

A new platform for NCN dimethylamino pincer complexes: Synthesis and structural studies

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Received 26 June 2007; received in revised form 2 August 2007; accepted 2 August 2007

Available online 9 August 2007

Abstract

The reaction of 2,6-(2-{Me₂NCH₂}C₆H₄)₂C₆H₃I (**2**) with Pd₂(dba)₃ produced the NCN diamine pincer complex [2,6-(2-Me₂{NCH₂}C₆H₄)₂C₆H₃PdI] (**3**) by an oxidative addition route. The structural analysis of ligand precursor **2** revealed a *syn*-conformation in the solid state. Single crystal X-ray analysis of complex **3** revealed a conventional square planar geometry about the palladium center and a global C₂ symmetric structure. Variable temperature and concentration NMR spectroscopic studies of complex **3** suggest an equilibrium between **3** and the dinuclear species [{2,6-(2-{Me₂NCH₂}C₆H₄)₂C₆H₃Pd}]₂μ²-I] in CDCl₃ solution. An unusual carbonate complex [{2,6-(2-{Me₂NCH₂}C₆H₄)₂C₆H₃Pd}]₃μ³-CO₃]I₃ (**4**) was also structurally characterized as a minor product during synthesis of **3**. © 2007 Elsevier B.V. All rights reserved.

Keywords: NCN pincer complexes; Palladium; Rigid structure; Twist angle; Catalysis

1. Introduction

The NCN diamine pincer ligand [2,6-(Me₂NCH₂)₂-C₆H₃][−] (**A**) (Chart 1, left) and its metal complexes (**B**) (Chart 1, right) were first introduced by van Koten et al. in the late 1970s [1,2]. Since then a large number of transition metal complexes with this ligand platform have been explored [3–11]. In particular, such pincer complexes are receiving attention for wide range applications such as catalysts for effecting carbon–carbon bond forming reactions [12], transfer hydrogenation reactions [13], and even gas sensing elements [14–16].

Although the analogous phosphine pincer ligands [2,6-(R₂PCH₂)₂C₆H₃][−] have perhaps received more attention [17], NCN pincer ligands are more stable towards moisture and air than their PCP counterparts. Such stability makes it easier to modify the NCN pincer platform by changing different functional groups within their multiple anchoring points [18,19]. These efforts have culminated in the construction of chiral pincer ligands and complexes that offer

promising utility in asymmetric catalytic synthesis. For example, modification of the methylene groups of the pincer ligand **A** can yield complexes of type **C** (Chart 2) [20]. Alternatively, one can build asymmetry into the N-donor site as examples **D** and **E** demonstrate (Chart 2) [21,22].

We have recently been pursuing the development of new pincer complexes having an expanded framework assembled around a *m*-terphenyl motif. PCP diphosphine and diphosphonite complexes (E = CH₂ and O) and NCN diimine complexes have thus been prepared (Chart 3, **F** and **G**, respectively) [23,24]. The materials were found to be conformationally rigid. In this report the detailed synthesis and characterization of analogous diamine pincer ligand and its complexation to palladium is described. In addition, the X-ray determined structures of the ligand and the palladium complexes are reported.

2. Results and discussion

2.1. Synthesis of NCN pincer ligand and complexes

A variety of routes have been employed to generate NCN pincer complexes [18,25,26]. Our earlier studies of

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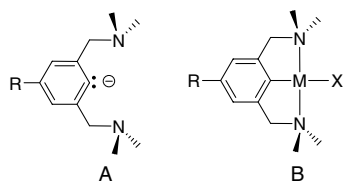


Chart 1.

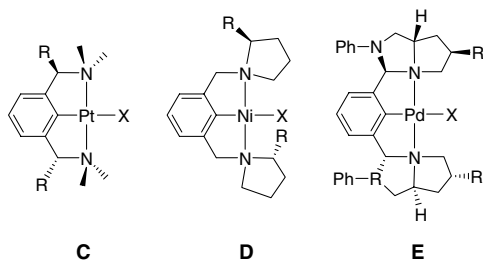


Chart 2.

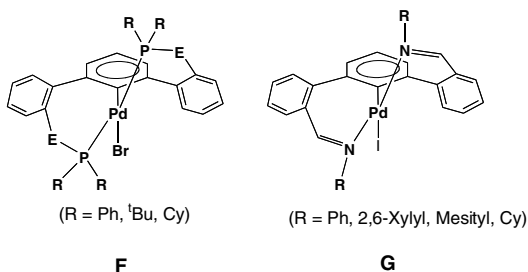


Chart 3.

