Coordination Behaviour of the New Multidentate Ligand 3,5-Bis(dimethylaminomethyl)pyridine with Palladium(II) and Platinum(II) Metal Centres

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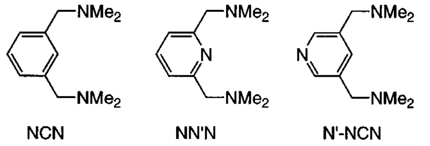
The synthesis of the new potentially tridentate ligand 3,5-bis(dimethylaminomethyl)pyridine (**3**) is described. Coordination chemistry of this ligand has been investigated with Pd^{II} and Pt^{II} precursor compounds. Both a bidentate bridging bonding motif and a monodentate bonding mode is observed. The latter compounds incorporate **3** by coordination through the pyridinic N atom only. The former complexes contain ligand **3** bonded to 2 metal centres by bridging through coordination of one trialkyl N donor atom and the pyridinic N atom. The solid-state structure of a ligand bridged Pd dimer has been elucidated by single-crystal X-ray diffraction and corroborates with the solid-state IR data that suggested a *trans*-$PdCl_2$ unit was present.

Introduction

Organometallic and main-group complexes containing the terdentate ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ (NCN: "pincer" ligand; Scheme 1) have been extensively investigated in this laboratory over the past decade.[1][2] This work has involved a systematic study of the reactivity of these compounds with a concurrent investigation of their catalytic and electronic characteristics. Recently, we have begun to expand this chemistry to include functionalized versions of the NCN ligand containing synthetically useful groups in the *para* position of the arene ring. This has enabled the attachment of organometallic compounds to a variety of polymeric[3] and dendrimeric supports.[4] *para*-Substituted NCN ligands have also provided a convenient gateway into bi- and trimetallic systems,[5][6][7][8][9][10] and to hydrogen-bonded transition-metal networks ("molecular wires").[11][12] The introduction of a heteroatom in the aromatic ring, as in the case of the pyridine compound $[2,6\text{-}(Me_2NCH_2)C_5H_3N]$ (NN′N; Scheme 1), represents a neutral version of the NCN ligand and results in modified reactivity of the resulting complexes incorporating this so-called "pyridine pincer".[13] Recent work has demonstrated that derivatives of NN′N containing a d^6 Ru^{II} metal centre present interesting structural and catalytic properties.[14]

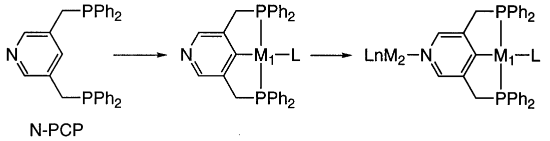
Scheme 1



Milstein and co-workers have recently described several rhodium and palladium complexes containing the related monoanionic diphosphanylpyridine ligand $[3,5\text{-}(Ph_2PCH_2)_2C_5H_2N]^-$ (N-PCP; Scheme 2). Subsequent coordination of the palladium compound [(N-PCP)PdCl] through the pyridinic nitrogen atom to a second metal center (M_2) was shown to influence the electron density of the coordinated Pd atom.[15a]

The reactivity of structurally similar pyridinium salts (specially of those derived from 3,5-pyridinediamides) towards various nucleophiles to form 1,2- and 1,4-dihydropyridines has also attracted recent attention. These compounds serve as models for NAD/NADH systems.[16] In this respect, the study of a ligand system derived from a 3,5-disubstituted aminopyridine presents an additional reason for investigation.

Scheme 2



We report herein the synthesis of the neutral pyridine-based ligand $[3,5\text{-}(Me_2NCH_2)_2C_5H_3N]$ (N′-NCN: **3**; Scheme 1), a potentially bridging ligand, and examine its coordination properties towards platinum and palladium in the 2+ oxidation state. Several coordination motifs are possible for this neutral N′-NCN ligand. Here the effect of the different Lewis basicity of the donor atoms (i.e. pyridine N vs. trialkyl amine N) towards various palladium and platinum precursors is investigated. Coordination through the trialkyl N atoms of the pincer "arms" or through the pyridinic N have been achieved depending on the reaction conditions. We have combined different NCN-based ligands in the same molecule, and have studied the reactivity of NCN-N′-metalated species (pyridinium ions) towards other metal precursors.

