New *cis*- and *trans*-Arylplatinum(II) Acetylide Compounds Containing a Bis(imino)aryl [NCN] Ligand

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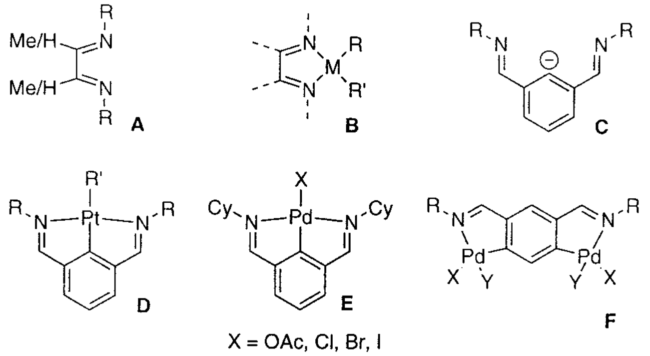
*Summary: The first platinum(II) halogenide compounds containing the (σ^3-N,C,N)isophtalaldimine ligand, **2a** and **2b**, have been prepared via an oxidative addition of the bromoisophthalaldimine ligands **1a** and **1b** to a Pt(0) precursor. Depending on the imine substituents, the reaction of these compounds with $LiC{\equiv}CSiMe_3$ in THF results in a monomeric trans-diorganoplatinum(II) compound (**3**) or a dimeric cis-diorganoplatinum(II) compound (**4**). Both **3** and **4** have been characterized by means of an X-ray crystal structure determination.*

Introduction

Cis- as well as *trans*-diorganometallic compounds of palladium and platinum are relevant to mechanistic considerations concerning C−C bond formation and C−C bond activation reactions.[1,2] Recently, we have worked on the organometallic chemistry of late transition metals involving bidentate nitrogen ligands. Apart from the coordination chemistry of α-diimine ligands (**A**, Chart 1) such as DAB and BIAN, the use of many Pd and Pt complexes containing such ligands in carbon−element bond forming reactions has been studied.[3] Employing bidentate coordinating α-diimine ligands, exclusively compounds with *cis* configuration can be obtained in a square planar diorganometallic compound **B** (Chart 1). In contrast, by using a meridional coordinating ligand of type **C** (Chart 1) in principle a *trans*-diorganoplatinum compound **D** (Chart 1, R′ = a carbon fragment) can be synthesized.

Ligand **C** can be seen as a meridional coordinating ligand of type $[D{-}C{-}D]^-$, in which two imine moieties are used as donor groups. Since the first publication by Shaw[4] concerning a $[P{-}C{-}P]^-$ ligand, the organometallic chemistry of tridentate ligands of this type has rapidly expanded. Apart from $[P{-}C{-}P]^-$ [1,5] also $[N{-}C{-}N]^-$,[6] $[S{-}C{-}S]^-$,[7] and $[O{-}C{-}O]^-$ [8] ligands have been investigated. Whereas the bis(amino) $[N{-}C{-}N]^-$ ligand has extensively been investigated, to our knowledge the tridentate coordination chemistry of the bis(imino) $[N{-}C{-}N]^-$ ligand, **C**, has hardly been studied.[9] Only one publication by Vila et al. has appeared concerning palladium(II) derivatives of **C** (**E**, Chart 1),[10a] which have not been further investigated.[10b] Other examples containing 1,3-bis(imino)aryl ligands are limited to compounds **F** (Chart 1), where the ligand bridges two metals after a double ortho-metalation reaction.[11]

Chart 1



As indicated above, we are particularly interested in *trans*-diorganoplatinum compounds of type **D** (Chart 1), which should be accessible by transmetalation of a

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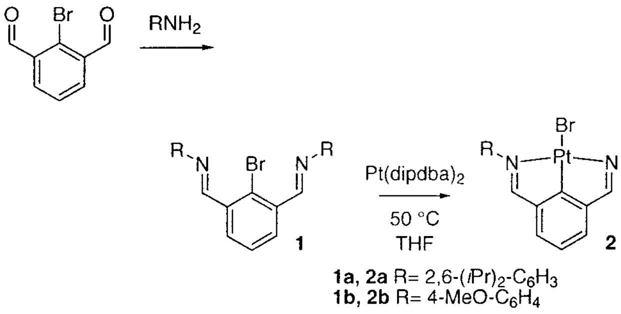
Scheme 1