NCN diimine complexes **G** showed that successful synthesis of pincer complexes could be best achieved by use of NC(I)N precursors, as oxidative addition of NC(Br)N ligand precursors to Pd₂(dba)₃ failed. We thus initiated synthesis of the diamine NC(I)N ligand precursor **2**. Conveniently, compound **1** was available from the synthesis of related NC(I)N diimine ligand precursors [23,24]. Compound **1** can be readily converted to the ligand precursor **2** by a titanium mediated addition of dimethylamine hydrochloride (Scheme 1) [27]. This reaction yields a viscous oil that could be induced to crystallize from diethyl ether or 2-propanol at $-5\text{ }^{\circ}\text{C}$. Interestingly, both ¹H and ¹³C

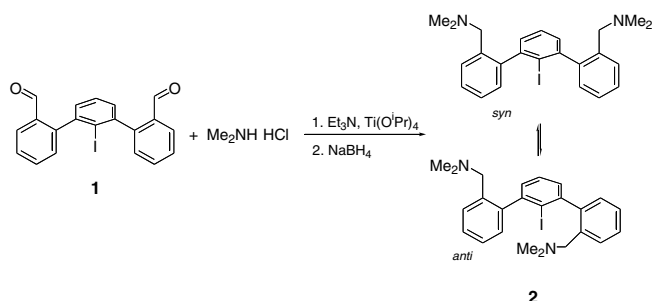
NMR spectroscopy of pure **2** show a single set of resonances. Specifically, only one resonance is observed for the *N*-methyl groups (δ 2.16 ppm in ¹H NMR and δ 46.2 ppm in ¹³C{¹H} NMR spectra). Related *m*-terphenyl PC(Br)P and NC(I)N (diimine) ligand precursors, however, showed evidence for two isomers in solution (*syn* and *anti*). It seems reasonable to assume that **2**, having smaller donor substituents, might undergo faster equilibration between *syn*- and *anti*-conformations and thus yield time averaged NMR spectra (Scheme 1). Further characterization by X-ray crystallography reveals that crystals of **2** grown from 2-propanol exist as the *syn*-isomer (vide infra) in the solid state.

The reaction of **2** with two equivalents of Pd₂(dba)₃ in THF slowly yielded pincer complex **3** in 73% yield (Scheme 2). A reduced yield is obtained if one equivalent of Pd₂(dba)₃ is used, and unreacted **2** is found to be present. It is worth mentioning that reaction of **2** and Pd₂(dba)₃ in benzene does not occur, which is puzzling since this solvent was used for previously reported related diphosphine and diimine pincer complexes **F** and **G**. Compound **3** is air stable crystalline material.

2.2. X-ray crystallography studies

A single crystal of **2** was grown by slow evaporation of 2-propanol solution of **2** at $-5\text{ }^{\circ}\text{C}$ and subjected to analysis by X-ray diffraction techniques. Crystallographic experimental details are shown in Table 1. The results of the analysis are shown in Fig. 1 and they reveal that the structure of **2** adopts a *syn*-conformation of the dimethylamine groups with respect to the central phenyl ring. The attached tolyl residues are nearly perpendicular to the central phenyl ring, with dihedral angles are 87.8° and 82.5° being observed. There are no special interactions between the two amine groups, and it appears that the nitrogen lone pairs are projected in opposite directions from one another. The remainder of the structure of **2** is unexceptional.

A light yellow crystal of **3** was grown by vapor diffusion of hexane into a CHCl₃ solution of **3** at room temperature, and its structure determined by X-ray diffraction methods. There are four independent molecules in the asymmetric unit; only one is shown in Fig. 2, and selected bond lengths and angles for those four molecules are given in Table 2. The average C1–Pd distance of 1.995 Å is slightly longer than those palladium carbon distances in the



Scheme 1. Synthesis of diamine NCN pincer ligand.

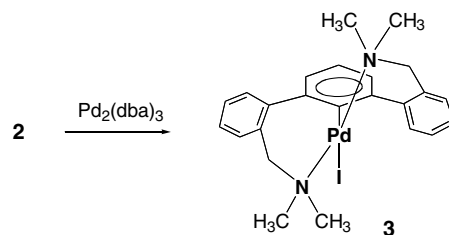
Scheme 2. Synthesis of diamine NCN pincer complex **3**.

