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Neutral Pyridyl-Functionalized *C,N-ortho*-Chelated Aminoaryl Platinum(II) Corner Building Blocks for Application in Coordination Reactions

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Two homoleptic pyridyl-functionalized *C,N-ortho*-chelating aminoaryl platinum(II) complexes, *cis*-[Pt(η^2-C,N)] (**3a**,**b**), were prepared via an unconventional method involving the initial synthesis of a bromide-functionalized *C,N*-chelating aminoaryl platinum(II) precursor complex **8**, to which subsequently pyridyl groups were attached via a Suzuki–Miyaura C–C coupling reaction. The electron-donating properties of the pyridyl nitrogen atoms of the resulting complexes (**3a**,**b**) were used in complexation reactions with monocationic NCN-pincer (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) platinum(II) (**11a**) and palladium(II) (**12a**) nitrate complexes [M(NCN)(NO_3)], thereby obtaining four trimetallic coordination complexes **16**–**19**. The difference in the pyridine–metal coordination behavior between platinum and palladium was studied by varying the ratios of the reagents and by variable-temperature NMR experiments. IR and Raman analyses of **11a** and **12a** were performed to determine the coordination behavior of the nitrate counteranion, and it was found that both NO_3^- and H_2O coordinate to the metal centers. The crystal structure determinations of free pyridyl complex **3a**, [Pt(NCN)(NO_3)] (**11a**), and [Pt(NCN)(NO_3)]·(H_2O) (**11b**), as well as the crystal structure of trisplatinum coordination complex **16**, are reported.

Introduction

Since the first report of a self-assembled metallasupramolecular square,[1] the synthesis of self-assembled molecular squares, cycles, and cages has received considerable attention[2] not only because of their novel structural features but also for their potential applications in the field of host−guest chemistry, catalysis, and luminescent materials and for molecular recognition and sensing.[3] The two most important factors for the rational design of these coordination-based supramolecular entities are the symmetry and shape of the resulting assembly. These two factors are determined solely by the type and properties of the building blocks. For two-dimensional structures, two types of building blocks are required: (1) linear ditopic units, which contain reactive sites with a 180° orientation relative to each other, and (2) angular ditopic units, possessing reactive sites with other desirable fixed angles. Generally, a building block consists of electron-deficient metal centers or organic ligands with Lewis base donor functionalities (often pyridine). Square-planar platinum(II) and palladium(II) centers with coordination angles of 180° or 90° are frequently used as either linear or corner acceptor units, respectively. Only in a few cases have organometallic complexes been used as donor building blocks. In these cases, the metal center itself is not used as the acceptor unit but only as a center for determining the orientation of the donor units via its attached ligands. The advantages of such complexes are their predefined structures,

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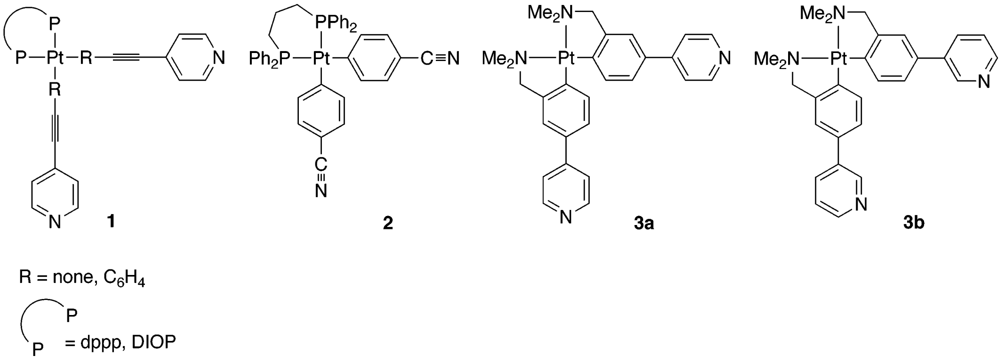
Chart 1. Organometallic Corner Complexes



e.g., in the case of square-planar complexes linear or angular, and their high chemical and physical stability compared to coordination complexes. An additional feature is that especially the 90° angle is rarely observed in pure organic donor compounds. Examples of right-angled electron-donating structures are complexes **1** and **2** (Chart 1) reported by Stang and Ferrer.[4]

For our research, we aimed at the use of the predefined 90° angle of organometallic *cis*-platinum(II) complexes as molecular building blocks representing a right-angled corner. The homoleptic platinum(II) complex $[\mathrm{Pt(dmba)_2}]$ (dmba = $[\mathrm{C_6H_4\{CH_2NMe_2\}\text{-}2}]^-$)[5] was chosen as the corner building block. On the basis of this complex, we reported in a previous paper the synthesis of functionalized *cis*- and *trans-C,N-ortho*-chelated aminoaryl platinum(II) compounds.[6] The functionalities on the aryl groups (halides or methyl-, naphthyl-, or (dimethylamino)methyl groups) were used to influence the cis/trans ratio and for additional functionalization of these complexes by means of lithiation, transmetalation, and C−C coupling reactions. We describe here the synthesis of pyridyl-functionalized *cis-C,N-ortho*-chelated aminoaryl platinum(II) corner complexes (**3a**,**b**, Chart 1) and their use as molecular building blocks with donor functionalities in self-assembly reactions with electron-deficient metal centers.

A common route for the synthesis of organometallic complexes comprises the construction of the organic backbone, followed by the introduction of the metal center in the final step. However, for successful synthesis of complexes **3a** and **3b**, we had to apply an unconventional synthesis route, which implies the use of metal-catalyzed C−C coupling reactions of pyridyl reagents with organoplatinum precursor complexes. The reactivity of these donor complexes in assembly reactions was tested with monocationic platinum(II) and palladium(II) NCN-pincer nitrate complexes (NCN = $[\mathrm{C_6H_3(CH_2NMe_2)_2\text{-}2,6}]^-$). For the latter complexes, the coordination behavior of the nitrate counteranion was investigated.

Experimental Section

General Procedures. 1-Bromo-2-(bromomethyl)-4-iodobenzene (**4**),[7] 4-bromo-2-[(dimethylamino)methyl]iodobenzene (**9**),[6] 4-pyridylborane pinacol ester,[8] 3-pyridylborane pinacol ester,[9] $[\mathrm{Pt(NCN)(H_2O)}](\mathrm{BF_4})$ (**11c**),[10] $[\mathrm{Pd(NCN)(H_2O)}](\mathrm{BF_4})$ (**12c**),[10] [PtCl(NCN)] (**13**),[10] and [PdCl(NCN)] (**14**)[11] were synthesized according to (modified) literature procedures. All solvents and other reagents were obtained from commercial sources and were used without further purification unless stated otherwise. Reactions involving organolithium derivatives were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Et_2O and THF were distilled from Na/benzophenone prior to use. ^1H, ^{13}C, and ^{195}Pt NMR spectra were recorded at 300, 75.5, and 64.3 MHz, respectively, at 25 °C. Chemical shifts are reported in ppm. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Raman spectra of solids were measured on a Perkin-Elmer 2000 FT-Raman spectrometer (excitation wavelength 1064 nm) and those of aqueous solutions on a Kaiser RXN 532-nm dispersive instrument. The applied optical resolution was 4 cm^{-1}. Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium (Mülheim a.d. Ruhr, Germany).

1-Bromo-2-[(dimethylamino)methyl]-4-iodobenzene (5). To a solution of **4** (17.1 g, 45.5 mmol) was added dimethylamine (60 mL, 865 mmol, 19 equiv) in Et_2O (250 mL) at room temperature. After 2 h, the salts were removed by filtration and the reaction mixture was concentrated in vacuo. The resulting oil was purified by flash distillation. Yield: 12.6 g (37.0 mmol, 81%). ^1H NMR ($CDCl_3$): δ 2.30 (s, 6H, NCH_3), 3.46 (s, 2H, CH_2N), 7.26 (d, $^3J_{H,H}$ = 8 Hz, 1H, ArH-6), 7.42 (d, $^3J_{H,H}$ = 10 Hz, 1H, ArH-5), 7.78 (s, 1H, ArH-3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.7 (NCH_3), 62.9 (CH_2N), 92.8 (ArC-4), 124.3 (ArC-1), 134.4, 137.4, 139.5, 140.7 (ArC-3). Anal. Calcd for $C_9H_{11}NBrI$: C, 31.79; H, 3.26; N, 4.12. Found: C, 31.87; H, 3.35; N, 4.18.

1-Bromo-2-[(dimethylamino)methyl]-4-(*p*-pyridyl)benzene (6). Compound **5** (1.39 g, 4.09 mmol), 4-pyridylborane pinacol ester (0.88 g, 4.29 mmol, 1.05 equiv), $[\mathrm{PdCl_2(dppf)}]$ (0.4 mmol, 10 mol

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%), and Na_2CO_3 (2.6 g, 24.5 mmol, 6 equiv) were brought into a Schlenk flask and evacuated for 30 min. To this was added a degassed mixture of DME (60 mL) and H_2O (30 mL). The reaction mixture was stirred at 90 °C for 40 h. The reaction mixture was cooled to room temperature, extracted with Et_2O (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The product was purified by column chromatography (silica, 94:3:3 $CH_2Cl_2/NEt_3/MeOH$). Compound **6** was isolated as a light yellow oil. Yield: 0.69 g (2.37 mmol, 58%). ^1H NMR ($CDCl_3$): δ 2.33 (s, 6H, NCH_3), 3.58 (s, 2H, CH_2N), 7.37 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH-6), 7.50 (dd, $^3J_{H,H} = 6$ Hz, $^2J_{H,H} = 2$ Hz, 2H, ArH-8,11), 7.65 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH-5), 7.73 (s, 1H, ArH-3), 8.64 (dd, $^3J_{H,H} = 6$ Hz, $^2J_{H,H} = 2$ Hz, 2H, ArH-9,10). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.5 (NCH_3), 64.4 (CH_2N), 121.8, 125.8, 127.7, 129.1, 129.9, 138.3, 140.1, 148.4, 150.3. Anal. Calcd for $C_{14}H_{15}N_2Br$: C, 57.75; H, 5.19; N, 9.62. Found: C, 58.02; H, 5.31; N, 9.49.

