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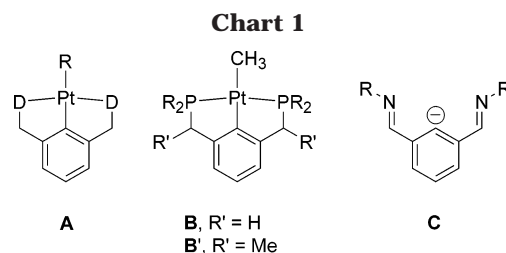
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Summary: The synthesis and the first X-ray crystal structure of stable *trans*-arylplatinum methyl complexes [Pt(CH₃)NCN] with imine type N ligands are reported. These are interesting examples of compounds on the reaction coordinate of C–C bond-forming and bond-breaking reactions, which have so far not been observed in the known series of Pt(II) complexes featuring an amine type N–C–N “pincer” ligand. Due to the strong C(sp²)–C(sp³) bond, only very few transition-metal compounds having an aryl as well as a methyl group bonded to the same metal atom are known and, usually, reductive elimination occurs. In case of the title compounds, this is prevented due to the *trans* disposition of the methyl and aryl groups and the rigid coplanarity of the chelate rings. This prevents deformation of the N–C–N tridentate ligand in the coordination plane.

Geometric isomers of the square-planar diorgano-platinum(II) compounds PtR₂L₂ are relevant to mechanistic considerations concerning C–C bond formation^{1–4} and to fundamental structural investigations. The strong *trans* influence exerted by hydrocarbonyl ligands will bias the geometry of tetracoordinate diorganoplatinum(II) compounds toward *cis* complexes when L is a monodentate or L₂ is a bidentate ancillary ligand, and even when RL₂ is a tridentate ligand, unless chelate effects are overriding.^{5–7} Much fewer examples are known of *trans* diorganoplatinum(II) compounds. Some of these platinum compounds have two monodentate phosphine ligands,^{8–11} in which case isomerization to the thermodynamically more stable *cis*-diorganoplatinum(II) diphosphine compounds may occur.¹² In most



of the other known *trans*-diorganoplatinum(II) compounds the remaining two (neutral) ligands bound to the platinum are forced into a *trans* configuration by using a meridionally coordinating and covalently bound [D–C–D] ligand (A; Chart 1).

Since the first report of a platinum(II) [P–C–P] compound,¹³ many papers concerning platinum(II) [D–C–D] compounds, bearing different donor groups, have appeared; the forced *trans* coordinating mode of the donor groups has resulted in *trans*-diorganoplatinum(II) compounds which contain [P–C–P]^{14–16} and [N–C–N]^{17–19} ligands.

When platinum(II) *methyl* compounds containing a [D–C–D] ligand are considered, it appears that only two examples of *trans* isomers have been documented; these are the platinum [P–C–P] methyl compounds B and B' (Chart 1; R = Ph).^{14,16} However, none has been authenticated by means of a crystal structure determination. To the best of our knowledge, no *trans*-arylplatinum(II) methyl compound has ever been crystallographically authenticated. Only one crystal structure of a *trans* aryl–Pt–C(sp³) compound has appeared at all; in this diphenylphosphine-substituted [P–C–P] platinum compound,¹⁶ a σ-bonded *n*-C₃F₇ group is coordinated to platinum *trans* to the aryl carbon; i.e., electronic stabilization has been gained by introducing a perfluoroalkyl moiety.

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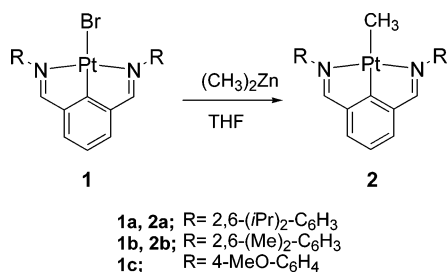
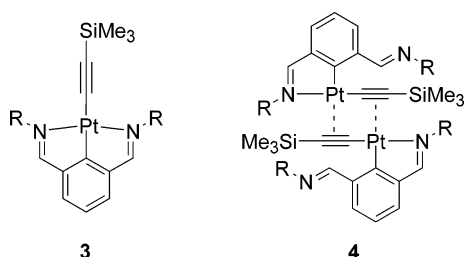
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Scheme 1. Synthesis of Title Compounds**Chart 2**

We now report the synthesis of thermally stable, novel *trans*-bis(imino)arylplatinum(II) methyl compounds **2** and the crystal structure of one of these, which were readily accessible from the corresponding platinum(II) halide compounds **1** (see Scheme 1) by transmetalation.