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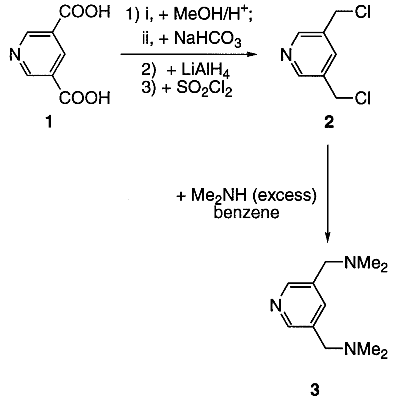
Results and Discussion

Ligand Synthesis

The starting compound 3,5-$(ClCH_2)_2C_5H_3N$ (**2**) was prepared from 3,5-$[HOC(O)]_2C_5H_3N$ (**1**) by a modified version of a previously published method (see Experimental).[16][17][18] The dimethyl ester of **1** was first reduced with excess of $LiAlH_4$ to the diol 3,5-$(HOCH_2)_2C_5H_3N$, which upon boiling with $SOCl_2$ gave compound **2** in 33% overall yield. The ligand 3,5-$(Me_2NCH_2)_2C_5H_3N$ (**3**) was synthesized in 90% yield by a reaction of **2** and an excess of Me_2NH in benzene (see Scheme 3). After subsequent drying ($MgSO_4$) and solvent evaporation, compounds **2** and **3** were assessed to be of sufficient purity by GC/MS, and ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy for further synthetic applications.

Scheme 3

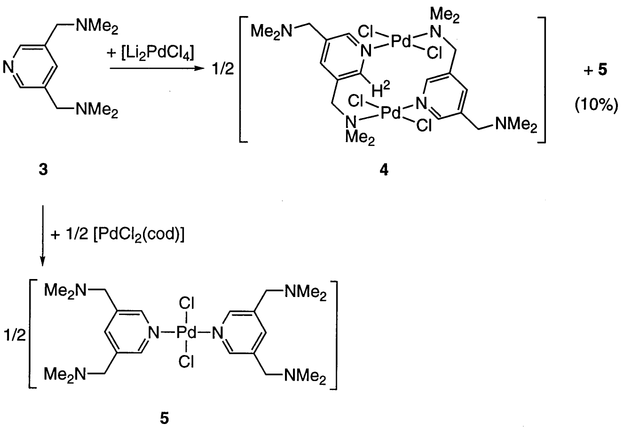


N′-NCN Coordination Compounds

With the aim of synthesizing orthometallated palladium complexes containing ligand **3**, the reaction between equimolar amounts of **3**, Li_2PdCl_4 and NaOAc in MeOH solution was investigated. Deprotonation of ligand **3** did not occur[15b] and immediate precipitation of compound **4** as a yellow solid took place (ca. 60% yield). Compound **4** could also be prepared in slightly higher yield by treating **3** with Li_2PdCl_4 (1:1) in MeOH. Small amounts of a second compound **5** were obtained in both these reactions (Scheme 4). This complex is the N(Py)-coordinated compound *trans*-$[Pd(N'\text{-}NCN)_2Cl_2]$ and was isolated in low yield (10%) from the mother liquor of the reactions. A high-yield synthesis of **5** is possible by using $PdCl_2(cod)$ (cod = cycloocta-1,5-diene) and excess **3**.

The ^1H-NMR spectra of compounds **4** and **5** show pronounced downfield shifts for hydrogen atoms assumed to be in close proximity to the metal atom compared with the corresponding values of free ligand **3**.