***cis*-[Pt(C_6H_3Br-4-{CH_2NMe_2}-2)$_2$] (8).** To a solution of **9** (2.11 g, 6.21 mmol) in Et_2O (20 mL) was added *n*-BuLi (6.2 mmol, 1.6 M in hexane, 3.9 mL, 1 equiv) at −78 °C. The reaction mixture was stirred for 5 min, after which a suspension of *cis*-[$PtCl_2$(cod)] (1.11 g, 2.97 mmol, 0.48 equiv) in Et_2O (10 mL) was added. The off-white suspension was allowed to warm to room temperature and stirred for 3 h. The precipitate was isolated by centrifugation and washed with water (6 mL, 3×) and acetone (6 mL, 2×) to give 1.70 g of **8** (2.74 mmol, 92%) as a white solid. The analytical data were identical with the data previously reported.[6]

***cis*-[Pt({4-pyridyl}-dmba)$_2$] (3a) and *cis*-[Pt({3-pyridyl}-dmba)$_2$] (3b).** Compound **8** (0.40 g, 0.64 mmol), 4- or 3-pyridylborane pinacol ester (0.33 g, 1.61 mmol, 2.5 equiv), [$PdCl_2$(dppf)] (33 mg, 0.044 mmol, 7%), and Na_2CO_3 (0.34 g, 3.24 mmol, 5 equiv) were brought into a Schlenk flask and evacuated for 30 min. To this was added a degassed mixture of DME (15 mL), THF (15 mL), and H_2O (15 mL). The reaction mixture was stirred at 70 °C until the reaction was complete (±3 h). The reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The product was purified by column chromatography (basic alumina, from pure CH_2Cl_2 to a mixture of 95:5 CH_2Cl_2/NEt_3) and subsequently washed with Et_2O (5 mL, 2×). Complexes **3a** and **3b** were isolated as light yellow solids. **3a.** Yield: 0.31 g (0.50 mmol, 78%). ^1H NMR (CD_2Cl_2): δ 2.86 (s, $^3J_{Pt,H} = 11$ Hz, 12H, NCH_3), 3.99 (s, $^3J_{Pt,H} = 16$ Hz, 4H, CH_2N), 7.35 (dd, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz, 2H, ArH-5), 7.40 (s, 2H, ArH-3), 7.53 (d, $^3J_{Pt,H}$ not observed, $^3J_{H,H} = 8$ Hz, 2H, ArH-6), 7.58 (dd, $^3J_{H,H} = 5$ Hz, $^2J_{H,H} = 2$ Hz, 4H, ArH-8,11), 8.59 (dd, $^3J_{H,H} = 5$ Hz, $J_{H,H} = 1$ Hz, 4H, ArH-9,10). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.3 (NCH_3), 73.7 ($^2J_{Pt,C} = 51$ Hz, CH_2N), 119.6 ($^3J_{Pt,C} = 37$ Hz, ArC-3), 121.0 (ArC-8,11), 124.4 ($^3J_{Pt,C} = 87$ Hz, ArC-5), 132.1 (ArC), 139.5 ($^2J_{Pt,C} = 48$ Hz, ArC-6), 141.9 (ArC$_{ipso}$), 148.6, 149.1 (ArC-2), 150.2 (ArC-9,10). ^{195}Pt NMR (CD_2Cl_2): δ −3367.0. Anal. Calcd for $C_{28}H_{30}N_4Pt$: C, 54.45; H, 4.90; N, 9.07. Found: C, 54.30; H, 4.98; N, 8.87. **3b.** Yield: 0.37 g (0.59 mmol, 92%). ^1H NMR (CD_2Cl_2): δ 2.84 (s, $^3J_{Pt,H}$ not observed, 12H, NCH_3), 3.96 (s, $^3J_{Pt,H}$ not observed, 4H, CH_2N), 7.22−7.30 (m, 6H, ArH-3,5,10), 7.57 (d, $^3J_{H,H} = 8$ Hz, $^3J_{Pt,H} = 68$ Hz, 2H, ArH-6), 7.87 (d, $^3J_{H,H} = 8$ Hz, 2H, ArH-11), 8.48 (d, $^3J_{H,H} = 4$ Hz, 2H, ArH-9), 8.85 (s, 2H, ArH-8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.3 (NCH_3), 73.7 (CH_2N), 119.8 (ArC-3), 123.5 (ArC-11), 124.5 (ArC-5), 131.8, 133.7 (Ar-10), 137.5, 139.4 (ArC-6), 139.9 (ArC$_{ipso}$), 147.5, 148.0, 148.5 (ArC-2). ^{195}Pt NMR (CD_2Cl_2): δ −3375.8. Anal. Calcd for $C_{28}H_{30}N_4Pt$: C, 54.45; H, 4.90; N, 9.07. Found: C, 54.32; H, 4.85; N, 8.87.

[Pt(NCN)(NO_3)] (11a) and [Pd(NCN)(NO_3)] (12a). A solution of **13** or **14** (0.75 mmol) and $AgNO_3$ (134 mg, 0.79 mmol, 1.1 equiv) in acetone (15 mL) was stirred for 16 h in the absence of light. The reaction mixture was filtered over Celite, concentrated in vacuo, and washed with Et_2O (3 mL). Note: these reactions were performed in technical solvents, in open air. Complexes **11a** and **12a** were isolated as white solids. **11a.** Yield: 0.32 g (0.71 mmol, 95%). The analytical data were identical with the data previously reported.[12] ^{195}Pt NMR (acetone-d_6): δ −3299. IR (cm^{-1}, solid): 1417_s $\nu_1(A')$, 1281_{vs} $\nu_2(A'')$, 1014_m $\nu_3(A')$, 839_m $\nu_6(A'')$, 768_m $\nu_4(A')$ or $\nu_5(A')$ (NO_3^-). Raman (cm^{-1}): 1039_s $\nu_1(A'_1)$, 1014_s $\nu_3(A')$ (solid); 1046_{vs} $\nu_1(A'_1)$ (aqueous solution). **11a·H_2O.** IR (cm^{-1}): 3573_s ν_3, 3494_m ν_1, 1613_w ν_2 (H_2O); 1417_m $\nu_1(A')$, 1286_{vs} $\nu_2(A')$, 1008_m $\nu_3(A')$, 838_m $\nu_6(A'')$, 769_m $\nu_4(A')$ or $\nu_5(A')$ (NO_3^-). Raman (cm^{-1}): 1040_s $\nu_1(A'_1)$, 1013_s $\nu_3(A')$; 1046_{vs} $\nu_1(A'_1)$ (aqueous solution). **12a.** Yield: 0.24 g (0.68 mmol, 91%). ^1H NMR (acetone-d_6): δ 2.81 (s, 12H, NCH_3), 4.09 (s, 4H, CH_2N), 6.82 (d, $^3J_{H,H} = 8$ Hz, 2H, ArH-3,5), 6.98 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH-4). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 52.1 (NCH_3), 74.2 (CH_2N), 120.8 (ArC-3,5), 125.6 (ArC-4), 146.4 (ArC-2,6), 153.1 (C$_{ipso}$). IR (cm^{-1}, solid): 1411_m $\nu_1(A')$, 1289_{vs} $\nu_2(A')$, 1027_m $\nu_3(A')$, 840_m $\nu_6(A'')$, 764_m $\nu_4(A')$ or $\nu_5(A')$ (NO_3^-). Raman (cm^{-1}): 1038_s $\nu_1(A'_1)$, 1025_s $\nu_3(A')$ (solid); 1047_{vs} $\nu_1(A'_1)$ (aqueous solution). Anal. Calcd for $C_{12}H_{19}N_3O_3Pd$: C, 40.07; H, 5.32; N, 11.68. Found: C, 39.92; H, 5.26; N, 11.59.

Attempted Synthesis of [Pt(NCN)(H_2O)](NO_3) (11b) and [Pd(NCN)(H_2O)](NO_3) (12b). A solution of **11a** or **12a** in H_2O was stirred at room temperature for 16 h, after which the solvent was evaporated by means of freeze-drying. The products were isolated as white solids. **11b.** ^{195}Pt NMR (D_2O): δ −3351. IR (cm^{-1}, solid): 3572_w, 3494_w (H_2O); 1278_{vs} $\nu_2(A')$, 1014_m $\nu_3(A')$, 836_m $\nu_6(A'')$, 769_m $\nu_4(A')$ or $\nu_5(A')$ (NO_3^-). The $\nu_1(A')$ symmetric stretching could not be observed because of overlap with other vibrations. Raman (cm^{-1}): 1037_m $\nu_1(A'_1)$, 1016_m $\nu_3(A')$ (solid); 1047_{vs} $\nu_1(A'_1)$ (aqueous solution). **12b.** IR (cm^{-1}, solid): 3572_w (H_2O); 1292_{vs} $\nu_2(A')$, 1027_m $\nu_3(A')$, 841_m $\nu_6(A'')$, 763_m $\nu_4(A')$ or $\nu_5(A')$ (NO_3^-). The $\nu_1(A')$ symmetric stretching could not be observed because of overlap with other vibrations.