Pt(II) halogenide analogue of **E**. *Trans*-diorganometallic compounds of the related bis(dimethylamine) [N−C−N]$^-$ ligand have been synthesized and studied before, e.g., by van Koten et al.[12]

Results and Discussion

The synthesis of the platinum(II) bromide precursors is shown in Scheme 1. Starting from 2-bromoisophthalaldehyde,[13] the novel bisimines **1a** (R = 2,6-(*i*-Pr)$_2$-C$_6$H$_3$) and **1b** (R = 4-MeO-C$_6$H$_4$) were synthesized via a condensation reaction in good yields (76% and 94%, respectively). The oxidative addition reactions of the C−Br bond of **1a** and **1b** to a suitable Pt(0) precursor[6c] (Pt(dipdba)$_2$ [14]) in THF at 50 °C resulted in the formation of **2a** and **2b**. After separation from free dipdba by washing, compounds **2a** (63%, orange) and **2b** (64%, reddish brown) were isolated as air stable solids after crystallization.

From the ^{1}H and ^{13}C NMR spectra of **2a** and **2b** it can be concluded that the imine groups are equivalent and coordinating to the platinum atom, as appears from the isochronicity and the large couplings between the imine proton and the ^{195}Pt isotope. For **2a** and **2b** the $^3J(^1H,^{195}Pt)$ couplings are 144 and 139 Hz, respectively. In the ^{13}C NMR spectrum of **2a** and **2b** the *ipso* carbon bound to platinum is found at high frequency, and the expected large $^1J(^{13}C,^{195}Pt)$ coupling is observed (δ = 179 ppm, J = 927 Hz and δ = 175 ppm, J = 938 Hz, respectively).[12c]

After the synthesis of these platinum(II) bromide precursors, we reacted **2a** and **2b** with LiC≡CSiMe$_3$ to investigate whether *trans*-arylplatinum(II) acetylides compounds could be obtained. The reaction of **2a** and LiC≡CSiMe$_3$ in THF at −60 °C and warming up to 20 °C resulted in the complete conversion of **2a** to **3** (Scheme 2), as evidenced by an additional resonance in the ^{1}H NMR spectrum at δ = −0.42 ppm.[12b,c] It is noteworthy that the $^3J(^1H,^{195}Pt)$ of the imine proton decreases to 133 Hz due to the *cis* influence of the acetylide. In the ^{13}C NMR spectrum the *ipso* phenyl carbon bound to the platinum shifts to 199 ppm and the $^1J(^{13}C,^{195}Pt)$ decreases from 927 Hz in **2a** to 616 Hz in **3**, as a result of the strong *trans* influence of the acetylide. The molecular structure of **3** is depicted in Figure 1, and selected bond lengths and angles are given in the figure caption.

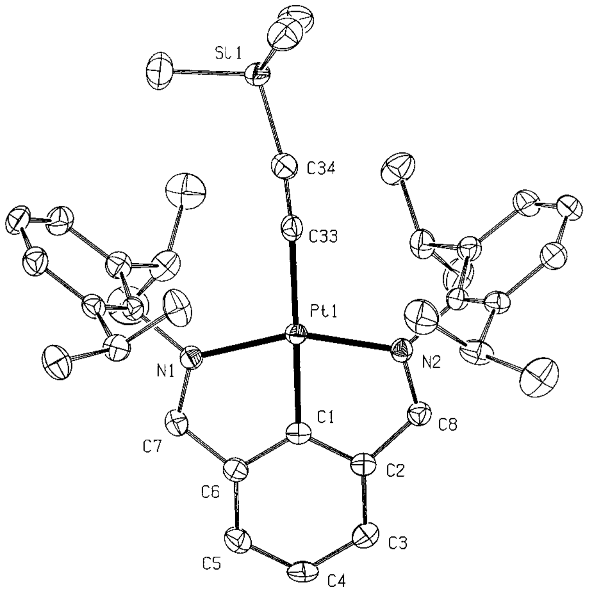
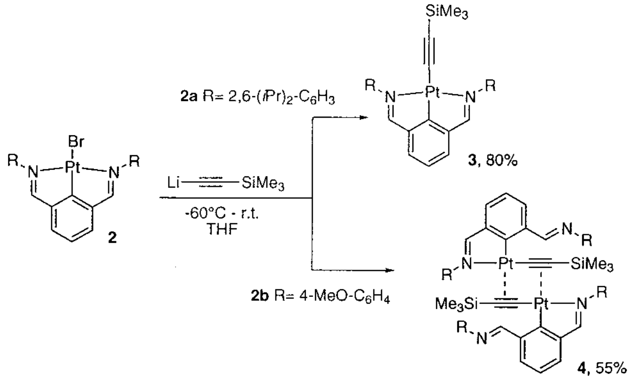