Scheme 4



The ^1H-NMR spectrum at room temperature of compound **4** presents four singlets for the CH_2 and CH_3 groups. These are assigned to the non-coordinated arm (δ = 3.45, 2.22) and at lower field to the coordinated one [δ = 3.85 (br.), 2.66]. The signals of the three pyridine protons appear as three singlets at δ = 11.51, 8.47, and 7.58 (2-H, 6-H, and 4-H, respectively). It is assumed that a fast flip of the 12-membered ring that contains the two Pd atoms occurs in solution on the NMR timescale. This would explain the chemical shift equivalence between both diastereotopic protons of the CH_2 and CH_3 groups of the coordinated arm. The pronounced downfield shift observed for pyridine 2-H atoms upon coordination ($\Delta\delta$ = 3.1) contrasts with the small shift of the 6-H protons ($\Delta\delta$ = 0.06; Table 1). Such a high deshielding may be due to the proximity of this proton with respect to both a Cl and a Pd atom, as indicated by the short H···Cl and H···Pd interactions present in the solid-state structure (vide infra). Large downfield shifts of protons situated close to a d^8 metal center and above the bonding plane (pseudoaxial position) have been described in the literature and are attributed to the paramagnetic anisotropy of the metal atom[19] or to the presence of weak CH···M agostic interactions.[20] A deshielding effect is also expected for H atoms involved in short C−H···Cl contacts or in hydrogen bonds. The $^{13}C\{^1H\}$-NMR spectrum of **4** does not present any unusual features, revealing only four singlets for the two inequivalent CH_2 and NCH_3 groups and five singlets for the aromatic C atoms, in support of the above discussion (Table 2). The IR spectrum of **4** contains a band at 343 cm^{-1} that is assigned to the Pd−Cl stretching vibration of *trans*-dichloride ligands.

The pyridinic 2,6-H and 4-H in compound **5** resonate as a doublet and a broad singlet at δ = 8.63 and 7.81, respectively in the ^1H NMR. The same resonances appear at δ = 8.41 and 7.62 in free **3**. The CH_2 and NCH_3 groups in **5** (singlets at δ = 3.45 and 2.26) have similar chemical shifts to those of **3** (Table 1). The $^{13}C\{^1H\}$-NMR spectrum of **5** presents five singlets of the coordinated ligand (Table 2). The *trans* configuration of compound **5** was supported by the presence of a single IR absorbance at 345 cm^{-1}, assigned to the Pd−Cl stretching vibration as in **4**.

(NCN)Pt(N′-NCN) Complexes

Previous publications have described the synthesis and reactivity of stable Pt complexes containing the monoanionic $[NCN]^-$ ligand. These compounds possess a variety of interesting properties involving the oxidative addition of halogens and alkyl halides (**6** and **7**: Scheme

Table 1. ^{1}H-NMR-spectroscopic data for compounds **3–5**, **8**, **9**[a]

	Py	Ph	(Ph)CH_2	(Py)NCH_2	(Ph)NCH_3	(Py)CH_3
3	8.41[b] (d; 2,6-H) 7.62[b] (t; 4-H)			3.42 (s)		2.23 (s)
4	11.51 (s; 2-H) 8.47 (s; 6-H) 7.58 (s; 4-H)			3.85 (br. s) 3.45 (s)		2.66 (s) 2.22 (s)
5	8.63[c] (d; 2,6-H) 7.81 (s[br]; 4-H)			3.45 (s)		2.26 (s)
8[d]	8.96[e] (m; 2,6-H) 8.01 (s [br]; 4-H)	7.05[f] (t; 4-H) 6.93[f] (d; 3,5-H)	4.30[g] (m)	3.63 (s)	2.89[h] (m)	2.25 (s)
9[d,i]	8.97 (s; 2,6-H)	7.20 (s; 2,6-H)	4.38[i] (m)	3.64 (s)	2.93[k] (m)	2.26 (s)

[a] ^{1}H-NMR data recorded at 200 or 300 MHz. Chemical shifts in ppm (δ from external SiMe$_4$ (δ = 0.0). CDCl$_3$ solutions were used except where noted. – [b] $^4J(^1H\text{-}^1H) = 3$ Hz. – [c] $^4J(^1H\text{-}^1H) = 1.4$ Hz. – [d] ^{1}H NMR in [D$_6$]acetone. – [e] $^4J(^1H\text{-}^1H) = 1.5$ Hz. $^3J(^{195}Pt\text{-}^1H) = 13.7$ Hz. – [f] $^3J(^1H\text{-}^1H) = 7$ Hz. – [g] $^3J(^{195}Pt\text{-}^1H) = 50$ Hz. – [h] $^3J(^{195}Pt\text{-}^1H) = 40$ Hz. – [i] $^{19}F\{^1H\} = -77.9$ (s, CF$_3$SO$_3$). – [i] $^3J(^{195}Pt\text{-}^1H) = 48$ Hz. – [k] $^3J(^{195}Pt\text{-}^1H) = 39$ Hz.