General Procedure for Coordination Reactions. To a mixture of **3a** or **3b** (7.7 mg, 12.5 μmol) and **11a** (11.5 mg, 26.0 μmol, 2 equiv) or **12a** (9.5 mg, 26.4 μmol, 2 equiv) was added acetone-d_6 (0.6 mL) and D_2O (0.3 mL). The solutions were analyzed by NMR spectroscopy. The products **16**−**19** were precipitated by slow diffusion of Et_2O in the reaction mixture, followed by decantation of the solvents. Drying of the residues in vacuo yielded solid compounds.

***cis*-[Pt(4-{*p*-pyridyl}dmba{[Pt(NCN)]}$_2$)$_2$](NO_3)$_2$ (16).** Yield: 15 mg (10 μmol, 80%). ^1H NMR (2:1 acetone-d_6/D_2O): δ 2.79 (s, 24H, NCH_3, η^3-NCN), 2.88 (s, 12H, NCH_3, η^2-CN), 3.95 (s, 4H, CH_2N, η^2-CN), 4.18 (s, 8H, CH_2N, η^3-NCN), 6.87 (d, $^3J_{H,H} = 8$ Hz, 4H, ArH-3,5, η^3-NCN), 6.97 (t, $^3J_{H,H} = 6$ Hz, 2H, ArH-4, η^3-NCN), 7.39−7.50 (m, 4H, ArH-5,6, η^2-CN), 7.59 (s, 2H, ArH-3, η^2-CN), 8.01 (d, $^3J_{H,H} = 5$ Hz, 4H, ArH-8,11, η^2-CN), 8.91 (d, $^3J_{H,H} = 5$ Hz, 4H, ArH-9,10, η^2-CN). $^{13}C\{^1H\}$ NMR (0.95:0.05 acetone-d_6/D_2O): δ 50.2 (NCH_3, η^2-CN), 53.9 (NCH_3, η^3-NCN), 73.7 (CH_2N, η^2-CN), 77.7 (CH_2N, η^3-NCN), 119.9, 123.4, 124.2, 125.4, 129.6, 139.7, 144.4, 145.4, 147.8, 150.9, 151.6, 151.9. ^{195}Pt NMR (0.95:0.05 acetone-d_6/D_2O): δ −3331.2, −3381.9. Anal. Calcd for $C_{52}H_{68}N_{10}O_6Pt_3$: C, 41.24; H, 4.53; N, 9.25. Found: C, 41.15; H, 4.47; N, 9.19.

***cis*-[Pt(4-{*p*-pyridyl}dmba{[Pd(NCN)]}$_2$)$_2$](NO_3)$_2$ (17).** Yield: 12 mg (9 μmol, 72%). ^1H NMR (2:1 acetone-d_6/D_2O): δ 2.64 (s,

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Table 1. Crystallographic Details

compd	**3a**	**11a**	**11a·H$_2$O**	**16**
formula	$C_{28}H_{30}N_4Pt$	$C_{12}H_{19}N_3O_3Pt$	$C_{12}H_{19}N_3O_3Pt \cdot H_2O$	$[C_{52}H_{68}N_8Pt_3](NO_3)_2$ + disordered solvent
fw	617.65	448.39	466.41	1514.43[a]
cryst color	yellowish	colorless	colorless	yellowish
cryst size [mm^3]	0.42 × 0.18 × 0.06	0.24 × 0.09 × 0.06	0.36 × 0.30 × 0.09	0.42 × 0.12 × 0.04
cryst syst	triclinic	orthorhombic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a [Å]	9.1884(10)	10.5554(4)	8.8915(3)	18.1883(3)
b [Å]	10.7555(17)	12.5362(4)	9.0104(2)	21.1087(4)
c [Å]	12.6573(10)	10.8290(2)	9.6808(2)	23.0192(4)
α [deg]	98.903(7)	90	77.947(2)	90
β [deg]	103.582(6)	90	87.790(2)	128.2015(6)
γ [deg]	92.374(10)	90	77.378(2)	90
V [Å^3]	1197.3(3)	1432.94(8)	740.14(3)	6945.1(2)
Z	2	4	2	4
D_x [g/cm^3]	1.713	2.078	2.093	1.448[a]
μ [mm^{-1}]	5.883	9.800	9.495	6.072[a]
abs corr	multiscan	analytical	analytical	analytical
abs corr range	0.29−0.70	0.19−0.55	0.08−0.48	0.21−0.81
refln measd/unique	17000/5481	11035/3247	18901/3401	70031/10269
$(\sin \theta/\lambda)_{max}$ [Å^{-1}]	0.65	0.65	0.65	0.56
param/restraints	302/58	176/1	193/0	612/32
R1/wR2 [$I > 2\sigma(I)$]	0.0267/0.0641	0.0214/0.0443	0.0134/0.0331	0.0405/0.1074
R1/wR2 [all reflns]	0.0326/0.0664	0.0273/0.0464	0.0142/0.0334	0.0567/0.1138
S	1.085	1.032	1.190	1.080
Flack x parameter[16]		-0.013(9)		
$\rho_{min/max}$ [e/Å^3]	−1.24/1.51	−1.31/0.70	−1.27/0.42	−0.73/2.46

[a] Derived quantities do not contain the contribution of the disordered solvent molecules.

24H, NCH_3, η^3-NCN), 2.78 (s, 12H, NCH_3, η^2-CN), 3.93 (s, 4H, CH_2N, η^2-CN), 4.04 (s, 8H, CH_2N, η^3-NCN), 6.80 (d, $^3J_{H,H} = 7$ Hz, 4H, ArH-3,5, η^3-NCN), 6.96 (t, $^3J_{H,H} = 7$ Hz, 2H, ArH-4, η^3-NCN), 7.36−7.53 (m, 6H, ArH, η^2-CN), 7.87 (bs, 4H, ArH-8,11, η^2-CN), 8.81 (bs, 4H, ArH-9,10, η^2-CN). $^{13}C\{^1H\}$ NMR (2:1 acetone-d_6/D_2O): δ 50.1, (NCH_3, η^2-CN), 52.2 (NCH_3, η^3-NCN), 73.5 (CH_2N, η^2-CN), 74.3 (CH_2N, η^3-NCN), 116.8, 120.2, 120.6, 122.5, 124.2, 125.9, 130.7, 136.2, 139.6, 146.3, 150.9, 151.1. Anal. Calcd for $C_{52}H_{68}N_{10}O_6Pd_2Pt$: C, 46.71; H, 5.13; N, 10.48. Found: C, 46.63; H, 4.97; N, 10.33.

***cis*-[Pt(4-{*m*-pyridyl}dmba{[Pt(NCN)]}$_2$)$_2$](NO$_3$)$_2$ (18).** Yield: 14 mg (9 μmol, 72%). ^1H NMR (2:1 acetone-d_6/D_2O): δ 2.79 (s, 12H, NCH_3, η^2-CN), 2.82 (s, 24H, NCH_3, η^3-NCN), 3.93 (s, 4H, CH_2N, η^2-CN), 4.20 (s, 8H, CH_2N, η^3-NCN), 6.88 (d, $^3J_{H,H} = 8$ Hz, 4H, ArH-3,5, η^3-NCN), 6.99 (t, $^3J_{H,H} = 7$ Hz, 2H, ArH-4, η^3-NCN), 7.28 (d, $^3J_{H,H} = 8$ Hz, 2H, ArH, η^2-CN), 7.46 (m, 4H, ArH, η^2-CN), 7.80 (t, $^3J_{H,H} = 5$ Hz, 2H, ArH-10, η^2-CN), 8.29 (d, $^3J_{H,H} = 8$ Hz, 2H, ArH-11, η^2-CN), 8.91 (d, $^3J_{H,H} = 5$ Hz, 2H, ArH-9, η^2-CN), 9.21 (s, 2H, ArH-8). $^{13}C\{^1H\}$ NMR (0.95:0.05 acetone-d_6/D_2O): δ 50.3 (NCH_3, η^2-CN), 54.0 ($^3J_{Pt,C} = 61.1$ Hz, NCH_3, η^3-NCN), 73.9 (CH_2N, η^2-CN), 77.8 (CH_2N, η^3-NCN), 120.1, 120.3, 124.5, 125.6, 127.9, 129.8, 136.7, 139.7, 139.9, 141.4, 144.2, 145.0, 145.6, 149.1, 149.6, 150.7. Anal. Calcd for $C_{52}H_{68}N_{10}O_6Pt_3$: C, 41.24; H, 4.53; N, 9.25. Found: C, 41.06; H, 4.61; N, 9.18.

***cis*-[Pt(4-{*m*-pyridyl}dmba{[Pd(NCN)]}$_2$)$_2$](NO$_3$)$_2$ (19).** Yield: 11 mg (8 μmol, 64%). ^1H NMR (2:1 acetone-d_6/D_2O): δ 2.71 (s, 24H, NCH_3, η^3-NCN), 2.77 (s, 12H, NCH_3, η^2-CN), 3.90 (s, 4H, CH_2N, η^2-CN), 4.05 (s, 8H, CH_2N, η^3-NCN), 6.80 (d, $^3J_{H,H} = 7$ Hz, 4H, ArH-3,5, η^3-NCN), 6.96 (t, $^3J_{H,H} = 8$ Hz, 2H, ArH-4, η^3-NCN), 7.24−7.42 (m, 6H, ArH, η^2-CN), 7.62 (bs, 2H, ArH-10, η^2-CN), 8.17 (bs, 2H, ArH-11, η^2-CN), 8.74 (bs, 2H, ArH-9, η^2-CN), 9.09 (bs, 2H, ArH-8, η^2-CN). $^{13}C\{^1H\}$ NMR (0.95:0.05 acetone-d_6/D_2O): δ 50.3 (NCH_3, η^2-CN), 52.3 ($^3J_{Pt,C} = 61$ Hz, NCH_3, η^3-NCN), 73.9 (CH_2N, η^2-CN), 74.5 (CH_2N, η^3-NCN), 120.2, 120.2, 124.6, 125.8, 128.1, 129.6, 136.9, 139.7, 139.9, 141.5, 144.1, 144.9, 145.6, 149.2, 149.8, 150.9. Anal. Calcd for $C_{52}H_{68}N_{10}O_6Pd_2Pt$: C, 46.71; H, 5.13; N, 10.48. Found: C, 46.54; H, 5.06; N, 10.36.