Figure 1. Displacement ellipsoid plot of **3** with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.050(2); Pt(1)−N(2) 2.043(2); Pt(1)−C(1) 1.945(2); Pt(1)−C(33) 2.065(3); C(33)−C(34) 1.200(4); N(1)−C(7) 1.306(3); N(2)−C(8) 1.303(3). N(1)−Pt(1)−N(2) 157.21(9); C(1)−Pt(1)−C(33) 178.41(9); C(1)−Pt(1)−N(1) 78.55(9); C(1)−Pt(1)−N(2) 78.76(9); Pt(1)−C(33)−C(34) 174.5(2); C(33)−C(34)−Si(1) 169.1(2).

Scheme 2



In the crystal structure the platinum has a distorted square planar environment with a sum of *cis* angles of 359.9°. The N−Pt−C angles of the five-membered chelate rings amount to 78.55(9)° and 78.76(9)°, which is significantly smaller than the ideal values of 90° and is caused by ring strain. This also leads to a distorted *trans* N−Pt−N angle of 157.21(9)°, which is slightly smaller compared to compounds derived from the bis(dimethylamine) [N−C−N]$^-$ ligand system, which is probably due to the higher strain arising from the shorter imine C=NR double bond as compared to the amine C−NR$_2$ single bond.[15] The Pt−C$_{aryl}$ and Pt−N bond lengths have expected values, 1.945(2) and 2.043(2)−2.050(2) Å, respectively. The acetylide group is coordinated *end-on* with a Pt−C$_{acetylide}$ bond length of 2.065(2) Å, which is relatively long,[16] probably caused

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by the small N−Pt−N angle and the *trans* influence of the aryl group.

The substituent on the imine group seems to have a distinct effect on the structure of the compounds formed in a reaction of **2a** and **2b** and $LiC{\equiv}CSiMe_3$. Whereas the reaction of **2a** (R = 2,6-(i-Pr)$_2$-C_6H_3) and $LiC{\equiv}CSiMe_3$ resulted in the formation of the *trans* diorganoplatinum compound **3**, in an analogous reaction of **2b** (R = 4-MeO-C_6H_4), a different reaction product was obtained.

^{1}H NMR spectroscopic analysis of the reaction mixture obtained by addition of $LiC{\equiv}CSiMe_3$ to **2b** (R = 4-MeO-C_6H_4) in THF at −60 °C and warming up to 20 °C showed two inequivalent imine moieties (HC=N at 10.1 and 7.4 ppm). The 10.1 ppm resonance belongs to an uncoordinated imine moiety, and for the coordinating imine moiety at 7.4 ppm, the small $^3J(^1H,^{195}Pt)$ of 73 Hz as compared to the starting material (139 Hz) pointed at an acetylide group *trans* to this imine. We suggested that the acetylide moiety was in a configuration *cis* to the central aryl carbon and that the compound had dimerized across the Pt−acetylide moiety to furnish **4** (Scheme 2). This was supported by the infrared spectrum of a solid sample in which the triple bond resonated at a lower wavenumber ($\nu_{C\equiv C}$ = 1949 cm^{-1}) compared to **3** ($\nu_{C\equiv C}$ = 2032 cm^{-1}), indeed pointing to a side-on coordination of the acetylide. FD-MS showed the existence of a dimeric species. The molecular structure of **4** was unambiguously proven by an X-ray structure analysis. From the above-mentioned ^{1}H NMR data, ^{1}H NOE experiments, and IR spectroscopy of a benzene solution of **4** it was concluded that **4** is also dimeric in solution.

The molecular structure of **4** is depicted in Figure 2, and selected bond lengths and angles are given in the figure caption. Compound **4** is a dimer with two acetylide units acting as bridging ligands. They are each coordinated *end-on* to one and *side-on* to the other platinum, respectively. The Pt1···Pt2 distance is 3.15573(19) Å, indicating that there is no bonding interaction. As expected, the Pt−C$_{acetylide}$ *end-on* distances of 1.945(3) and 1.935(4) Å are much smaller than the Pt−C$_{acetylide}$ *side-on* distances of 2.330(3)−2.397(3) Å. The different coordination mode of the acetylide unit in compounds **4** and **3** is not reflected in the C≡C distances, which are the same within standard deviations. The Pt−C$_{aryl}$ distance is slightly smaller in **3** than in **4**, which probably is a consequence of the tridentate coordination in **3** as compared to the bidentate coordination in **4**.