Table 2. $^{13}C\{^1H\}$-NMR-spectroscopic data for compounds **3–5**, **8**, **9**[a]

	Py + Ph	(Ph)CH_2	(Py)CH_2	(Ph)NCH_3	(Py)NCH_3
3	149.2 (2,6-Py), 137.3 (4-Py), 133.8 (3,5-Py)		61.3		45.3
4	156.1, 153.7, 141.6, 135.7, 132.1		66.3, 60.5		53.4, 45.3
5	152.0 (2,6-Py), 139.6 (4-Py), 135.9 (3,5-Py)		60.5		45.3
8	149.7, 143.5 (m; 2,6-Ph)[b], 142.8 (1-Ph), 139.7, 138.6, 125.2, 119.7	77.4	65.8	53.9	45.3
9[c]	150.9, 146.2 (m; 2,6-Ph)[d], 143.2 (1-Ph), 140.6, 140.3, 139.4, 119.0	78.0 (m)[e]	61.1	54.1	45.4

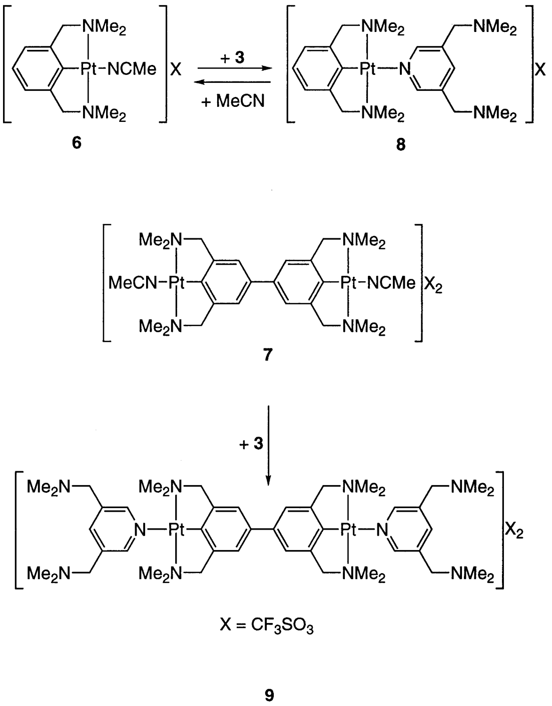
[a] $^{13}C\{^1H\}$-NMR data recorded at 50 or 75 MHz. Chemical shifts in ppm (δ) from external SiMe$_4$ (δ = 0.0) except where noted. Aromatic signals not all unequivocally assigned. All signals are singlets unless otherwise noted. – [b] $^2J(^{195}Pt\text{-}^{13}C) = 67$ Hz. – [c] $^{13}C\{^1H\}$ NMR in [D$_6$]acetone. – [d] $^2J(^{195}Pt\text{-}^{13}C) = 70$ Hz. – [e] $^2J(^{195}Pt\text{-}^{13}C) = 48$ Hz.

5).[1][10] Replacement of the coordinated MeCN ligands in complexes **6** and **7** by ligand **3** was therefore examined.

The starting compound **6** was prepared in situ by the reaction of the known complex PtCl[(Me$_2$NCH$_2$)$_2$C$_6$H$_3$][25] (**10**) with Ag(O$_3$SCF$_3$) in MeCN (see Experimental Section). Compound **3** was then reacted separately with the cationic platinum complexes **6** and **7** in dry acetone to give the corresponding products **8** and **9** (Scheme 5). Displacement of MeCN by **3** takes place only when an excess of the latter is used. The structure proposed for compounds **8** and **9**, in which the ligand **3** coordinates to platinum through the pyridinic nitrogen atom, was confirmed by ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy. These spectra show similar features to those of the parent compounds **7** and **10**, in addition to the resonances expected for coordinated **3**. Appropriate downfield shifts of the pyridinic 2,6-H and 4-H atoms with respect to **3** is observed, in addition to the presence of ^{195}Pt satellites associated with the resonance assigned to the 2,6-H of the pyridine ring (Table 1).