The bis(imino)arylplatinum(II) bromide compounds **1a,c** were described in our recent paper on acetylide derivatives **3** and **4** (see Chart 2);²⁰ **1b** was prepared similarly.

Synthesis of the thermally stable methyl derivatives **2** was attempted first by transmetalation of the respective bis(imino)arylplatinum(II) bromide compounds **1a–c** with methyllithium, an approach which has been successful in the case of [P–C–P] ligands.^{14,16} However, when compounds **1a,c** were reacted with methyllithium at low temperature in THF, the orange reaction mixture immediately turned green. No Pt–CH₃ resonance was observed in the ¹H NMR spectra of the reaction mixtures. Probably, only undesired reactions such as electron transfer, proton abstraction, and addition to the imine moiety had occurred. Next, dimethylzinc was applied as a less basic and less nucleophilic methyl transfer reagent. Indeed, the transmetalation of **1a** was successfully performed (Scheme 1) at room temperature in THF by addition of excess dimethylzinc, upon which the color of the light orange reaction mixture slowly turned to dark red. ¹H NMR spectroscopic analysis pointed to the clean formation of a new methylplatinum compound (a correctly integrated Pt–CH₃ resonance at 0.7 ppm, ³J(¹H, ¹⁹⁵Pt) = 53 Hz, C₆D₆) which has structural features similar to those of **1a**. Pure **2a** was isolated as red prisms in 95% yield. Similarly treating compound **1b** with an excess of dimethylzinc at room temperature afforded the analogous bis(imino)arylplatinum(II) methyl compound **2b** in 80% isolated yield.

It appeared that such bis(imino)arylplatinum(II) methyl compounds could be isolated only for sterically demanding aryl substituents on the imine moieties; for compound **1c** (R = 4-methoxyphenyl) the platinum(II) methyl compound **2c** was observed by ¹H NMR in a

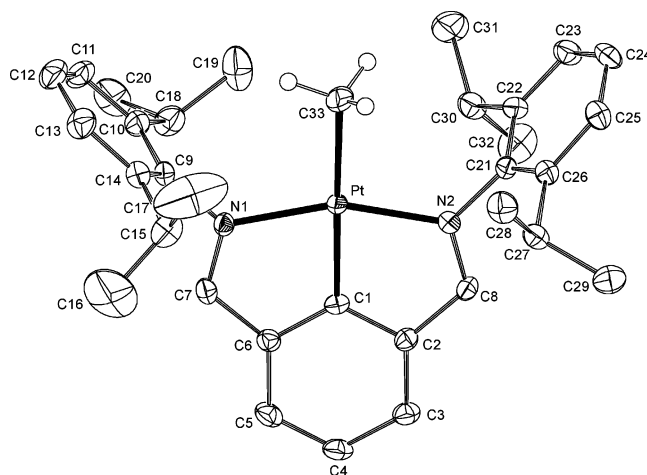


Figure 1. Displacement ellipsoid plot of **2a**, drawn at the 50% probability level. All hydrogen atoms except those of the methyl group have been omitted for clarity. Selected distances (Å), angles (deg), and torsion angles (deg): Pt–N1 = 2.045(2), Pt–N2 = 2.036(2), Pt–C1 = 1.944(2), Pt–C33 = 2.156(3), N1–C7 = 1.314(3), N1–C9 = 1.442(3), N2–C8 = 1.304(3), N2–C21 = 1.439(3); N1–Pt–N2 = 157.63(8), N1–Pt–C1 = 78.93(9), N1–Pt–C33 = 102.22(10), C1–Pt–C33 = 173.49(12), N2–Pt–C1 = 78.80(9), N2–Pt–C33 = 100.15(10), C7–N1–C9 = 118.9(2), C8–N2–C21 = 120.7(2); Pt–C1–C2–C8 = –5.2(3), Pt–C1–C6–C7 = 4.2(3).

sample of the reaction mixture, but it readily decomposed and could not be isolated.

The ³J(¹H, ¹⁹⁵Pt) values of the imine protons of **2a,b** (125 Hz) are substantially lower than those of **1a,b** (144 Hz) due to the larger cis influence of the methyl group compared to the bromide. In agreement with the nephelauxetic effect previously discussed,²¹ the ¹⁹⁵Pt chemical shift increases from –3563 ppm in **1a** (–3517 ppm in **1b**) to –3096 ppm in **2a** (–3074 ppm in **2b**).