The core of compound **4** can be considered as a six-membered Pt−C−C−Pt−C−C ring. This ring is not planar, but severely puckered with a dihedral angle of 75.07(12)° between the two Pt−C−C−Pt units. This means that the $Pt_2(C{\equiv}C)_2$ core is much more puckered than in a structure published by Forniés,[17] in which the analogous dihedral angle is 45°. We conclude that this geometry is strongly dependent on the steric demands of the ligand system.

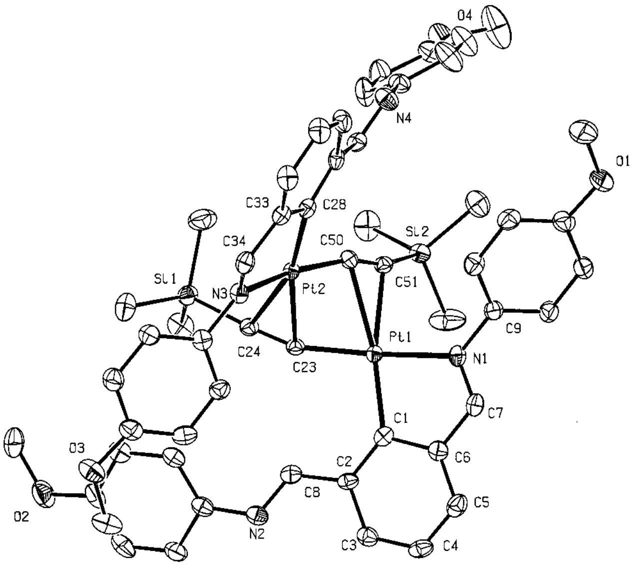

Figure 2. Displacement ellipsoid plot of **4** with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.087(3); Pt(2)−N(3) 2.090(3); Pt(1)−C(1) 2.018(3); Pt(2)−C(28) 2.010(3); Pt(1)−C(23) 1.945(3); Pt(2)−C(50) 1.935(4); Pt(1)−C(50) 2.376(3); Pt(1)−C(51) 2.330(3); Pt(2)−C(23) 2.397(3); Pt(2)−C(24) 2.335(3); C(23)−C(24) 1.228(5); C(50)−C(51) 1.231(5). C(1)−Pt(1)−N(1) 81.01(12); C(28)−Pt(2)−N(3) 80.54(13); N(1)−Pt(1)−C(23) 170.93(14); N(3)−Pt(2)−C(50) 169.65(13); C(1)−Pt(1)−C(23) 102.20(13); C(28)−Pt(2)−C(50) 99.69(14); Pt(1)−C(23)−C(24) 161.7(3); Pt(2)−C(50)−C(51) 165.0(3); Pt(1)−C(23)−Pt(2) 92.63(12); Pt(1)−C(50)−Pt(2) 93.57(14); C(23)−C(24)−Si(1) 158.1(3); C(50)−C(51)−Si(2) 159.5(3).

Although organometallic compounds that are dimers via π-coordination of a M−C≡C moiety are known (M = Ti,[18] Zr,[19] Rh, Ir,[20] Re,[21] and Pt[17,22]), such compounds remain relatively rare. Moreover, most of these were synthesized from dimeric precursors ($[L_xM{-}Cl]_2$, Ir, Rh, Ti, Zr) or by exchange of the acetylide between the two metal centers (Pt, Zr). Clearly in the case of **4** the $Pt_2(C{\equiv}C)_2$ core results from a dimerization of two independently formed Pt−C≡C−R units.

Conclusion

It is shown that the coordination properties of the imine moiety are strongly influenced by the electronic and steric effects of its substituent. The difference in lability of the imine moieties bearing 2,6-(i-Pr)$_2$-C_6H_3 or 4-MeO-C_6H_4 groups directs the reaction pathway to the formation of **3** or **4**, respectively.

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Experimental Section

General Comments. All reactions were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use, according to standard methods. In NMR spectra positive chemical shifts (δ) are denoted downfield from an external TMS reference. HRMS measurements were performed on a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system. IR spectra were measured on a Biorad FTS-7 spectrophotometer of a KBr pellet, unless stated otherwise. Elemental analyses were carried out at H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr. Melting points are uncorrected.