Table 1
Structure refinement details for compound 2–4

Complex	2	3	4 · (THF) ₂
Empirical formula	C ₂₄ H ₂₇ IN ₂	C ₂₄ H ₂₇ IN ₂ Pd	C ₈₁ H ₉₇ I ₃ N ₆ O ₅ Pd ₃
Formula weight	470.38	576.78	1934.55
Temperature (K)	100	100	100
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>			
<i>a</i>	16.2484(3)	15.4830(2)	15.0361(3)
<i>b</i>	16.8777(3)	15.6181(2)	16.0807(3)
<i>c</i>	7.8974(1)	19.6522(3)	17.5379(3)
α	90.00	74.624(1)	74.418(1)
β	101.108(1)	76.617(1)	74.891(1)
γ	90.00	89.867(1)	76.753(1)
Volume (Å ³)	2125.17(6)	4448.8(1)	3885.3(1)
<i>Z</i>	4	8	2
Density (calc., g/cm ³)	1.470	1.722	1.654
Absorption coefficient (mm ⁻¹)	1.517	2.234	1.933
<i>F</i> (000)	952	2272	1924
Crystal size (mm)	0.12 × 0.08 × 0.06	0.06 × 0.30 × 0.33	0.05 × 0.08 × 0.13
Crystal color and shape	Colorless block	Light yellow plate	Pale orange block
θ Range data collection	1.28–28.29	1.11–28.33	1.23–28.31
Limiting indices	–21 < <i>h</i> < 21, –22 < <i>k</i> < 22, –10 < <i>l</i> < 10	–20 < <i>h</i> < 20, –20 < <i>k</i> < 20, –26 < <i>l</i> < 26	–20 < <i>h</i> < 20, –21 < <i>k</i> < 21, –23 < <i>l</i> < 23
Reflections collected	35762	118856	77176
Independent reflections [<i>R</i> _{int}]	5274 [0.0591]	22093 [0.0336]	19215 [0.0825]
Refinement method	Full-matrix least-square on <i>F</i> ²		
Data/restraints/parameters	5274/0/248	22093/0/1025	19215/15/878
Goodness-of-fit on <i>F</i> ²	1.109	1.147	1.113
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0303 <i>wR</i> ₂ = 0.0657	<i>R</i> ₁ = 0.0348 <i>wR</i> ₂ = 0.0794	<i>R</i> ₁ = 0.0616 <i>wR</i> ₂ = 0.1657
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0491 <i>wR</i> ₂ = 0.0836	<i>R</i> ₁ = 0.0471 <i>wR</i> ₂ = 0.0852	<i>R</i> ₁ = 0.1018 <i>wR</i> ₂ = 0.1920

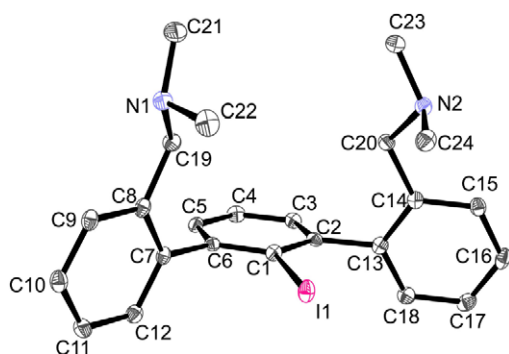


Fig. 1. An ORTEP drawing (40% probability thermal ellipsoids) of **2** with atom labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–I1, 2.102(3); N1–C19, 1.464(3); N1–C21, 1.458(4); N1–C22, 1.459(4); N2–C23, 1.460(4); N2–C24, 1.458(4); N1–C19–C8, 112.7(2); N2–C20–C14, 113.9(2); C8–C7–C6–C1, 89.5; C14–C13–C2–C1, 83.7.

m-xylyl based pincer complexes [**2**,6-(Me₂NCH₂)₂C₆H₃]-PdI] · 2I₂ (1.920(8) Å) [28] and [**2**,6-(Me₂NCH₂)₂C₆H₃]-Pd(OPh)] (1.910(2) Å) [29], as well as to two other *para*-substituted examples [**4**-NH₂-2,6-(Me₂NCH₂)₂-C₆H₃]PdBr] (1.921(2) Å) [30] and [**4**-NO₂-2,6-(Me₂NCH₂)₂-C₆H₃]PdBr] (1.913(2) Å) [7]. The average N1–Pd1–N2

bond angle of 170.4° for **3** is notably closer to linear than those values reported [7,28–30] for *m*-xylyl based NCN diamine pincer complexes, which range from 161° to 163°. The reasons for these differences could be rationalized by the increased size of the chelating rings (from 5 to 7). The palladium (II) centers in **3** are slightly distorted from perfectly square planar geometries, as evidenced by the average C1–Pd1–I1 bond angles (160.4°) being more acute than seen for C–Pd–X bond angles in the *m*-xylyl based pincer complexes