Crystal Structure Determinations. X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating-anode and graphite monochromators ($\lambda = 0.710\,73$ Å) at a temperature of 150(2) K. The structures were solved with automated Patterson methods[13] and refined with SHELXL-97[14] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. The crystal structure of **16** contains large voids (1957.1 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by Fourier backtransformation using the routine SQUEEZE of the PLATON[15] package resulting in 636 electrons/unit cell.

Geometry calculations, drawings, and checks for higher symmetry were performed with the PLATON[15] package. Further crystallographic details are given in Table 1.

Results and Discussion

Synthesis and Characterization of Pyridyl-Functionalized Organoplatinum Complexes. Platination of *ortho*-chelating aminoaryl ligands is generally achieved via a sequence of two reactions involving the regioselective *ortho*-lithiation of the ligand first, followed by subsequent transmetalation with a *cis*- or *trans*-[PtX_2L_2] salt (X = Br, Cl, L = cod, SEt_2, SMe_2).[5,17] Initially, this route was applied for the synthesis of pyridyl-functionalized *C,N-ortho*-chelated

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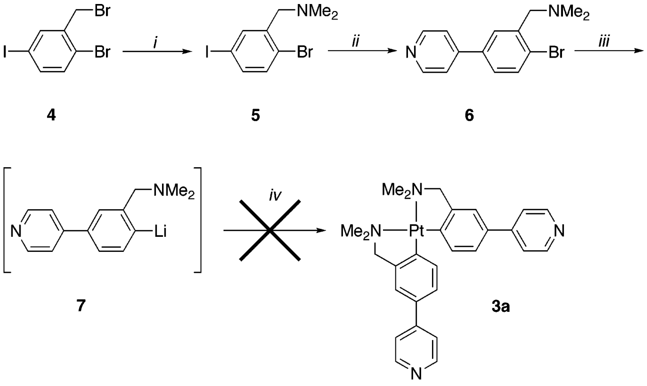
Scheme 1. Attempted Synthesis of 4-Pyridyl-Functionalized Corner Building Block **3a**[a]

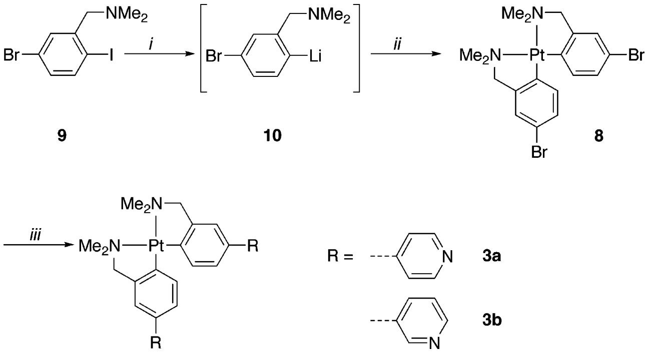


[a] (i) HNMe$_2$, Et$_2$O, RT, 2 h. (ii) 4-Pyridylborane pinacol ester, [PdCl$_2$(dppf)], Na$_2$CO$_3$, DME/THF/H$_2$O, ΔT, 40 h. (iii) *n*-BuLi, Et$_2$O, −78 °C, 10 min. (iv) [PtCl$_2$(cod)], Et$_2$O, −78 °C → RT, 3 h.

aminoaryl platinum(II) corner complexes, starting from 1-bromo-2-(bromomethyl)-4-iodobenzene (**4**)[7] (Scheme 1). The positions of the iodide and bromide substituents were chosen such that the *para*-position could be selectively addressed by a Suzuki−Miyaura C−C coupling reaction with 4-pyridylborane pinacol ester because of the higher reactivity of the C−I bond over the corresponding C−Br bond in C−C cross-coupling reactions. The Suzuki−Miyaura coupling reaction yielded **6** as an oil after purification via column chromatography in 65% yield. Chemoselective lithiation of **6** at the C−Br position was achieved by reacting **6** with 1 equiv of *n*-BuLi in Et$_2$O at −78 °C for 10 min. Quenching an aliquot of the reaction mixture with S$_2$Me$_2$, followed by analysis with ^{1}H NMR and GC−MS spectroscopy, confirmed that complete exchange of the bromo substituent for a methyl sulfide group had occurred. Under these reaction conditions, no trace of products resulting from the reaction of *n*-BuLi with the pyridyl ring was observed. However, the platination reaction of intermediate lithium complex **7** with 0.5 equiv of [PtCl$_2$(cod)] did not result in the formation of the *cis*-platinum(II) complex **3a**. Instead, the protonated ligand was obtained after workup. Variation in the reaction temperatures (−10 °C to reflux) and prolonged reaction times did not improve this result.

The alternative route toward the synthesis of functionalized organometallic complexes would involve the synthesis of the organometallic complex containing metal−carbon bonds prior to the subsequent organic functionalization reaction, via either lithiation or a metal-catalyzed C−C bond formation reaction. These kinds of nucleophilic substitution reactions are rarely performed on organometallic complexes, and the lithiation reactions have thus far been reported by Roper and co-workers and our group only.[6,18,19] Furthermore, a few examples of C−C cross-coupling reactions on organometallic complexes have been reported, i.e., Suzuki−Miyaura and Sonogashira reactions on organoosmium(IV) and -ruthenium(II) complexes.[20] We recently reported the palladium-catalyzed Suzuki−Miyaura cross-coupling reaction of a SCS-pincer borane compound (SCS = [C$_6$H$_3$(CH$_2$S*t*Bu)$_2$-1,3]$^-$) with bromide-functionalized [Pt(C,N)$_2$] complex **8**.[6] Following the same reaction procedure (Scheme 2), the synthesis of pyridyl-substituted [Pt(C,N)$_2$] (C,N = *C,N-ortho*-chelating ligand) complexes **3** could be achieved. Complex **8**, synthesized in 92% yield by the reaction of 0.5 equiv of [PtCl$_2$(cod)] with lithium complex **10**, is stable under basic conditions, which allows it to be used in a subsequent Suzuki−Miyaura coupling reaction. The reaction of **8** with either 4- or 3-pyridylborane pinacol ester in a mixture of DME, THF, and H$_2$O (1:1:1), with Na$_2$CO$_3$ and [PdCl$_2$(dppf)] (dppf = (diphenylphosphino)ferrocene) as the catalysts, was completed at 70 °C within 3 h. It is noteworthy that no decomposition of **8** was observed and conversion to *cis*-[Pt(4-{*p*-pyridyl}-dmba)$_2$] (**3a**) and *cis*-[Pt(4-{*m*-pyridyl}-dmba)$_2$] (**3b**) was quantitative (Scheme 2). Purification of the reaction mixtures by column chromatography afforded **3a** and **3b** in moderate to good yields as air- and moisture-stable, light-yellow-colored solids. No cis-to-trans isomerization of the complexes was observed during the reactions or purification of the products.

Scheme 2. Synthesis of Pyridyl-Functionalized Corner Molecules **3a** and **3b**[a]



[a] (i) *n*-BuLi, Et$_2$O, −78 °C, 10 min. (ii) *cis*-[PtCl$_2$(cod)], Et$_2$O, −78 °C, RT, 3 h. (iii) 4- or 3-pyridylborane pinacol ester (**a** and **b**, respectively), [PdCl$_2$(dppf)], Na$_2$CO$_3$, DME/THF/H$_2$O, 70 °C, 3 h.