The addition of a drop of MeCN to a solution of **8** in [D$_6$]acetone resulted in partial conversion of **8** into the starting complex **6**, with liberation of free ligand **3**. This was observed in situ by ^{1}H-NMR spectroscopy. Compounds **8** and **9** are moisture-sensitive as slow ligand exchange processes between **3** and H$_2$O have likewise been observed (^{1}H NMR).

Scheme 5



The high lability of ligand **3** in compounds **8** and **9** made it difficult to draw conclusions concerning the subsequent coordination of **3** through the N atoms of the "arms". Thus, reaction of **9** with 2 equivalents of PtCl$_2$(SEt$_2$)$_2$ in dry acetone gave, among other non identified compounds, the neutral complex [ClPt(NCN–NCN)PtCl][10] which precipitated from the reaction mixture and was identified by its ^{1}H-NMR spectrum in CDCl$_3$.

In a subsequent reaction, ligand **3** and compound **8** were allowed to react with 1 equiv. of [Pd(MeCN)$_4$](BF$_4$)$_2$ in

[D$_6$]acetone. After 15 min, the ^{1}H-NMR spectrum of the reaction mixture showed the presence of at least three compounds. The most abundant product being complex **6**. Unfortunately, the minor components of the mixture could not be unequivocally assigned.

An ORTEP diagram representing the solid-state molecular structure of compound **4** in the crystal is depicted in Figure 1. Selected bond lengths and angles are listed in Table 3. The molecule of **4** has an inversion center at the center which is also a crystallographic inversion center. A distorted square-planar coordination at the Pd metal centre is observed. The value of the angles N1−Pd1−N3a are smaller than 180° [174.51(4)° and 172.9(1)°, respectively] and N3a is positioned significantly (0.24 Å) out of the plane determined by Pd1, Cl1, Cl2, and N1 (mean plane deviation 0.001 Å). This plane forms an angle of ca. 53° with the pyridine ring. The Pd1−Cl (average) and Pd1−N1 atom distances in complex **4** are 2.298(1) and 2.031(3) Å, respectively, and lie within the range observed in other *trans*-dichloropalladium(II) complexes containing pyridine ligands: 2.289−2.310 Å and 2.024−2.043 Å respectively.[21] The Pd1−N3a atom distance in **4** [2.102(3) Å] is similar to that found in related aryldimethylaminopalladium complexes.[10][22]

Figure 1. An ORTEP diagram (50-% probability level) of the molecular structure of complex **4** showing the adopted numbering scheme

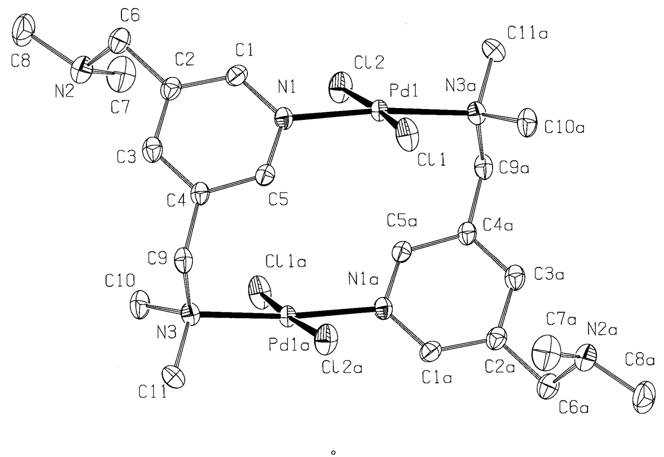


Table 3. Selected bond lenghts [Å] and angles [°] of compound **4**

Pd(1)−Cl(1)	2.2882(11)	Cl(1)−Pd(1)−Cl(2)	174.51(4)
Pd(1)−Cl(2)	2.3086(11)	Cl(1)−Pd(1)−N(1)	87.73(9)
Pd(1)−N(1)	2.031(3)	Cl(1)−Pd(1)−N(3a)	94.74(9)
Pd(1)−N(3)a	2.102(3)	Cl(2)−Pd(1)−N(1)	86.78(9)
		Cl(2)−Pd(1)−N(3a)	90.69(9)
		N(1)−Pd(1)−N(3a)	172.92(14)