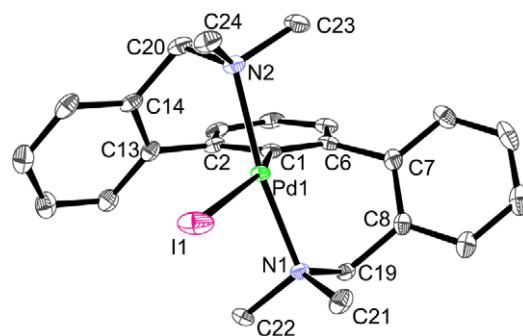


Fig. 2. ORTEP drawing (40% probability ellipsoids) of the molecular structure of **3**. Hydrogen atoms are omitted for clarity, and only one of the four independent molecules in the asymmetric unit is shown.

Table 2
Selected bond lengths (Å) and angles (°) of complex **3** (four independent molecules in the asymmetric unit)

	3a	3b	3c	3d
Pd1–C1	1.995(4)	1.995(4)	1.998(4)	1.994(4)
Pd1–I1	2.8018(4)	2.8170(4)	2.8238(4)	2.8199(4)
Pd1–N1	2.121(3)	2.126(3)	2.158(3)	2.162(3)
Pd1–N2	2.167(3)	2.167(3)	2.118(3)	2.125(3)
C1–Pd1–N1	88.76(14)	89.04(14)	89.26(13)	86.55(13)
C1–Pd1–N2	88.75(14)	86.36(14)	86.64(14)	88.52(13)
N1–Pd1–I1	91.72(9)	91.16(9)	91.22(9)	95.11(9)
N2–Pd1–I1	94.98(9)	96.31(9)	95.73(9)	92.18(9)
N1–C19–C8	112.9(3)	114.0(3)	114.0(3)	111.9(3)
N2–C20–C14	112.0(3)	112.7(3)	112.0(3)	112.9(3)
C1–Pd1–I1	160.72(12)	159.27(11)	160.05(11)	161.50(11)
N1–Pd1–N2	171.31(13)	169.93(13)	170.05(13)	170.42(13)
Twist angle	74.2	72.8	73.4	74.2

[7,28–30] which range from 172° to 179°. The nature of the *m*-terphenyl scaffold enforces non-planarity of the N-donor atoms and the central Pd-coordinated phenyl ring. We have described this structure type by a “twist angle Φ ” that relates the angles between the plane containing the metal, two donor atoms and attached carbon atom and the plane of the attached phenyl ring and attached metal atom [23,24]. The twist angle Φ determined for **3** is thus 74°, a value that is close to the values determined for PCP pincer complexes **F** (~76°), but larger than for NCN diimine pincer complexes **G** (61–65°).

The N1–C19–C8 and N2–C20–C14 bond angles (112.7(2)° and 113.9(2)°, respectively) in **2** change little upon coordination in complex **3** is formed (112.5(4)° and 112.9(4)°, respectively). For the *m*-xylyl based NCN pincer systems the corresponding bond angles change from ~113° to ~108° upon formation of the pincer complexes [28,31].

During efforts to purify compound **3** and grow crystals suitable for X-ray analysis, small amounts of a second type of crystals (pale orange) were observed. Crystals of this minor component, obtained by vapor diffusion of hexane into THF solution of **3** at –5 °C, were subjected to X-ray analysis. The results of the crystal structure determination revealed an unusual trimetallic complex **4**, containing three [NCNPd]⁺ units triply bridged by a carbonate group (Fig. 3). The charge of the cation {[NCNPd]₃(μ₃-CO₃)⁺ is balanced by an I₃[–] counter anion. The three [NCNPd]⁺ units in each individual trimer have the same chirality, and a pseudo-three fold symmetry axis (i.e., non-crystallographic) that passes through the carbon atom of the carbonate and perpendicular to the plane of the carbonate relates each of the [NCNPd]⁺ units. The selected bond lengths and angles are presented in Table 3. The geometry of the palladium center also is slightly distorted from square planar, and the Pd–C1 and Pd–N1 bond lengths are comparable to those found in complex **3**. However, the C1–Pd1–O1 and N1–Pd1–N2 bond angles are closer to linear than the C1–Pd1–I1 and N1–Pd1–N2 bond angles in complex **3**, possibly due to the smaller size of coordinat-