Proof of the cis configuration of **3** was provided by the X-ray crystal structure of **3a**. Single crystals of **3a** suitable for an X-ray crystal structure determination were obtained by slow vapor diffusion of Et$_2$O into a saturated solution of **3a** in CH$_2$Cl$_2$. The molecular structure is depicted in Figure 1, and relevant bond lengths, bond angles, and torsion angles are listed in Table 2. The molecular structure of **3a** shows a slightly distorted square-planar platinum center bonded to two bidentate, *C,N*-chelating aminoaryl ligands in a cis configuration. This is reflected by the acute bite angles of the two *C,N* ligands at the platinum center, 80.44(14)° (N11−Pt1−C11) and 81.16(14)° (N21−Pt1−C21). These values are comparable to N−Pt−C angles of similar [*cis*-Pt(C,N)$_2$]

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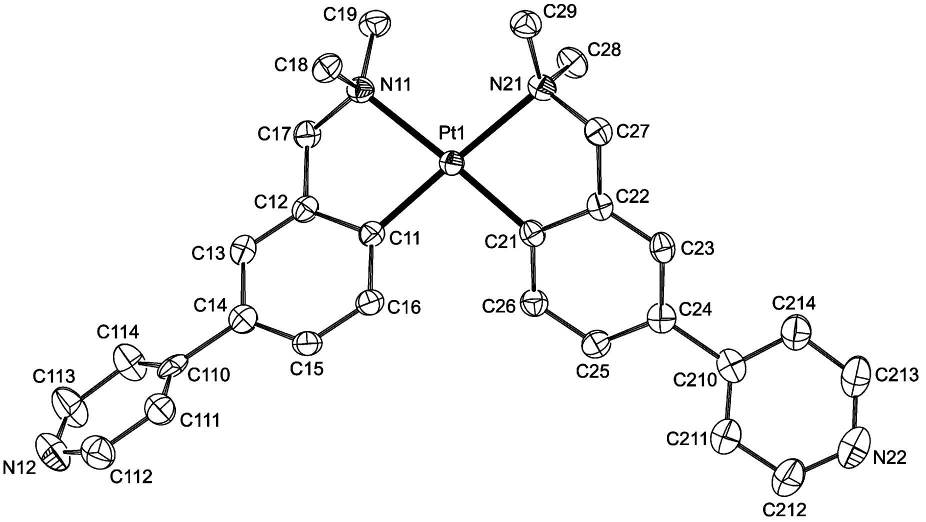

Figure 1. Displacement ellipsoid plot (50% probability level) of the molecular structure of **3a** in the crystal, with the adopted labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **3a**

Interatomic Distances			
Pt1−N11	2.191(3)	Pt1−N21	2.202(3)
Pt1−C11	1.980(4)	Pt1−C21	1.981(4)
Interatomic Angles and Torsion Angles			
N11−Pt1−N21	102.39(12)	C11−Pt1−C21	97.28(15)
N11−Pt1−C11	80.44(14)	N21−Pt1−C21	81.16(14)
N11−Pt1−C21	171.04(14)	N21−Pt1−C11	171.21(14)
N11−Pt1−C11−C12	15.4(3)	N21−Pt1−C21−C22	12.2(3)
C11−Pt1−C21−C26	29.8(4)	C21−Pt1−C11−C16	32.8(4)
C111−C110−C14−C15	33.5(6)	C211−C210−C24−C25	−26.9(6)

complexes (79.57−80.97°).[6] The two five-membered metallacycles are puckered, which is shown by the torsion angles of 15.4(3)° and 12.2(3)° for N11−Pt1−C11−C12 and N21−Pt1−C21−C22, respectively. The torsion angles around the platinum center are 32.9(4)° and 29.8(4)° for C21−Pt1−C11−C16 and C11−Pt1−C21−C26, respectively, showing that the structure is not completely flat (see Figure 4). The angles between the aryl and pyridyl rings of 33.5(6)° and −26.9(6)° (C15−C14−C110−C111 and C25−C24−C210−C211, respectively) fall in the range normally observed for similar compounds.[6] In the crystal of **3a**, there are short intermolecular contacts between the platinum center and the benzylic hydrogen atoms H17A and H27B, respectively, with distances of 2.81 and 2.92 Å, which is shorter than the sum of their contact radii.

Only one set of signals for both aminoaryl ligands was observed in the ^{1}H NMR spectra of **3** in CD_2Cl_2, indicating that in solution both complexes have an apparent C_{2v} symmetry on the NMR time scale. In the ^{1}H NMR spectra of **3a** and **3b**, singlets for CH_2NMe_2 protons with low $^3J_{Pt-H}$ couplings constants (11−16 Hz) were observed (Table 6), which confirmed the anticipated cis configuration of **3a** and **3b**.[5,6] Variable-temperature ^{1}H NMR experiments in the range of room temperature to −80 °C did not result in decoalescence of the singlet resonances of the benzylic protons, which demonstrates that even at low temperatures the interconversion process between the two possible diastereomers Δ and Λ is fast on the NMR time scale, as was already observed for precursor **8**.[6] The flexibility of **3a** and **3b** points to the possibility of using these complexes as flat corner molecules in closed molecular structures.

Synthesis and Characterization of $[M(NCN)(NO_3)]$ Complexes. To test the coordinative properties of the pyridyl nitrogen atoms in **3a**,**b**, complexation reactions with platinum and palladium NCN complexes were performed. Terdentate coordinating, monoanionic ECE-pincer ligand complexes (E = SR, NR_2, and PR_2) have been used in self-assembly reactions with Lewis bases to form coordination complexes,[21] polymers,[22] a triangle,[23] and organometallic dendrimers.[24] Recently, the use of the strong coordination bond between a NCN-pincer platinum(II) cation and pyridine in a template-assisted synthesis of heteromacrocycles has been reported.[10] Because the strength of complexation of a pyridine ligand to a metal center depends on the metal being used,[21c] we have chosen to use both cationic platinum(II) and palladium(II) pincer complexes, $[M(NCN)(NO_3)]$ (M = Pt (**11a**), Pd (**12a**)). These complexes were prepared from [MCl(NCN)] (M = Pt (**13**), Pd (**14**), respectively) via halide abstraction with silver nitrate (Scheme 3), according to the procedure reported for the synthesis of $[M(NCN)(OH_2)](BF_4)$ (M = Pt (**11c**), Pd (**12c**); Chart 2).[25]

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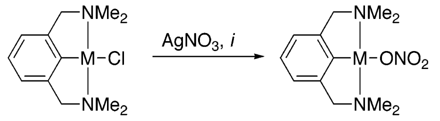
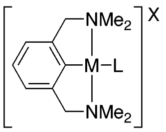
Scheme 3. Synthesis of Cationic Pincer Nitrate Complexes **11a** and **12a**[a]



M = Pt (**13**), Pd (**14**) M = Pt (**11a**), Pd (**12a**)

[a] (i) Acetone, RT, 16 h.

Chart 2. Pincer Platinum(II) and Palladium(II) Complexes **11** and **12**



M	L	X	
Pt	ONO_2^-	–	**11a**
Pt	OH_2	NO_3^-	**11b**
Pt	OH_2	BF_4^-	**11c**
Pd	ONO_2^-	–	**12a**
Pd	OH_2	NO_3^-	**12b**
Pd	OH_2	BF_4^-	**12c**

The coordinated nitrate anions can easily be replaced by pyridyl groups in self-assembly reactions (vide infra),[26] which are often carried out in aqueous solutions because of the good solubility of nitrate complexes in that environment. Although nitrate counteranions are commonly reported to be coordinated to platinum(II) and palladium(II) centers,[26] it has also been reported that in water-containing solutions the nitrate ligand can be replaced by a water molecule depending on the conditions employed, e.g., the water concentration.[27−29]

To investigate the nature of ligand coordination in aqueous media, i.e., to answer the question of whether the complexes are neutral with formula [M(NCN)(NO_3)] (M = Pt (**11a**), Pd (**12a**); Chart 2) or cationic with formula [M(NCN)(OH_2)](NO_3) (M = Pt (**11b**), Pd (**12b**)), we studied a series of Pt and Pd complexes by means of X-ray diffraction and IR and Raman spectroscopy.

Crystallization of water-free complex **11a** was carried out in both the absence and presence of H_2O. The X-ray crystal structure determination of **11a** with crystals obtained by layering a concentrated solution of **11a** in acetone with Et_2O showed it to be the expected monomeric nitrate complex. However, layering a concentrated solution of **11a** in an acetone/H_2O mixture (9:1, v/v) with Et_2O afforded suitable crystals of the water adduct of **11a**, [Pt(NCN)(NO_3)]·(H_2O) (**11a**·H_2O). The molecular structures are depicted in Figure 2, and relevant bond lengths, bond angles, and torsion angles are listed in Table 3. The molecular structures reveal platinum centers that are ligated by terdentate η^3-*N,C,N*-bound NCN ligands and monodentate η^3-*O*-bound NO_3^- anions. The Pt−O bond lengths (2.180(3) and 2.1780(17) Å for **11a** and **11a**·H_2O, respectively) are comparable to values reported for platinum(II)/nitrate complexes (2.135−2.18 Å).[30] The puckered five-membered chelate ring conformations, bond lengths, and bond angles of the Pt−NCN moieties fall in the range normally observed for square-planar platinum(II) complexes containing this type of ligand.[25,31] In the solid state, **11a**·H_2O is self-assembled into centrosymmetric dimers by hydrogen bonding between the H_2O molecules as the donor and the O atom from the nitrate group as the acceptor; i.e., it is the H_2O molecule that forms the bridges between two neutral [Pt(NCN)(NO_3)] entities. The interatomic distances between H1O···O3 and H2O···O1 are 2.20(4) and 2.12(5) Å, respectively, and the contact angles between O4−H1O···O3 and O4−H2O···O1 are both 158(4)°. Similar assemblies of cationic platinum and palladium complexes have been reported before.[29] However, in most cases the anions were bridging two cationic aqua complexes via hydrogen bonding. For example, for pincer platinum and palladium complexes, this resulted in the formation of a dimeric structure in the case of [Pt(NCN)(H_2O)](OSO_2CF_3)[31b] (**15**) and a polymeric structure for [Pd(NCN)(H_2O)](BF_4) (**12c**)[32] in the solid state (Chart 3).

Similar to **3a**, the crystal structure of **11a** has short intermolecular contacts between the platinum center and the benzylic hydrogen atoms H7A and H10A, respectively, with distances of 2.96 and 2.90 Å, which are shorter than the sum of their contact radii.