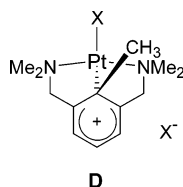
A single-crystal X-ray structure determination of **2a** provided proof of its molecular structure, which is depicted in Figure 1; it constitutes the first crystal structure of a mononuclear *trans*-arylplatinum methyl compound. The molecular structure of **2a** reveals bond lengths and angles that are similar to those in the acetylide **3**;²⁰ notably the lengths of their Pt–N bonds and the Pt–C_{aryl} bond. The platinum has a distorted-square-planar environment with a sum of cis angles of 360.1°. The short imine C=N bonds lead to a large deviation from linearity of the trans N–Pt–N angle, amounting to 157.63(89)° in **2a**, which is similar to that in **3** (157.21(9)°).

The Pt–C_{methyl} bond is relatively long (2.156(3) Å), in agreement with the large mutual trans influence of the aryl and methyl groups, and is significantly longer than in compounds with, for example, N ligands in trans positions and/or with cis hydrocarbyl groups.^{22–25} However, similar values have been reported for platinum methyl complexes with a trans phosphine ligand.^{26,27} A large trans influence has also been observed in the crystal structure of the *trans*-arylplatinum C₃F₇ compound,¹⁶ where the Pt–CF₂R bond length is 2.186(8) Å. The five- and six-membered rings in the coordination plane of platinum are almost planar; for the Pt(1), N(1), C(1), C(6), C(7) plane, the largest deviation is 0.026(2)

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Chart 3



Å, for the Pt(1), N(1), C(1), C(2), C(8) plane this is 0.034(2) Å, and for the aryl ring the largest deviation from planarity is 0.009(2) Å. These three planes are almost coplanar, the angles between these rings varying from 0.71(10) to 2.97(11)°.

In compounds **2a,b** the trans disposition of the aryl and the methyl groups is dictated by the strong coordination of the chelating imine moieties. Possibly, the relative stability of **2a,b** can be ascribed to the rigidity of the fused five-membered-ring systems, which, due to the imine moieties, must remain essentially coplanar, allowing only small deviations from planarity.

Furthermore, since compound **2c** could not be isolated, the presence of large ortho substituents on the N-aryl ring probably also plays a role in preventing decomposition.

For related amine type N–C–N (“pincer”) compounds, arylplatinum(II) methyl derivatives have been neither observed nor isolated. Instead, Pt(II)–arenium compounds of type **D** (see Chart 3) have been isolated, which arise via oxidative addition of methyl halide to a Pt(II) precursor, followed by a 1,2-methyl shift from the resulting Pt(IV) to the ipso carbon of the arene ring.^{28–30} For phosphine type P–C–P compounds, a few arylmetal methyl compounds have been isolated, notably for Rh, but these are cis high-valent d⁶ complexes.^{4,31}

In conclusion, compounds **2a,b** constitute interesting examples of compounds on the reaction coordinate of C–C bond-forming and bond-breaking reactions, which have so far not been observed in the known series of Pt(II) complexes featuring an amine type N–C–N or phosphine type P–C–P “pincer” ligand.

Experimental Section

General Comments. All reactions involving air-sensitive compounds were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and

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distilled prior to use, according to standard methods.³² ¹⁹⁵Pt NMR spectroscopy was measured via a normal HMQC sequence on a Bruker DRX300 spectrometer at 64.3 MHz at 298 K. Positive chemical shifts (δ) are denoted for high-frequency shifts relative to a TMS reference (¹H, ¹³C) and an Na₂PtCl₆ reference (¹⁹⁵Pt). HRMS measurements were performed on a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. For fast atom bombardment (FAB) mass spectrometry, the samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used.

Materials. 2-Bromoisophthalaldehyde³³ and Pt(dipdba)₂³⁴ were prepared according to literature procedures. Molecular sieves (3 Å) were activated by heating at 150 °C in vacuo overnight. All other starting materials were obtained from commercial sources and used as received.

Bis(N-2,6-dimethylphenyl)-2-bromoisophthalaldimine. To a solution of 2-bromoisophthalaldehyde (1.5 g, 7.0 mmol) in 50 mL of toluene was added 2,6-dimethylaniline (2 mL, 2.1 g, 17.6 mmol) and 3 Å molecular sieves. The reaction mixture was stirred overnight at 60 °C and filtered, after which the solvent was evaporated under reduced pressure. The residue was washed with 50 mL of pentane and dried in vacuo to yield 2.45 g (5.8 mmol, 84%) of a yellow solid which was identified by ¹H and ¹³C NMR spectroscopy as the pure compound. ¹H NMR (500 MHz, CDCl₃): δ 8.75 (s, 2H; HC=N), 8.41 (d, ³J_{HH} = 7.5 Hz, 2H), 7.58 (t, ³J_{HH} = 7.5 Hz, 1H), 7.11 (bs, 6H), 2.20 (s, 12H). ¹³C NMR (126 MHz, CDCl₃): δ 162.1 (C=N), 151.1 (C), 135.9 (C), 131.7 (CH) 128.7 (C–Br), 128.5 (CH), 128.2 (CH), 127.3 (C), 124.4 (CH), 18.7 (CH₃). HRMS (FAB): *m/z* calcd [M + H]⁺ C₂₄H₂₄N₂⁷⁹Br 419.1123, found 419.1124. Anal. Calcd for C₂₄H₂₃BrN₂: C, 68.74; H, 5.53; N, 6.68. Found: C, 68.88 H, 5.48; N, 6.65.