Materials. 2-Bromoisopthalaldehyde[13] and Pt(dipdba)$_2$ [14] were synthesized according to literature procedures, $LiC\equiv CSiMe_3$ was prepared from $HC\equiv CSiMe_3$ in THF and *n*-BuLi in hexane, and all other starting materials were obtained from commercial sources and used as received. The synthesis and characterization of compounds **1a**,**b** and **2a**,**b** is described in the Supporting Information.

***σ*-Trimethylsilylethynyl-*N*,*N*′-bis(2,6-diisopropylphenyl)isophthalaldimine-2-ylplatina(II) (3).** To a solution of **2a** (100 mg, 0.138 mmol) in THF (20 mL) at −60 °C was added a solution of $LiC\equiv CSiMe_3$ 0.068 M in THF (2.2 mL, 0.152 mmol, 1.1 equiv). After slow warming up to 20 °C the solvent was evaporated in vacuo and the residue was extracted with 10 mL of pentane. After evaporation of the solvent in vacuo the residue was crystallized from MeOH. After standing at −20 °C for 4 days, the orange crystals were isolated by the removal of the mother liquor. Washing with a little cold MeOH and drying in vacuo yielded 81.8 mg (0.11 mmol, 80%) of orange crystals. Mp: 160 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (s, $^3J(^1H^{195}Pt) = 133$ Hz, 2H; $HC{=}N$) 7.77 (d, $J = 7.8$ Hz, 2H) 7.35 (t, $J = 7.8$ Hz, 1H) 7.17 (m, 6H) 3.16 (septet, $J = 7$ Hz, 4H; CH_3CHCH_3) 1.26 (d, $J = 7$ Hz, 24H; CH_3CHCH_3) 1.16 (d, $J = 6.5$ Hz, 24H; CH_3CHCH_3) −0.42 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.9 ($^1J(^{13}C^{195}Pt) = 616$ Hz, C−Pt) 179.8 ($^2J(^{13}C^{195}Pt) = 73$ Hz, $C{=}N{-}C$) 154.8 ($^1J(^{13}C^{195}Pt) = 1048$ Hz, Pt−*C*CSi) 147.3 ($C{=}N{-}C$) 144.5 ($^2J(^{13}C^{195}Pt) = 95$ Hz, C) 141.5 (C) 127.4 (CH) 127.2 (CH) 123.0 (CH) 123.0 (CH) 115.5 ($^2J(^{13}C^{195}Pt) = 211$ Hz, Pt-C*C*Si) 27.9 (CH_3CHCH_3) 24.4 (CH_3CHCH_3) 23.0 (CH_3CHCH_3) 1.24 ($Si(CH_3)_3$). HRMS(FAB): *m/z* calcd ($[M - H]^+$ $C_{37}H_{49}N_2SiPt$) 744.3315. Found: 744.3331. Anal. Calcd for $C_{37}H_{48}N_2PtSi$: C, 59.73; H, 6.50; N, 3.77. Found: C, 59.80; H, 6.55; N, 3.82. Single crystals suitable for X-ray structure determination were obtained by slow cooling of a methanolic solution from 20 to −20 °C.