The 12-membered ring containing the Pd atoms adopts a strained zigzag "chair"-like conformation which brings H51 close to both the Pd1a and the C11 atoms with H···Cl [2.73(3) Å] and H···Pd [2.69(2) Å] interatomic distances considerably shorter than the sum of the corresponding Van der Waals radii[23] (indicated by dotted lines in the Figure). Similar short Pd···H contacts have been identified in other Pd^{II} complexes.[19a][21b][21c][24] The C5−H51···C11 angle in complex **4** [109.6(19)°] is too far from linearity as to be considered a typical hydrogen bond. The intramolecular Pd···Pd distance [4.5997(8) Å] is virtually identical to the sum of their contact radii (4.6 Å).[23] Some of these features are comparable to those observed in other dipalladium ring systems described by Constable et al., e.g. [Pd$_2$Cl$_4${Me$_2$N(CH$_2$)$_n$NMe$_2$}$_2$] (n = 5, 7)[25] and [Pd$_2$Cl$_4${Me$_2$NN=CH(CH$_2$)$_3$CH=NNMe$_2$}$_2$].[25b] The higher thermodynamic stability of these 16- and 20-membered cyclic systems with respect to their open-chain analogues has been explained in terms of entropy and conformational effects. Such influences can be derived from the presence of bulky NMe$_2$ groups occupying "corner positions" in the ring, the existence of double bonds in the ligand system, and/or the formation of short H···H and H···Pd attractive transannular interactions (e.g. 2.4 Å and 2.6−2.7 Å, respectively in [Pd$_2$Cl$_4${N(NMe$_2$)=CH(CH$_2$)$_3$CH=N(NMe$_2$)}$_2$]).[25b] In spite of the obvious similarities between both our ligand system and complexes **3** and **4** and those studied by Constable et al., we suggest that short intramolecular interactions present in complex **4** (a more rigid system) may be due to geometrical contraints within the molecule, and not to forces of attractive nature. However, it is noticeable that although a certain degree of flexibility of the ring at room temperature in solution has been shown by ^{1}H-NMR spectroscopy (vide supra), short H···Cl and/or H···Pd contacts still appear to be important in solution.

Conclusions

It has been demonstrated that the potentially multidentate ligand 3,5-bis(dimethylaminomethyl)pyridine (**3**) can be synthesized in good yield from the corresponding bis(chloromethyl)pyridine. The coordination versatility of **3** has been shown in complex **4**, where N$_{py}$−Pd and Me$_2$N−Pd bonds are present, and in complexes **5**, **8**, and **9** in which only bonding through N$_{Py}$ are observed. The three latter complexes represent a linear geometry of the NCN and N′-NCN ligands and thus are a potential starting point for the synthesis of organometallic chains. Our attempts to ligate the free NMe$_2$ groups of **8** and **9**, and hence to increase the number of metal centres, has not so far been successful. This may be a manifestation of the inherit lability of the N$_{py}$−M bond in these compounds.

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Experimental Section

General: All experiments were conducted under dry nitrogen using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. − Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). − ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded at 298 K with a Bruker AC200 or AC300 spectrometers. − Infrared spectra were recorded as Nujol mulls deposited on disposable polyethene substrates (700−100 cm^{-1}) with a Perkin Elmer Model 2000 FT-IR spectrometer equipped with a MIRTGS (for MIR) and FIRTGS (for FIR) detector. The instrument was flushed with nitrogen and connected to a PC under SPECTRUM software. − Melting (decomposition) points were measured using a Büchi melting-point apparatus. The boiling point of compound **3** was determined by the Siwoloboff method. − GC/MS analyses were recorded with a Unicam Automass instrument using electron impact (EI, 70eV). − Starting materials: $[Li_2PdCl_4]$[26] and $[PdCl_2(cod)]$[27] were prepared according to literature procedures. $Ag(O_3SCF_3)$ was purchased from Aldrich and $C_5H_3N(CO_2H)_2$-3,5 (**1**) from Avocado.