[κC,κN,κN-Bis(N-2,6-dimethylphenyl)isophthalaldimine-2-yl]platinum(II) Bromide (1b). To a solution of bis(N-2,6-dimethylphenyl)-2-bromoisophthalaldimine (1.0 g, 2.4 mmol) in 30 mL of THF was added Pt(dipdba)₂ (3.5 g, 3.0 mmol), and the reaction mixture was stirred overnight at 60 °C. ¹H NMR spectroscopic analysis showed a partial conversion, and therefore another portion of Pt(dipdba)₂ (1.1 g, 1.4 mmol) was added. When the reaction was complete, the reaction mixture was cooled to room temperature, upon which the product crystallized. The reaction mixture was filtered over Celite, and the product was extracted from the residue with dichloromethane. The solvent was evaporated under reduced pressure, and the product was dried in vacuo to yield 1.3 g (2.1 mmol, 88%) of a bright orange solid which was identified by ¹H, ¹³C, and ¹⁹⁵Pt NMR spectroscopy as pure **1b**. ¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, ³J_{HPT} = 144 Hz, 2H; HC=N), 7.71 (d, ³J_{HH} = 7.5 Hz, 2H), 7.32 (t, ³J_{HH} = 7.5 Hz, 1H), 7.10 (bs, 6H), 2.27 (s, 12H; CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 179.1 (²J_{CPT} = 106 Hz, C=NC), 178.4 (C–Pt, ¹J_{CPT} = 935 Hz), 148.1 (C=NC), 142.1 (³J_{CPT} = 116 Hz, C), 131.3 (³J_{CPT} = 10 Hz, C), 128.1 (CH), 128.0 (CH), 127.5 (CH), 123.0 (CH), 18.5 (CH₃). ¹⁹⁵Pt NMR (CDCl₃): δ –3562. HRMS (FAB): *m/z* calcd [M + H]⁺ C₂₄H₂₄N₂⁷⁹Br¹⁹⁵Pt 614.0773, found 614.0714.

Methyl [κC,κN,κN-bis(N-2,6-diisopropylphenyl)isophthalaldimine-2-yl]platinum(II) (2a). To a solution of **1a** (113 mg, 0.16 mmol) in 20 mL of THF was added dimethylzinc (2 mL of a 2.0 M solution in toluene, 4 mmol). In 10 min the orange reaction mixture turned red, and the reaction was very gently quenched with water. Most of the THF was evaporated

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under reduced pressure, and the mixture was extracted three times with 30 mL of pentane. The organic layer was washed subsequently with water and a concentrated NaHCO_3 solution and dried on MgSO_4 . After filtration the solvents were evaporated in vacuo. The residue was extracted with 200 mL of pentane. The pentane was removed under reduced pressure, and the solid material was washed two times with a small amount of pentane and dried in vacuo to yield 98 mg (0.15 mmol, 95%) of an orange-red solid which was identified by ^1H , ^{13}C , and ^{195}Pt NMR spectroscopy as pure **2a**. ^1H NMR (300 MHz, C_6D_6): δ 8.14 (s, $^3J_{\text{HPt}} = 125$ Hz, 2H; $\text{HC}=\text{N}$), 7.42 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.07 (m, obscured by solvent), 6.92 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 3.31 (septet, $^3J_{\text{HH}} = 6.8$ Hz, 4H; CH_3CHCH_3), 1.28 (d, $^3J_{\text{HH}} = 7$ Hz, 12H; CH_3CHCH_3), 0.98 (d, $^3J_{\text{HH}} = 7$ Hz, 12H; CH_3CHCH_3), 0.67 (s, $^3J_{\text{HPt}} = 53$ Hz, $\text{Pt}-\text{CH}_3$). ^{13}C NMR (126 MHz, C_6D_6): δ 204.6 ($\text{C}-\text{Pt}$), 180.3 ($^2J_{\text{CPt}} = 56$ Hz, $\text{C}=\text{N}$), 146.7 (C), 143.2 ($^2J_{\text{CPt}} = 89$ Hz, C), 141.4 (C), 127.4 (CH), 126.6 (CH), 123.1 (CH), 121.7 (CH), 27.6 (CH_3CHCH_3), 24.2 (CH_3CHCH_3), 22.8 (CH_3CHCH_3), 10.2 ($^1J_{\text{CPt}} = 623$ Hz, $\text{Pt}-\text{CH}_3$). ^{195}Pt NMR (C_6D_6): δ -3074. HRMS (FAB): m/z calcd ($[\text{M} + \text{H}]^+$ $\text{C}_{33}\text{H}_{43}\text{N}_2\text{Pt}$) 662.3077, found 662.3040. Calcd for $\text{C}_{33}\text{H}_{42}\text{N}_2\text{Pt}$: C, 59.89; H, 6.40; N, 4.23. Found: C, 60.09; H, 6.35; N, 4.17. Single crystals suitable for X-ray structure determination were obtained by cooling a concentrated toluene solution.