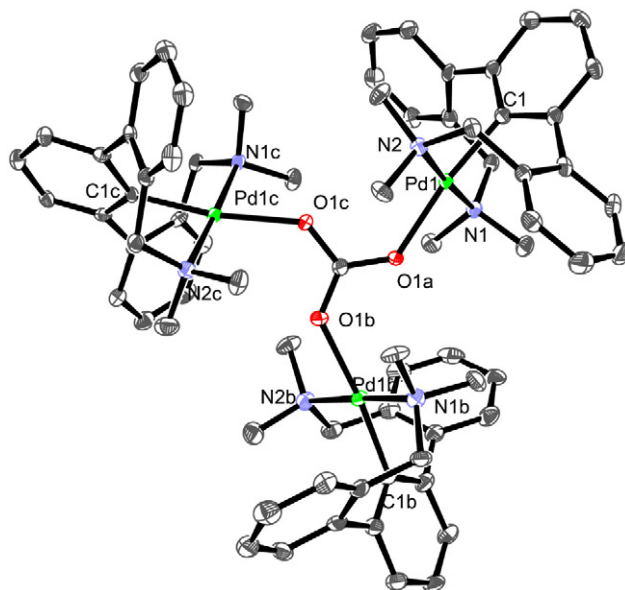


Fig. 3. ORTEP drawing (40% probability ellipsoids) of the molecular structure of **4**. Solvent molecules (THF), counter anion (I₃[–]) and hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°): Pd1–C1, 1.992(6); Pd1–O1a, 2.116(4); Pd1–N1, 2.145(5); Pd1–N2, 2.117(5); C1–Pd1–O1a, 172.1(2); N1–Pd1–N2, 176.8(2).

ing oxygen than iodine in complex **3**. The formation of such trinuclear complex **4** might be accounted for by the reaction of complex **3** with CO₂ (in the atmosphere) and OH[–] (from water and base). The μ₃-coordination mode of carboxylate ligands has been known, especially for Cu [32] and Zn [33] complexes. Complex **4** reported here is the first sample of such μ₃-CO₃ bridged tripalladium complex. Dipalladium μ₂-carbonato complexes, however, have been structurally characterized [34].

2.3. NMR spectroscopic studies

The ¹H NMR spectra of **2** reveal one singlet at 2.16 ppm assignable to the methyl groups. The resonances for the methylene protons appear as two doublets at 3.11 ppm and 3.31 ppm having coupling constants of 13.6 Hz. After forming the pincer complex **3**, the resonances of the methylene protons have shifted to 2.64 ppm and 3.03 ppm with coupling constants of 12.0 Hz. The methylene protons H20A and H19B are pointing at either side of the center benzene ring with a relatively close distance of about 3.0 Å (Fig. 4, hydrogen atoms are at idealized locations). Due to the ring current effects, protons H20A/H19B are shifted upfield relative to protons H20B/H19A.

The *N*-methyl signals resonate at two different frequencies as well (δ 2.46 ppm and 3.05 ppm). Such a large difference may be caused by similar difference of environments of one pair of methyl groups (C22 and C23) nearer the central benzene ring and the other methyl groups (C21 and C24) nearer to the iodine atom. The chemical shifts for the methylene and methyl groups in the *m*-xylyl based

Table 3
Selected bond lengths (Å) and angles (°) of complex 4

Pd1–C1	1.992(6)	Pd1–O1a	2.116(4)	C1–Pd1–O1a	172.1(2)
Pd1b–C1b	1.984(6)	Pd1b–O1b	2.109(4)	C1b–Pd1b–O1b	174.4(2)
Pd1c–C1c	1.986(5)	Pd1c–O1c	2.120(4)	C1c–Pd1c–O1c	171.1(2)
Pd1–N1	2.145(5)	Pd1–N2	2.117(5)	N1–Pd1–N2	176.8(2)
Pd1b–N1b	2.132(6)	Pd1b–N2b	2.136(6)	N1b–Pd1b–N2b	178.0(2)
Pd1c–N1c	2.133(5)	Pd1c–N2c	2.126(5)	N1c–Pd1c–N2c	178.3(2)