Synthesis of 3,5-$(ClCH_2)_2C_5H_3N$ (**2**):[28] To a suspension of $LiAlH_4$ (1 g, 26.3 mmol) in Et_2O (25 ml) was added 3,5-$[MeO(O)C]_2C_6H_3N$ (1.7 g, 8.7 mmol).[29] The resulting yellow mixture was stirred for 15 h and MeOH (50 ml) was then added slowly to destroy excess $LiAlH_4$. The solvent was then removed in vacuo and the residue extracted in a Soxhlet apparatus with MeOH (12 h). The solution was subsequently concentrated to to give 3,5-$(HOCH_2)_2C_5H_3N$ as a yellow oil [^1H NMR (CD_3OD, 300 MHz), δ = 8.42 (s, 2 H, 2,6-Py*H*), 7.82 (s, 1 H, 4-Py*H*), 4.66 (s, 4 H, CH_2)]. Thionyl chloride (150 ml) was then added to the oil and the mixture refluxed for 18 h yielding a brown suspension. Excess of $SOCl_2$ was distilled off (vacuo) and the flask placed in an ice bath. Aqueous NaOH (100 ml; 4 M) was added slowly to the residue. The aqueous layer was then extracted with CH_2Cl_2 (4 × 25 ml) and the combined organic layers were dried with $MgSO_4$. The solvent was then removed in vacuo to give **2** as an off-white solid (2.9 g, 47% yield based on the starting ester). Mp: 86°C. − MS (EI, 70 eV); *m/z* (%): 175 (22.1) [M^+], 140 (100), 104 (11.0), 77 (25.0), 51 (16.3).

Synthesis of 3,5-$(Me_2NCH_2)_2C_5H_3N$ (N′-NCN; **3**): A three-necked round-bottom flask was placed in an ice bath and charged with benzene (20 ml) and Me_2NH (17 ml, 255 mmol). A solution of **2** (2.4 g, 13.8 mmol) in 200 ml of benzene was then added via a dropping funnel during 30 min. The reaction mixture was allowed to reach room temperature and then stirred for 1 h yielding a yellow suspension which was concentrated in vacuo to ca. 100 ml and subsequently filtered. The filtrate was concentrated to dryness to give the product **3** as an orange liquid, which was dissolved in pentane and dried with $MgSO_4$ overnight (yield: 2.4 g, 90%). Bp: 178−180°C.[24] − MS (EI, 70 eV); *m/z* (%): 193 (3.8) [M^+], 150 (100), 105 (73.1), 77 (40.4), 58 (99.0).

Synthesis of μ-$[\{\eta^1$-N,N′-3,5-$(Me_2NCH_2)_2C_6H_3N\}(PdCl_2)]_2$ (**4**): To a solution of $[Li_2PdCl_4]$ (0.19 mg, 0.724 mmol) in MeOH was added **3** (0.14 mg, 0.724 mmol). The resulting yellow suspension was stirred overnight and then filtered. The solid thus obtained was then washed with MeOH and Et_2O and subsequently dried in vacuo. Compound **4** was isolated as a yellow solid, which was recrystallized from CH_2Cl_2 /Et_2O and dried on P_2O_5 (yield: 0.18 g, 67%). Mp: 179−180 (dec.)°C. − IR [υ(PdCl)]: $\tilde{\nu}$ = 343 cm^{-1}. − $C_{22}H_{38}Cl_4N_6Pd_2$: calcd. C 35.65, H 5.16, N 11.34; found: C 35.31, H 5.23, N 11.08.

Synthesis of trans-$[\{\eta^1$-3,5-$(Me_2NCH_2)_2C_6H_3N\}_2PdCl_2]$ (**5**): To a solution of $[PdCl_2(cod)]$ (63 mg, 0.22 mmol) in CH_2Cl_2 was added an excess of **3** (172 mg, 0.891 mmol). After 30 min, the solution was concentrated in vacuo to approximately 2−3 ml and Et_2O was then added to precipitate the product (**5**) as a pale yellow solid. This was washed with Et_2O and dried (yield 70 mg, 60% yield). Mp: 110°C (dec). − IR [υ(PdCl)]: $\tilde{\nu}$ = 345 cm^{-1}. − $C_{22}H_{38}Cl_2N_6Pd$: calcd. C 46.86, H 6.79, N 14.90; found: C 46.53, H 6.92, N 14.47.