Methyl[κ -C κ -N, κ -N-bis(N-2,6-dimethylphenyl)isophthalaldimin-2-yl]platinum(II) (2b). Compound **2b** was prepared, in analogy to **2a**, from **1b** (159.1 mg, 0.259 mmol) and dimethylzinc (2 mL of a 2.0 M solution in toluene, 4 mmol). During the workup, hexane was used instead of pentane. The yield was 114 mg (0.21 mmol, 80%) of an orange-red solid which was identified by ^1H , ^{13}C , and ^{195}Pt NMR spectroscopy as pure **2b**. The workup has to be performed quickly, since otherwise an increasing amount of a decomposition product, which is insoluble in hexane, is formed. ^1H NMR (300 MHz, C_6D_6): δ 7.63 (s, $^3J_{\text{HPt}} = 125$ Hz, 2H; $\text{HC}=\text{N}$), 7.42 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 6.95 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.86 (br s, 6H), 2.07 (s, 12H), 0.66 (s, $^3J_{\text{HPt}} = 53$ Hz, $\text{Pt}-\text{CH}_3$). ^{13}C NMR (126 MHz, C_6D_6): δ 204.0 ($^1J_{\text{CPt}} = 591$ Hz, $\text{C}-\text{Pt}$), 180.6 ($^2J_{\text{CPt}} = 52$ Hz, $\text{C}=\text{N}$), 149.2, 143.4 ($^2J_{\text{CPt}} = 91$ Hz), 131.1, 129.3, 126.6, 126.5, 121.6, 18.4 ($\text{Ar}-\text{CH}_3$), 8.7 ($^1J_{\text{CPt}} = 604$ Hz, $\text{Pt}-\text{CH}_3$). ^{195}Pt NMR (C_6D_6): δ -3096. HRMS (FAB): m/z calcd ($[\text{M} - \text{CH}_3]^+$ $\text{C}_{24}\text{H}_{23}\text{N}_2\text{Pt}$) 535.1590, found 535.1579.

Crystal Data for 2a: $\text{C}_{33}\text{H}_{42}\text{N}_2\text{Pt}$, fw = 661.78, red block, $0.18 \times 0.10 \times 0.09$ mm³, orthorhombic, $P2_12_1$ (No. 19), $a =$

11.2859(1) Å, $b = 14.6377(1)$ Å, $c = 17.7437(1)$ Å, $V = 2931.25(4)$ Å³, $Z = 4$, $D_x = 1.500$ g/cm³, $\mu = 4.810$ mm⁻¹. A total of 34 018 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $((\sin \theta)/\lambda)_{\text{max}} = 0.65$ Å⁻¹; 6705 reflections were unique ($R_{\text{int}} = 0.036$). An analytical absorption correction was applied (0.47–0.72 transmission). The structure was solved with automated Patterson methods (DIRDIF-97)³⁵ and refined with SHELXL-97³⁶ against F^2 values of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. H atoms of the imine group were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups (334 refined parameters, no restraints). R values ($I > 2\sigma(I)$): $R_1 = 0.0153$, $wR_2 = 0.0359$. R values (all reflections): $R_1 = 0.0158$, $wR_2 = 0.0361$. The Flack x parameter³⁷ is $-0.016(4)$, the GOF value is 1.050, and the residual electron density is between -0.67 and 0.57 e/Å³. Molecular illustration, structure checking and calculations were performed with the PLATON package.³⁸

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Supporting Information Available: X-ray CIF file for **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 215854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

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