, Z. Murtaza, Inorg. Chem. 32 (1993) 4721;
(c) R. Provencher, P.D. Harvey, Inorg. Chem. 35 (1996) 2113.

[11] (a) Y. Yamamoto, H. Yamazaki, Inorg. Chem. 25 (1986) 3327;
(b) T. Tanase, T. Fukushima, T. Nomura, Y. Yamamoto, Inorg. Chem. 33 (1994) 32.

[12] M. Jautelat, K. Ley, Synthesis (1970) 593.

[13] (a) For related reactions using TMSCN, see: N. Chatani, T. Hanafusa, Tetrahedron Lett. 27 (1986) 4201;
(b) T. Kusumoto, T. Hiyama, K. Ogata, Tetrahedron Lett. 27 (1986) 4197.

[14] (a) J. Tsuji, T. Nogi, J. Am. Chem. Soc. 88 (1966) 1289;;
(b) E.M. Campi, G.D. Fallon, W.R. Jackson, Y. Nilsson, Aust. J. Chem. 45 (1992) 1167;
(c) T. Joh, K. Doyama, K. Onitsuka, T. Shiohara, S. Takahashi, Organometallics 10 (1991) 2493;
(d) T. Joh, H. Nagata, S. Takahashi, Inorg. Chim. Acta 220 (1994) 45;
(e) K. Fuji, T. Morimoto, K. Tsutsumi, K. Kakiuchi, Chem. Commun. (2005) 3295.

[15] (a) H.W. Sternberg, J.G. Shukys, C.D. Donne, R. Markby, R.A. Friedel, I. Wender, J. Am. Chem. Soc. 81 (1959) 2339;
(b) O.S. Mills, G. Robinson, Inorg. Chim. Acta 1 (1967) 61.

[16] (a) R.J. Puddephatt, M.A. Thomson, Inorg. Chem. 21 (1982) 725;
(b) M.J. Irwin, G. Jia, J.J. Vittal, R.J. Puddephatt, Organometallics 15 (1996) 5321.

[17] W.D. Jones, W.P. Kosar, Organometallics 5 (1986) 1823.

[18] R.A. Stockland, G.K. Anderson, N.P. Rath, J. Am. Chem. Soc. 121 (1999) 7945.