Raman and IR spectra of nitrate complexes have been widely used to gain information about the mode of coordination of the nitrate anion and the covalent character of the O−M bond. The planar symmetric free nitrate ion (NO_3^-) has four fundamental frequencies of absorption according to its D_{3h} symmetry.[33−35] However, when monodentate coordinated to a metal center, the symmetry of the nitrate is lowered to C_{2v} or C_s (as we observed) and the N−O(M) bond order is also reduced. As a result, variations on the modes and frequencies of vibration of the nitrate ligand will be observed. For instance, the degenerated modes (E′) of the free nitrate anion will split into the asymmetric and symmetric modes upon coordination.[36−39]

Solid-state IR spectra of complexes **11c** and **12c** with noncoordinating BF_4^- anions, which were used as models

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(35) Although the mode $\nu_1(A'_1)$ (NO stretching) is expected to be only active in Raman, it has been shown experimentally that this mode can be weakly IR-active because of the deformation of the nitrate ion in the molecular field of the crystals. See: Mizushima, S. I.; Quagliano, J. V. *J. Am. Chem. Soc.* **1953**, *75*, 4870.

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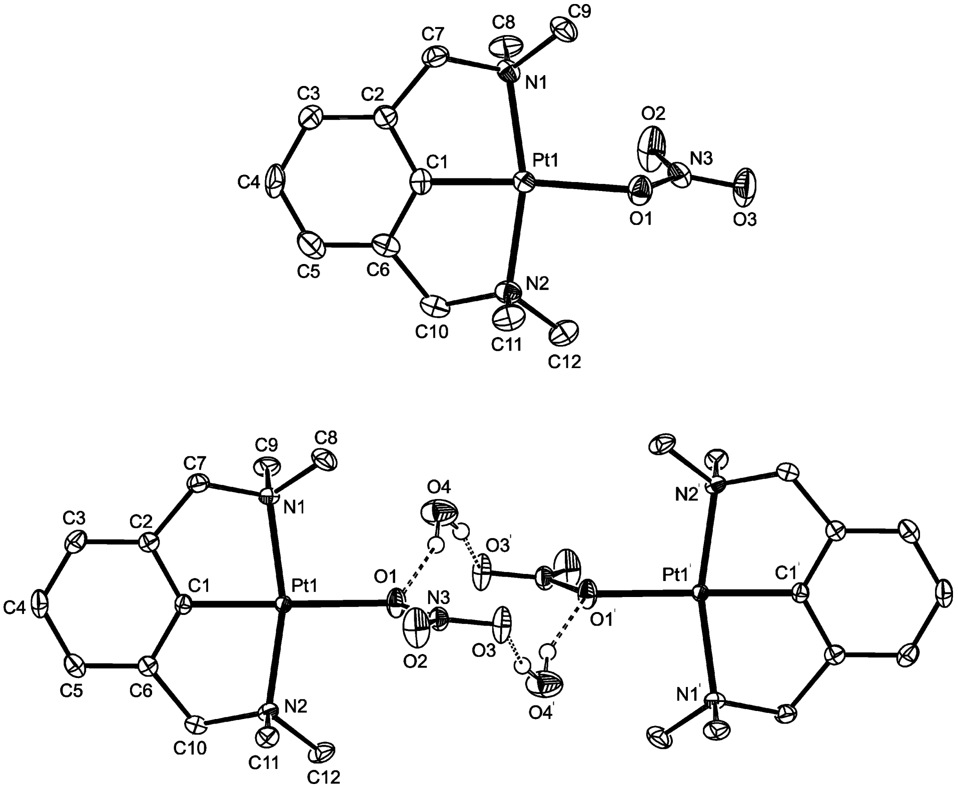

Figure 2. Displacement ellipsoid plot (50% probability level) of the molecular structure of **11a** (top) and a dimeric **11a**·H_2O (bottom), with the adopted labeling schemes. Hydrogen atoms (except for the water molecule) have been omitted for clarity (symmetry operation *i*: $1 - x$, $1 - y$, $1 - z$). Note that the H_2O molecules represent the bridges between the neutral [Pt(NCN)(NO_3)] entities.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **11a** and **11a**·H_2O

	11a	**11a**·H_2O
Interatomic Distances		
Pt1−N1	2.089(4)	2.0847(18)
Pt1−N2	2.087(4)	2.0847(18)
Pt1−C1	1.923(3)	1.908(2)
Pt1−O1	2.180(3)	2.1780(17)
O4−H1O, O4−H2O		0.81(4), 0.81(5)
H1O···O3^i, H2O···O1		2.20(4), 2.12(5)
O4····O3^i, O4····O1		2.972(3), 2.884(3)
Interatomic Angles and Torsion Angles		
N1−Pt1−N2	163.82(14)	164.25(8)
C1−Pt1−O1	173.0(4)	173.58(7)
N1−Pt1−C1	81.9(4)	82.35(9)
N2−Pt1−C1	82.0(4)	81.95(9)
O4−H1O···O3, O4−H2O···O1		158(4), 158(4)
N1−Pt1−C1−C2	−13.4(7)	−11.19(18)
N2−Pt1−C1−C6	−12.4(7)	−14.65(18)

of aqua-coordinated compounds, showed the typical intense absorption of H_2O at 3428 and 3468 cm^{-1}, respectively (Table 4). Complexes **11a** and **12a**, which were synthesized in technical acetone, did not show any significant H_2O absorptions, and the absorptions of coordinated nitrate ligands were unambiguously identified in the IR spectra. In general, the symmetric stretching band $\nu_1(A'_1)$ in the free NO_3^- ion appears around 1050 cm^{-1}, while for a purely covalent (N)O−C bond (O_2NOCH_3), this stretching band is observed at 854 cm^{-1}.[40] The energy difference Δ between the asymmetric and symmetric stretching modes $\nu_1(A')$ and $\nu_2(A')$ (in C_s symmetry), respectively, of the same compound, which appears for η^1-coordinated nitrate compounds as a result of the loss of degeneracy of the $\nu_3(E')$ mode of the nitrate ion, has also been used to measure the covalent character of the (N)O−M bond.[33,41] For example, the Δ value of nitromethane is 385 cm^{-1}, while for the free ion, it is zero. The observed energy differences $\Delta(\nu_1(A') - \nu_2(A'))$ and $(\nu_1(A'_1) - \nu_3(A'))$ between the symmetric stretching band of the free NO_3^- ion and the N−O(M) stretching of the coordinated nitrate ligand are listed in Table 4.

The split between the asymmetric and symmetric stretching modes $\nu_1(A')$ and $\nu_2(A')$ is larger in **11a** than in **12a**. The same trend is observed for the difference $\nu_1(A'_1) - \nu_3(A')$, indicating a more covalent character of the (N)O−Pt bond in comparison to (N)O−Pd.

The IR spectrum of crystals of the water adduct complex **11a**·H_2O showed only a small variation for the bands of the nitrate ligand in comparison to the water-free analogue **11a**, indicating NO_3 coordination to the metal. Two well-defined bands, for the asymmetric and symmetric (ν_3 and ν_1) O−H stretching modes, were observed for the water molecule. A thin weak absorption at 1613 cm^{-1} was also detected, which is characteristic for the bending mode of water in the crystal lattice. The appearance of these fine resolved bands can be the result of interactions of the water molecule through

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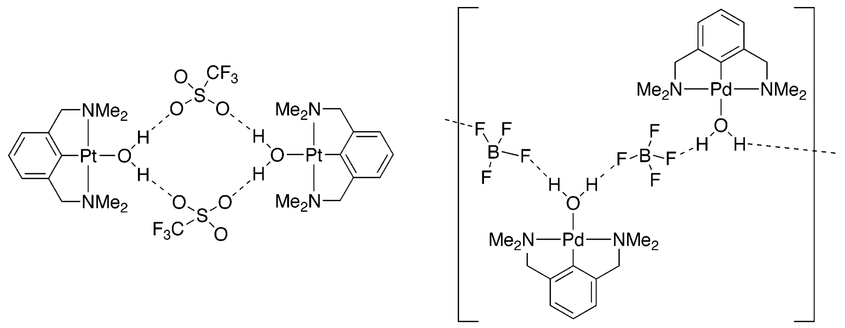
Chart 3. Hydrogen-Bonded Assemblies of **15** and **12c** in the Solid State[a,31b,32]



15

12c

[a] Note that the anions form the bridges between the $[M(NCN)(H_2O)]^+$ cations.

Table 4. Selected IR Bands (cm^{-1})[a] of NCN−Pt^{II} and −Pd^{II} Complexes[33]

complex	$\nu(H_2O)$ $(\nu_3)_{as}$, $(\nu_1)_{ss}$, $(\nu_2)_b$	$\nu_1(A')$ $(NO_2)_{as}$	$\nu_2(A')$ $(NO_2)_{ss}$	$\nu_3(A')$ $(N-OM)_s$	$\Delta(\nu_1(A') - \nu_2(A'))$	$\nu_1(A'_1)_{ss}$ (free NO_3)[b] − $\nu_3(A')_s$ (η^1-ON)
11a[c]		1417_s	1281_{vs}	1014_m	136	36
12a		1411_s	1289_{vs}	1027_m	122	23
11a·H_2O[c]	3573_s, 3494_m, 1613_w	1417_m	1286_{vs}	1008_m	131	42
11c	$3428_{vs(\nu3+\nu1)}$					
12c	$3468_{br(\nu3+\nu1)}$					

[a] Solid state. IR intensities: vs = very strong, s = strong, m = medium, w = weak, br = broad. Type of vibration: as = asymmetric stretching, ss = symmetric stretching, s = stretching, b = bending. [b] $\nu_1(A'_1) = 1050$ cm^{-1} for the free NO_3^- ion. [c] Samples measured from crystals obtained for X-ray spectroscopy.

hydrogen bonding with the nitrate ligand.[33] In contrast, for compounds **11c** and **12c** with water coordinated to the metal center, the stretching vibrations ν_3 and ν_1 appear as one broad signal.