***σ*,*μ*^{2}-Trimethylsilylethynyl-*N*,*N*′-bis(4-methoxyphenyl)isophthalaldimine-2-ylplatina(II) Dimer (4).** To a solution of **2b** (101.6 mg, 0.164 mmol) in THF (25 mL) at −60 °C was added a solution of $LiC\equiv CSiMe_3$ 0.068 M in THF (2.7 mL, 0.18 mmol, 1.1 equiv). After stirring at −60 °C for 30 min, the mixture was allowed to warm to 20 °C. After stirring at 20 °C for 16 h, the solvent was evaporated. The residue was extracted with 15 mL of a 1:1 pentane/CH_2Cl_2 mixture. After evaporation of the solvent in vacuo the residue was washed twice with pentane (10 mL) and crystallized by a slow diffusion of pentane into a concentrated CH_2Cl_2 solution. Washing of the product with 10 mL of pentane and drying in vacuo yielded 58 mg (0.91 mmol, 55%) of the dimeric product as a dark brown solid. Mp: 220 °C decomp. ^{1}H NMR (500 MHz, C_6D_6): δ 10.1 (s, 2H; $HC{=}N$) 8.96 (d, $J = 8$ Hz, 2H) 7.42 (s, $^3J(^1H^{195}Pt) = 73$ Hz, 2H; $HC{=}N$) 7.41 (d, $J = 9$ Hz, 4H) 7.11 (dd, $J = 8$ Hz, $J = 7$ Hz, 2H) 7.08 (d, $J = 9$ Hz, 4H) 6.99 (d, $J = 7$ Hz, 2H) 6.82 (d, $J = 9$ Hz, 4H) 6.77 (d, $J = 9$ Hz, 4H) 3.37 (s, 3H; OCH_3) 3.26 (s, 3H; OCH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 176.9 ($C{=}N{-}Pt$) 164.8 ($C{=}N$) 159.2 ($COCH_3$) 158.4 ($COCH_3$) 153.7 (C−Pt) 148.9 ($C{-}C{=}N{-}Pt$) 146.0 ($C{-}N{=}C$) 142.2 ($C{-}N{-}Pt$) 141.3 ($C{-}C{=}N{-}C$) 132.5 (CH) 130.8 (CH) 124.6 (CH) 125.9 (CH) 123.5 (CH) 114.6 (CH) 114.1 (CH) 111 (Pt*C*CSi) (PtC*C*Si not observed) 55.1 (OCH_3) 54.8 (OCH_3) 0.6 ($Si(CH_3)_3$). MS(FD): *m/z* calcd ($[M]^+$ $C_{54}H_{56}N_4O_2Pt_2Si_2$) 1271. Found: 1271. Anal. Calcd for $C_{54}H_{56}N_4O_2Pt_2Si_2$: C, 51.01; H, 4.44; N, 4.41. Found: C, 51.02; H, 4.51; N, 4.45. Single crystals suitable for X-ray structure determination were obtained by slow diffusion of pentane into a diluted CH_2Cl_2 solution.

Crystal Structure Determinations. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150 K. The structures were solved with Patterson methods (DIRDIF97[23]) and refined with SHELXL97[24] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined freely with isotropic displacement parameters in compound **3** and as rigid groups in **4**. Molecular illustrations, structure checking, and calculations were performed with the PLATON package.[25]

Crystal Data and Details on Data Collection and Refinement: Compound 3. $C_{37}H_{48}N_2PtSi$, fw = 743.95, orange needle, 0.38 × 0.22 × 0.21 mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 9.9706(3)$ Å, $b = 11.1440(3)$ Å, $c = 17.3043(5)$ Å, $\alpha = 82.8786(10)°$, $\beta = 79.7901(13)°$, $\gamma = 65.0548(10)°$, $V = 1713.14(9)$ Å^3, $Z = 2$, $\rho = 1.442$ g/cm^3; 31 975 reflections were measured; 7825 reflections were unique ($R_{int} = 0.056$). The θ range was 1.20−27.49° with indices *hkl* −12/12, −14/14, −22/22. An analytical absorption correction was applied (program PLATON,[3] routine ABST, $\mu = 4.16$ mm^{-1}, 0.24−0.49 transmission); 562 refined parameters, no restraints. *R*-values [$I > 2\sigma(I)$]: R1 = 0.0198, wR2 = 0.0505. *R*-values [all reflns]: R1 = 0.0228, wR2 = 0.0540. GoF = 1.119. The residual electron density is between −1.10 and 1.14 e/Å^3.

Compound 4. $C_{54}H_{56}N_4O_4Pt_2Si_2$, fw = 1271.39, red plate, 0.21 × 0.17 × 0.09 mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 11.5121(2)$ Å, $b = 13.4158(3)$ Å, $c = 16.3824(2)$ A, $\alpha = 88.2974(11)°$, $\beta = 82.1793(11)°$, $\gamma = 84.6873(7)°$, $V = 2495.49(8)$ Å^3, $Z = 2$, $\rho = 1.692$ g/cm^3; 34 245 reflections were measured; 11 344 reflections were unique ($R_{int} = 0.063$). The θ range was 1.25−27.51° with indices *hkl* −14/14, −17/17, −21/21. The applied absorption correction was based on multiple measured reflections (program PLATON,[3] routine MULABS, $\mu = 5.70$ mm^{-1}, 0.47−0.61 transmission); 605 refined parameters, no restraints. *R*-values [$I > 2\sigma(I)$]: R1 = 0.0280, wR2 = 0.0663. *R*-values [all reflns]: R1 = 0.0366, wR2 = 0.0699. GoF = 1.042. The residual electron density is between −1.82 and 1.48 e/Å^3.

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Supporting Information Available: Experimental details for the synthesis and characterization of **1a**,**b** and **2a**,**b**, X-ray CIF files, and tables giving atomic coordinates, displacement parameters, and bond distances and angles for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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