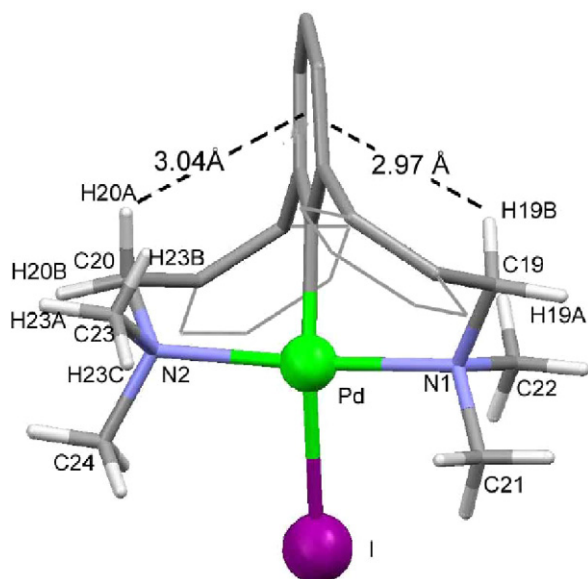


Fig. 4. Illustration of the proximity of protons to the central benzene ring in complex 3.

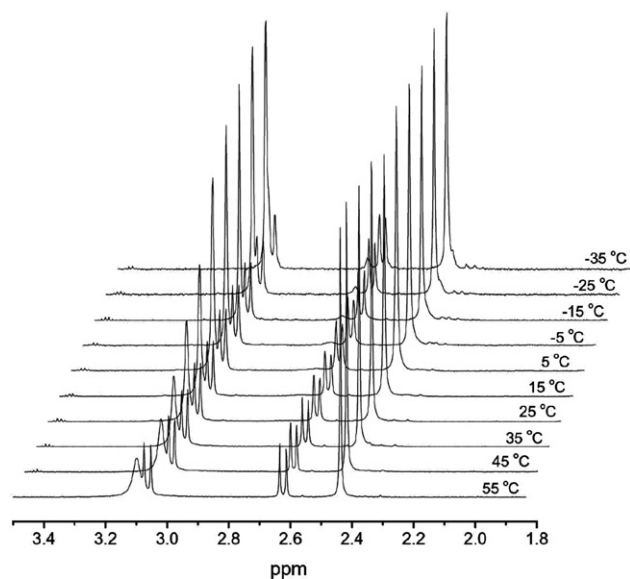


Fig. 5. Variable temperature NMR spectra of complex 3 (CDCl_3 , 600 MHz).

NCN pincer complex $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdI}$ appear as singlets at δ 4.00 ppm and 3.03 ppm, respectively. These chemical shifts are not affected much by the coordination of halogen atoms (Table 4).

One set of the *N*-methyl resonances, however, (δ 3.05 ppm) is broad relative to the other. Variable temperature NMR experiments were thus conducted on complex 3 (Fig. 5). As the temperature decreases the resonance at 3.05 ppm sharpens, while at higher temperatures the resonance further broadens. This phenomenon was found to be concentration dependent, as further NMR experiments on 3 showed (Fig. 6). During these experiments, the tem-

perature was fixed at 25 °C and the sample concentration was changed from 54 mmol/L to 0.79 mmol/L. The resonance at 3.05 ppm was most broadened for the most concentrated samples, suggesting a bimolecular process.

These results suggest the presence of the equilibrium portrayed in Scheme 3. At higher temperatures or lower concentrations, the dimeric species $[\{2,6-(2-(\text{Me}_2\text{NCH}_2)-\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3\text{Pd}\}_2\mu^2-\text{I}]\text{I}$ (5) is more dissociated into 3. The related $[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Pd}\}_2\mu^2-\text{Cl}]^+$ cation has been prepared by halide abstraction from $[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{PdCl}\}]$ [9]. The more facile dissociation of halide from 3 may reflect the greater steric crowding

Table 4
Selected ^1H NMR data for *m*-xylyl based NCN pincer complexes and 3

Complex	δCH_2 (J_{HH}/Hz)	δCH_3	Ref.
$[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdCl}$	3.98	2.93	[25]
$[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdBr}$	4.00	2.97	[25]
$[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdI}$	4.00	3.03	[25]
$[4\text{-}^t\text{BuSi}(\text{Me})_2\text{O}-2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdI}$	3.94	3.01	[35]
$[4\text{-NMe}_2-2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdBr}$	3.95	2.96	[30]
$[4\text{-NO}_2-2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PdBr}$	4.05	2.99	[30]
$[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Pd}(\text{H}_2\text{O})]\text{BF}_4$	4.17	2.87	[25]
$[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Pd}\}_2(\mu\text{-Cl})]\text{BF}_4$	4.13	2.83	[9]
3	2.64(12), 3.03(12)	2.46, 3.05(br)	