Attempts to synthesize and isolate the cationic aqua complexes **11b** and **12b** in aqueous solution were carried out by dissolving complexes **11a** and **12a** in water and stirring for 16 h, followed by freeze-drying of the reaction mixtures. The IR spectra of the products pointed to coordination of an NO_3^- anion to the metal center. A weak band at 3571 cm^{-1} corresponding to the water molecule was also observed but could not unambiguously be determined as being from an aqua complex or free water.

Raman analysis was also carried out for complexes **11a**, **11b**, **12a**, and the crystals of **11a**·H_2O, both in the solid state and in aqueous solution to verify the presence of free NO_3^- anions. For all platinum compounds **11a**, **11a**·H_2O, and **11b**, two bands were observed in the solid state at ∼1039 and ∼1015 cm^{-1}, which correspond to free and coordinated NO_3^- anions, $\nu_1(A'_1)$ and $\nu_3(A')$, respectively. The peaks appeared in similar ratios with respect to each other (∼1:1). For the palladium complex **12a**, analogous peaks at 1038 and 1025 cm^{-1} were observed. On the other hand, Raman spectra of aqueous solutions of the complexes **11a**, **11a**·H_2O, **11b**, and **12a** showed only a strong signal at ∼1046 cm^{-1}, which is indicative of the presence of only noncoordinated nitrate anions.

IR measurements pointed toward the existence of pure $[M(NCN)(NO_3)]$ complexes **11a** and **12a** in the solid state because no significant signals for water were observed for **11a** and **12a**. The presence of aqua complexes $[M(NCN)(H_2O)](NO_3)$ in the samples of **11a** and **12a** was not observed by IR because of the fact that the symmetric NO stretching ($\nu_1(A'_1)$) of free nitrate is not IR-active.[35] The other vibration modes $\nu_3(E')$, $\nu_2(A''_2)$, and $\nu_4(E')$, which are active, were not observed because of overlap. On the contrary, from the Raman analysis, it can be concluded that both $[M(NCN)(NO_3)]$ and $[M(NCN)(H_2O)](NO_3)$ complexes were present in the samples of **11a** and **12a** because the signals of both free and coordinated nitrate were observed. It is likely that a dynamic exchange process between nitrate-to-metal (**11a** and **12a**) and water-to-metal (**11b** and **12b**) coordination exists during the synthesis or isolation of the complexes. This was also demonstrated by the Raman analysis in aqueous solutions, in which only complexes **11b** and **12b** were observed, indicating a complete shift of the equilibrium to water-to-metal coordination. This behavior was also observed for dissolution of $[PdL(NO_3)_2]$ (L = 1-methyl-2,2′-bipyridin-3-ylium) in water.[42]

It should be noted that the absence of coordinated water in the crystals of **11a** and **11a**·H_2O, measured with X-ray crystallographic studies, does not exclude the presence of the aqua complex **11b**. Attempts to crystallize complexes **11b** and **12b** from aqueous solutions were without success. These results indicate that only IR analysis and/or X-ray crystallography are not sufficient to confirm the presence or absence of water in these kinds of complexes, although conclusions have been drawn from results obtained by these techniques.[29,42,43] By Raman analysis, however, noncoordinated nitrate groups can be easily observed in the sample, providing definite proof for the presence of (non)coordinating nitrate anions.

Coordination Reactions with $[M(NCN)(NO_3)]$. The coordination reactions between solutions of **3a**,**b** and 2 equiv

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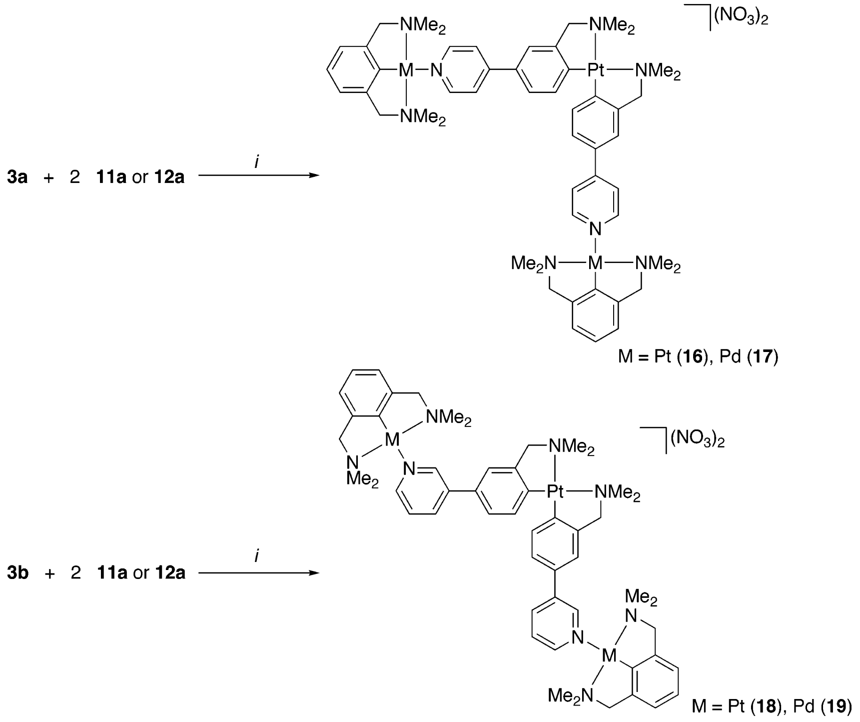
Scheme 4. Coordination Reactions of **3a** and **3b** with Cationic Platinum(II) and Palladium(II) Pincer Nitrate Complexes[a]



[a] (i) Acetone, H_2O, RT, 30 min.

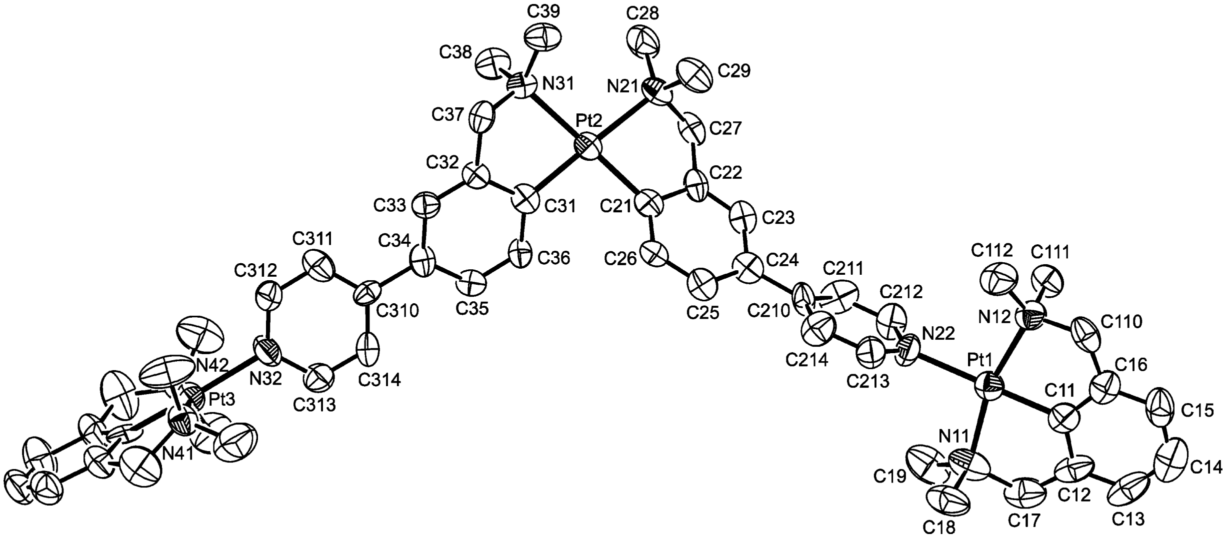


Figure 3. Displacement ellipsoid plot (50% probability level) of the molecular structure of the dication of trisplatinum complex **16**, with the adopted labeling scheme. Hydrogen atoms, disordered solvent molecules, and nitrate anions have been omitted for clarity.

of **11a** or **12a** in deuterated solvents (Scheme 4) were performed by stirring the mixtures for 30 min at room temperature, after which ^{1}H NMR spectra were recorded. The spectra showed in each reaction the formation of a single compound, i.e., corner complexes coordinated with the pyridyl groups to two metal pincer entities. The thus-formed dicationic trinuclear complexes **16**−**19** were isolated as light-yellow solids by slow precipitation with Et_2O.