Synthesis of $[\{\eta^1$-3,5-$(Me_2NCH_2)_2C_6H_3N\}Pt\{\eta^3$-NCN-2,6-$(Me_2NCH_2)_2C_6H_3\}](CF_3SO_3)$ (**8**): To a solution of [(η^3-NCN-2,6-$\{Me_2NCH_2\}_2C_6H_3$)PtCl][18] (96.4 mg, 0.228 mmol) in MeCN was added $Ag(O_3SCF_3)$ (64.4 mg, 0.250 mmol). The resulting suspension was stirred for 10 min and then filtered through a plug of Celite. The filtrate was concentrated to dryness and washed with Et_2O to give compound **6** as a colorless solid. Complex **6** was then dissolved in dry acetone and **3** (74 mg, 0.38 mmol) was added to the solution. Upon addition of Et_2O to the reaction mixture, compound **8** precipitated as a colourless solid, which was filtered, washed with Et_2O, and dried in vacuo (yield: 140 mg, 85%). Mp: 165°C (dec). − $C_{24}H_{38}F_3N_5O_3PtS$: calcd. C 39.56, H 5.26, N 9.61; found C 39.32, H 5.36, N 9.42.

Synthesis of $[\{\eta^1$-3,5-$(Me_2NCH_2)_2C_6H_3N\}Pt\{\eta^3$-NCN-2,6-$(Me_2NCH_2)_2C_6H_2\}]_2(CF_3SO_3)_2$ (**9**): To a solution of **7** (51.9 mg, 0.045 mmol)[10] in dry acetone was added an excess of **3** (80 mg, 0.41 mmol). The resulting yellow solution was stirred at room temperature for 30 min. The solvent was then removed in vacuo and the residue washed with Et_2O (2 × 5 ml) to give **9** as a pale yellow solid (yield: 50 mg, 76%). Mp: 137−140°C (dec). − $^{19}F\{^1H\}$ NMR [$(CD_3)_2CO$, 200 MHz], δ = −77.9 (s, CF_3SO_3). − $C_{48}H_{74}F_6N_{10}O_6Pt_2S_2$: calcd. C 39.61, H 5.12, N 9.62; found C 39.54, H 5.04, N 9.46.

X-ray Structure Determination of Complex **4**: X-ray data were collected for an orange needle-shaped crystal at 150 K with an Enraf-Nonius CAD4T on rotating anode. Numerical data on the structure determination are collected in Table 4. The unit-cell parameters were derived from the 25 SET4[30] setting angles. The structure was solved with automated Patterson techniques using DIRDIF96[31] and refined on F^2 using the program SHELX96.[32] All other calculations (including the ORTEP illustration) were done with PLATON.[33]

Table 4. Crystal data and details on the structure determination of complex **4**

Empirical formula	$C_{22}H_{38}Cl_4N_6Pd_2$
Formula weight	741.23
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a [Å]	10.0020(6)
b [Å]	13.3358(18)
c [Å]	12.5944(14)
β [°]	120.186(7)
V [Å^3]	1452.1(3)
Z	2
$D_{calcd.}$ [g cm^{-3}]	1.695
F (000)	744
μ(Mo-K_α) [cm^{-1}]	16.3
Crystal size [mm]	0.10×0.13×0.38
Temperature [K]	150
Radiation, λ [Å] (graphite-monochromated)	Mo-K_α, 0.71073
θ (min., max.) [°]	2.4, 27.5
Scan (type and range) [°]	0.75 + 0.35tanθ
Dataset	−12/12; 0/17; −16/16
Tot., uniq. data, *R* (int)	7017, 3324, 0.049
Observed data [$I > 2.0\sigma(I)$]	2486
N_{ref}, N_{par}	3324, 167
R, *wR*	0.0348, 0.0620[a]
S	1.00
Max. and av. shift/error	0.00, 0.00
Min. and max. resd. electron dens. [e/Å^3]	−0.51, 0.48

[a] $w = 1/[\sigma^2(F_o^2) + (0.0172\ P)^2]$; where $P = (F_o^2 + 2\ F_c^2)/3$.

Hydrogen atoms were located at calculated positions and refined riding on their carrier atoms. A final difference map did not show any significant residual density. The structure contains no residual solvent-accessible voids as indicated by the PLATON/SOLV option.[33]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no. CCDC-100824. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. code + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.co.uk].

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