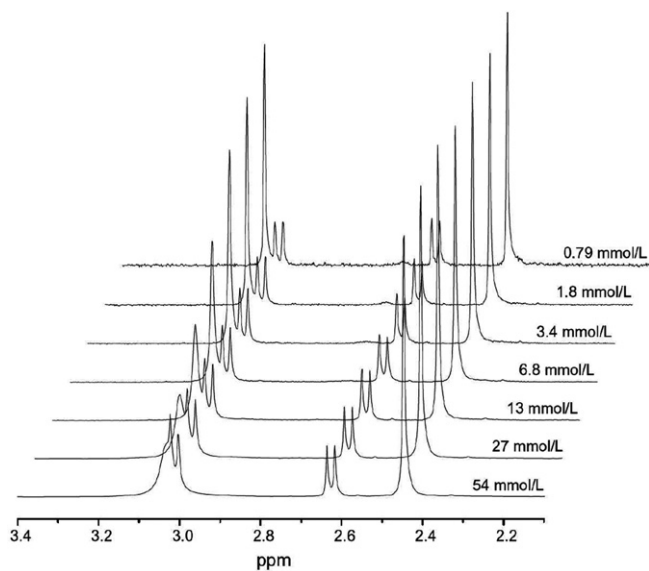
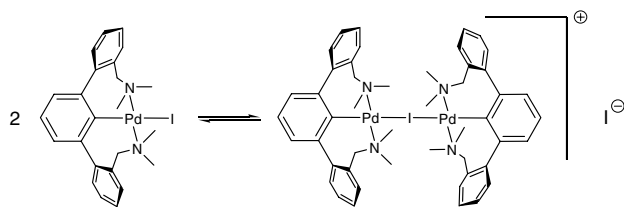


Fig. 6. Variable concentration NMR spectra of complex **3** (CDCl_3 , 600 MHz).



Scheme 3. Proposed equilibrium of **3** in solution.

present in **3** compared to $[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{PdCl}\}]$ and the weaker nucleophilicity of I^- relative to Cl^- .

3. Conclusion

In summary, a *m*-terphenyl diamine NCN pincer ligand and palladium complexes have been synthesized. Structural studies of these diamine NCN pincer complexes reveal an approximately C_2 symmetric environment. Variable temperature and variable concentration NMR spectroscopic studies demonstrate that complex **3** equilibrates in solution with a dimer of the form $[\{2,6-(2-\{\text{Me}_2\text{NCH}_2\}\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3\text{Pd}\}_2\mu^2\text{-I}]\text{I}$. The lability of the iodide in **3** is further demonstrated by the structural characterization of trimeric μ^3 -carbonato complex **4**.

4. Experimental

Experiments involving manipulation of air- and water sensitive materials were carried out using Schlenk techniques or in a glove box under nitrogen. Certified A.C.S. grade solvents (CH_2Cl_2 , hexanes, ethanol and methanol) from Fisher were used as received. THF was distilled from Na/benzophenone prior to use. The NMR spectroscopy measurements were recorded on Varian Inova 400 or 600 MHz spectrometers. Chemical shifts were referenced

to residual solvent signals (^1H , ^{13}C NMR). Elemental analyses were performed by Quantitative Technologies, Inc. NJ. The compound $2,6-\{2\text{-CH(=O)CH}_2\text{C}_6\text{H}_4\}_2\text{-C}_6\text{H}_3\text{I}$ (**1**) was synthesized by the literature methods [24].

4.1. $2,6-(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3\text{I}$ (**2**)