Single crystals of complex **16** suitable for an X-ray crystal structure determination were obtained by slow diffusion of Et_2O into a concentrated acetone/H_2O (2:1) mixture. The molecular structure is depicted in Figure 3, and relevant bond lengths, bond angles, and torsion angles are listed in Table 5. The molecular structure of **16** shows the same cis conformation of the central moiety as was present in **3a**, with similar angles and distances. To both pyridyl groups is coordinated the NCN-platinum(II) complex in a trans fashion (179.1(3)° N22−Pt1−C11 and 177.2(3)° N32−Pt3−C41). The pincer platinum moieties are placed nearly perpendicular to the pyridyl planes, with torsion angles of 91.1(7)° and 83.6(7)° for N11−Pt1−N22−C213 and N41−Pt3−N32−C313, respectively. These values are consistent with those observed for related NCN−Pt-pyridyl complexes.[10] The Pt−N(pyridyl) distances (2.141(6) Å for both Pt1−N22 and Pt3−N32) agree with those observed for *trans*-pyridyl-coordinated N∧C∧N ligands ([Pt(pip$_2$NCN)(py)]$^+$ (2.138−2.159 Å)[21b,d]

Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **16**

Interatomic Distances			
Pt2−N21	2.197(7)	Pt2−N31	2.203(8)
Pt2−C21	1.997(12)	Pt2−C31	1.973(7)
Pt1−N11	2.073(7)	Pt3−N41	2.074(7)
Pt1−N12	2.072(7)	Pt3−N42	2.073(7)
Pt1−N22	2.141(6)	Pt1−C11	1.942(11)
Pt3−N32	2.141(6)	Pt3−C41	1.820(9)
Interatomic Angles and Torsion Angles			
N21−Pt2−N31	102.1(3)	C21−Pt2−C31	97.2(4)
N21−Pt2−C31	170.4(3), 171.2(3)	N21−Pt2−C21	80.9(4)
N31−Pt2−C21		N31−Pt2−C31	81.2(3)
N11−Pt1−N12	164.8(4)	N22−Pt1−C11	179.2(3)
N41−Pt3−N42	164.4(3)	N32−Pt3−C41	177.2(4)
N11−Pt1−C11	82.9(4)	N41−Pt3−C41	83.5(3)
N12−Pt1−C11	82.0(4)	N42−Pt3−C41	80.9(3)
C21−Pt2−C31−C36	−31.0(8)	C31−Pt2−C21−C26	−36.2(8)
C211−C210−C24−C23	−29.4(15)	C311−C310−C34−C33	23.5(11)
N11−Pt1−C11−C12	11.1(7)	N41−Pt3−C41−C42	−2.8(6)
N12−Pt1−C11−C16	9.3(7)	N42−Pt3−C41−C46	−11.3(7)
N11−Pt1−N22−C213	91.1(7)	N41−Pt3−N32−C313	83.6(7)

Table 6. Selected ^{1}H NMR Data for Complexes **3** and **16**−**21**[a]

	NMe$_2$ ($^3J_{\mathrm{Pt-H}}$)		CH$_2$N ($^3J_{\mathrm{Pt-H}}$)		pyridyl protons	
complex	η^2-CN	η^3-NCN	η^2-CN	η^3-NCN	α	β
3a[b]	2.86 (11)		3.99 (16)		8.59 (d)	7.58 (d)
3b[b]	2.84		3.96		8.85, 8.48 (d)	7.87
16[c]	2.88	2.79	3.95	4.18	8.91 (d)	8.01 (d)
17[c]	2.78	2.64	3.93	4.04	8.81 (bs)	7.87 (bs)
18[c]	2.79	2.82	3.93	4.20	9.21, 8.91 (d)	8.29 (d)
19[c]	2.77	2.71	3.90	4.05	9.09 (bs), 8.74 (bs)	8.17 (bs)
20[c]	2.79	2.79	3.92, 3.93	4.18	8.90 (d), 8.46 (d)	8.00 (d), 7.59 (d)
21[c]	2.78	2.67	3.92	4.08	8.74 (bs)	7.80 (bs)

[a] Chemical shifts in ppm, coupling in hertz, singlet resonances unless stated otherwise, doublet (d), broad singlet (bs), 25 °C. [b] In CD$_2$Cl$_2$ solutions. [c] In acetone-d_6/D$_2$O (2:1) solutions.

and [Pt(NCN)(py)]$^+$ (2.183−2.192 Å).[10,21c] The puckered five-membered chelate ring conformations, bond lengths, and bond angles of the Pt−NCN moieties fall in the range normally observed for square-planar platinum(II) complexes containing this type of ligand.[25,31]

Although both complexes **3a** and **16** have distorted square-planar geometries with torsion angles between 29.8(4)° and 36.2(7)° (Figure 4) for the aryl rings around the platinum center, this should not hamper the possible formation of closed and flat molecular structures such as molecular squares. These complexes have proven to be very flexible in solution because twisting of the arene rings with respect to each other was even observed at low temperatures (vide infra).[6]

Structure in Solution. The ^{1}H NMR spectra of complexes **16**−**19** were recorded in an acetone-d_6/D$_2$O mixture (2:1). The signals attributable to the NMe$_2$ and benzylic protons of the *cis*-coordinated dmba ligands are similar to those observed for complexes **3a** or **3b**, respectively (see Table 6). The pyridyl resonances appear as a set of doublets for **16** and two broad singlets for **17**. For **18**, these resonances appear as two doublets, a triplet, and a singlet, and for **19**, four broad signals were observed. With respect to the corresponding free pyridine complexes, a downfield shift for the resonances attributable to the α protons of the pyridyl groups was observed for platinum complexes **16** and **18** (Δδ(H) = 0.32−0.43 ppm), confirming coordination of the pyridyl groups to the platinum centers.[21b,d] The α proton pyridyl resonances of palladium complexes **17** and **19** showed a similar downfield shift, although considerably smaller (Δδ(H) = 0.22−0.26 ppm), while the signals are more broadened. This is a consequence of the weaker nitrogen-to-metal coordination bond in the case of palladium.

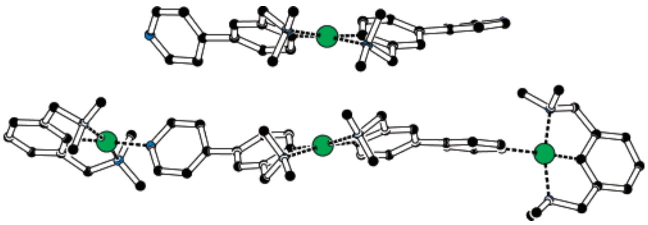


Figure 4. PLUTON plot of the side views of **3a** (top) and the dication of **16** (bottom).

To determine the difference in the coordination behavior of the analogous palladium complex versus the cationic platinum pincer complex, **11** and **12** were reacted in a 1:1 ratio with **3a**, forming [*cis*-Pt(4-{*p*-pyridyl}dmba)$_2$[Pt(NCN)]](NO$_3$) (**20**) and [*cis*-Pt(4-{*p*-pyridyl}dmba)$_2$[Pd(NCN)]](NO$_3$) (**21**), respectively. In the case of the mono-NCN-platinum complex **20**, ^{1}H NMR spectroscopy revealed two sets of sharp resonances for coordinated and noncoordinated pyridyl groups in a 1:1 ratio, indicating that the exchange reaction for the coordination complex in solution is slow or nonexistent on the NMR time scale. In contrast, the mono-NCN-palladium complex **21** undergoes a fast exchange reaction, showing in its ^{1}H NMR spectrum an average resonance pattern for the α and β protons from the coordinated and noncoordinated pyridyl groups at 7.80 and 8.74 ppm. This is an upfield shift $\Delta\delta$(H) amounting to 0.07 ppm, as compared to **17**.[21c]

In addition, variable-temperature ^{1}H NMR experiments were carried out to further monitor the coordination behavior of **16**−**19**. For the platinum complexes **16** and **18**, no significant spectral differences were observed in a temperature range of −35 to +55 °C. A small upfield shift of $\Delta\delta$(H) ∼ 0.03 ppm of the α protons of the pyridyl groups was noted upon warming of solutions of **16** and **18** in a mixture of acetone-d_6 and D_2O (2:1, v/v) from −35 to +55 °C. At +55 °C, the resonances still appear as sharp signals, indicating that exchange reactions are still slow at this temperature. It can, therefore, be concluded that the Pt−N bond strength is larger than that of the Pd−N bond. The palladium complexes **17** and **19** showed a significantly larger shift of 0.18−0.28 ppm upon increasing the temperature from −35 to +55 °C, while sharpening of these signals was also observed. Variable-temperature ^{1}H NMR experiments for the mono-NCN-platinum complex **20** showed in the temperature range of −35 to +55 °C no significant chemical shift changes. However, the ^{1}H NMR spectrum of **21** at −35 °C showed four resonances for coordinated and noncoordinated pyridyl groups in a 1:1 ratio at 8.90, 8.44, 7.97, and 7.59 ppm, identical with the chemical shifts of **20** at 25 °C. This indicates that below −35 °C the exchange reaction reaches the slow exchange limit. As was observed for complexes **3**, the assembled complexes **16**−**19** have a C_{2v} symmetry in solution in the complete measured temperature region. As expected, the pincer metal groups do not hinder twisting of the arene rings around the platinum center.

Conclusions

Two neutral homoleptic, pyridyl-functionalized bis(*C*,*N*-*ortho*-chelated aminoaryl) platinum(II) corner complexes were synthesized via an unconventional procedure, which implies first the synthesis of a homoleptic bromide-functionalized precursor platinum(II) complex and second the subsequent functionalization with pyridyl groups in Suzuki−Miyaura C−C coupling reactions. The pyridyl-functionalized corner complexes were active as 2-fold Lewis bases in coordination reactions with the cations of NCN-platinum(II) and palladium(II) nitrate complexes, resulting in the formation of dicationic trimetallic coordination complexes. The pyridyl-functionalized corner complexes show excellent potential to be used as Lewis base functionalized corner complexes for the synthesis of larger self-assembled molecular architectures. Further studies in this direction are currently under investigation. With IR and Raman analysis, it was found that for the NCN−Pt^{II} and −Pd^{II} complexes **11** and **12** both nitrate anions and water molecules are coordinated to the metal centers. In aqueous solutions, however, only aqua complexes [M(NCN)(OH_2)](NO_3) were observed, indicating a complete shift in the equilibrium toward water-to-metal coordination.

Acknowledgment. M.L. and A.L.S. kindly acknowledge the Netherlands Organization for Scientific Research (NWO) for financial support.

Supporting Information Available: CIF data for **3a**, **11a**, **11a**·H_2O, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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