To a solution of **1** (2.00 g, 4.85 mmol) in 15 mL THF in a 100 mL round bottom flask, a mixture of $\text{Ti}(\text{O}^i\text{Pr})_4$ (5.71 g, 20.1 mmol), Me_2NHHCl (1.61 g, 19.7 mmol) and NEt_3 (1.23 g, 12.2 mmol) in 20 mL EtOH was added. This reaction mixture was stirred overnight at room temperature under N_2 . Then NaBH_4 (0.556 g, 14.7 mmol) was added. After being stirred for an additional 12 h, the reaction mixture was quenched by pouring into 30 mL of 2 M aqueous ammonium hydroxide and then filtered. The remaining solid was rinsed with 50 mL CH_2Cl_2 , and the filtrate was extracted by CH_2Cl_2 (2×50 mL). The solvent was removed in vacuo. The remaining sticky compound was dissolved in ether and filtered. The ether solution was kept in refrigerator (-5°C) overnight. Colorless crystalline solid of **2** was obtained (0.75 g, 33%). Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{I}$: C, 61.28; H, 5.79; N, 5.96. Found: C, 61.14; H, 5.64; N, 5.79%. ^1H NMR (CDCl_3 , 400 MHz): δ 2.16 (s, 12H, CH_3), 3.14 (d, $J_{\text{HH}} = 13.6$ Hz, 2H, $-\text{CH}_2-$), 3.31 (d, $J_{\text{HH}} = 13.6$ Hz, 2H, $-\text{CH}_2-$), 7.14–7.18 (m, 4H), 7.30–7.34 (m, 2H), 7.38–7.43 (m, 3H), 7.58–7.60 (m, 2H). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 46.2 (CH_3), 61.5 ($-\text{CH}_2-$), 107.3 (Ar(C)–I), 126.7, 127.5, 128.2, 128.7, 129.1, 129.5, 137.0, 145.3, 146.9.

4.2. $[2,6-(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3\text{PdI}]$ (**3**)

A mixture of **2** (0.20 g, 0.43 mmol) and $\text{Pd}_2(\text{dba})_3$ (0.23 g, 0.25 mmol) were dissolved into 15 mL anhydrous THF and stirred overnight at room temperature under N_2 . The reaction was monitored by ^1H NMR. After overnight stirring only half of the ligand **2** reacted. Another portion of $\text{Pd}_2(\text{dba})_3$ (0.46 g, 0.50 mmol) was added. After an additional 16 h of stirring, the resultant solution was filtered and the solvent was removed *in vacuo*. The product was purified by flash column chromatography using $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:20 v/v) as eluent. Yellow crystalline solid of **3** (0.18 g, 73%) was obtained. Analytically pure product was obtained via recrystallization from CH_2Cl_2 /hexanes. Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{IPd}$: C, 49.98; H, 4.72; N, 4.86. Found: C, 49.62; H, 4.57; N, 4.82%. ^1H NMR (CDCl_3 , 400 MHz): δ 2.46 (s, 6H, $-\text{CH}_3$), 2.64 (d, $J_{\text{HH}} = 11.6$ Hz, 2H, $-\text{CH}_2-$), 2.03 (d, $J_{\text{HH}} = 12$ Hz, 2H, $-\text{CH}_2-$), 3.04 (br 6H, $-\text{CH}_3$), 6.99 (d, $J_{\text{HH}} = 7.2$ Hz, 2H), 7.16 (t, $J_{\text{HH}} = 7.2$ Hz, 2H), 7.30 (d, $J_{\text{HH}} = 7.6$ Hz, 2H), 7.42–7.46 (m, 2H), 7.56–7.63 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 54.0 ($-\text{CH}_3$), 61.5 (br, $-\text{CH}_3$), 67.3 ($-\text{CH}_2-$), 125.0, 126.7, 127.4, 127.6, 129.5, 130.4, 134.5, 143.4, 148.0 (Ar(C)–Pd).

4.3. X-ray crystallographic studies

The X-ray intensity data were measured at 100 K on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 1500 watts power. The crystals of **2** and **4** were mounted on a MiTeGen micromount using paratone-N which was then frozen; crystal of **3** was mounted on glass fiber with epoxy. The detector was placed at a distance of 6.00 cm from the crystal. Data were measured using omega scans of 0.5° per frame for 10 s. The frames were integrated with the Bruker SAINT[®] build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using AXScale. The structures were solved and refined using the Bruker SHELXTL[®] (Version 6.14) software. The positions of all non-hydrogen atoms were derived from the direct methods (TREF) solution. With all non-hydrogen atoms being anisotropic and all hydrogen atoms being isotropic the structure was refined to convergence by least squares method on F^2 , XSHLL (Version 6.3.1), incorporated in SHELXTL (Version 6.14).

Acknowledgements

This work was supported by the ACS-PRF (PRF 44644-AC3) and by the National Science Foundation (CHE 0541766) for funds to for purchase of the X-ray diffractometer.

Appendix A. Supplementary material

CCDC 650758, 650759 and 650760 contain the supplementary crystallographic data for **2**, **3** and **4**. 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.08.004](https://doi.org/10.1016/j.jorganchem.2007.08.004).

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