$F(000) = 5012$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.714\ \mathrm{mm^{-1}}$. Crystal data for **8** ($C_{88}H_{164}Cr_7F_8NNiO_{32}$; $M_r = 2316.20$): dark-green plate, monoclinic, space group $P2_1/n$, $a = 26.067(2)$, $b = 20.3010(17)$, $c = 27.098(2)$ Å, $\beta = 112.258(1)°$, $V = 13271.5(19)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{calcd} = 1.159\ \mathrm{g\,cm^{-1}}$, $F(000) = 4876$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.700\ \mathrm{mm^{-1}}$. Crystal data for **9** ($C_{96}H_{180}Cr_7F_8NNiO_{32}$; $M_r = 2428.41$): dark-green plate, orthorhombic, space group $Pnma$, $a = 23.2504(15)$, $b = 21.0031(13)$, $c = 31.451(2)$ Å, $V = 15358.4(17)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{calcd} = 1.050\ \mathrm{g\,cm^{-1}}$, $F(000) = 5132$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.608\ \mathrm{mm^{-1}}$. Unit cell for **10**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.031(1)$, $b = 16.639(1)$, $c = 30.910(1)$ Å, $\beta = 110.03(1)°$. Unit cell for **11**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.061(4)$, $b = 16.622(3)$, $c = 30.960(5)$ Å, $\beta = 110.488(5)°$. Unit cell for **12**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.049(2)$, $b = 16.630(1)$, $c = 30.927(2)$ Å, $\beta = 110.18(3)°$. Unit cell for **13**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.173(7)$, $b = 16.629(5)$, $c = 31.135(8)$ Å, $\beta = 111.093(3)°$. Compounds **10**, **11**, **12**, and **13** are isostructural with **6**. Data were collected on a Bruker SMART CCD diffractometer ($\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71069$ Å). In all cases the selected crystals were mounted onto the tip of a glass pin using Paratone-N oil and placed in the cold flow (120 K) produced with an Oxford Cryocooling device. Complete hemispheres of data were collected using ω scans (0.3°, 30 s/frame). Integrated intensities were obtained with SAINT+[12] and corrected for absorption using SADABS.[12] Structure solution and refinement was performed with the SHELX-package.[12] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 to give for **4**: using 479 parameters and 55 restraints, $wR_2 = 0.5006$ (12935 unique reflections), $R_1 = 0.1806$ (11281 reflections with $I > 2\sigma(I)$); for **5**: using 299 parameters and 28 restraints, $wR_2 = 0.2937$ (7978 unique reflections), $R_1 = 0.0973$ (7306 reflections with $I > 2\sigma(I)$); for **6**: using 1204 parameters and 105 restraints, $wR_2 = 0.1716$ (20413 unique reflections), $R_1 = 0.0804$ (17353 reflections with $I > 2\sigma(I)$); for **7**: using 901 parameters and 108 restraints, $wR_2 = 0.3241$ (22002 unique reflections), $R_1 = 0.1140$ (13892 reflections with $I > 2\sigma(I)$); for **8**: using 827 parameters and 116 restraints, $wR_2 = 0.4806$ (30385 unique reflections), $R_1 = 0.1661$ (17629 reflections with $I > 2\sigma(I)$); for **9**: using 449 parameters and 76 restraints, $wR_2 = 0.5085$ (9688 unique reflections), $R_1 = 0.1780$ (7500 reflections with $I > 2\sigma(I)$). CCDC-191618–191623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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14-Electron Platinum(II) Complexes

Novel T-Shaped 14-Electron Platinum(II) Complexes Stabilized by One Agostic Interaction**

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Three-coordinate 14-electron d^8-ML_3 complexes, which are generally transient species generated in situ by ligand dissociation, have received much attention because of their key role in many stoichiometric and catalytic reactions.[1] Platinum(II) complexes of the form $[L_2PtR(\text{solvent})]^+$, which contain bidentate nitrogen ligands and a weakly bonded solvent molecule, have been found to be active in alkane C–H activation through the formation of the transient alkane σ-adduct $[L_2PtR(R'{-}H)]^+$.[2] Such species have eluded isolation because of the ease of displacement of the alkane moiety by solvent or anions in solution, and thus, several approaches have been used to examine their reactivity including the study of agostic complexes.[3] Orpen and Spencer have described a series of β-agostic platinum(II) complexes of the type $[Pt(R)(P{-}P)]^+$ (P–P = chelating diphosphane; R = alkyl), which are in equilibrium with the corresponding alkene–hydrido derivatives,[4] and which have been viewed as models for intermediates along the migratory insertion/β-elimination alkene-polymerization pathway.[3a,4c] The bulky phosphane P*t*Bu$_3$ has been used to stabilize 14-electron T-shaped platinum(II) species of the form *trans*-$[PtH(P\mathit{t}Bu_3)_2]X$ (X = noncoordinating anion), which have been characterized by NMR analysis.[5] It is noteworthy that the analogous derivatives bearing PCy_3 or P*i*Pr$_3$ moieties led to the four-coordinate complexes *trans*-$[PtH(PR_3)_2(\text{solvent})][BAr^f_4]$ (R = Cy,[6a] *i*Pr;[6b] $Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$), with dichloromethane as solvent.

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[**] This work was supported by Ministero della Ricerca Scientifica e Tecnologica (MURST), University of Sassari and the Bayerische Forschungsstiftung (FORKAT; X-ray equipment).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Among the phosphanes used to stabilize low-coordinated species, those containing the 2,6-dimethylphenyl group appear very effective since the *o*-methyl groups can easily interact in an agostic fashion. In fact, we have recently isolated a rare example of a 14-electron ruthenium(II) complex $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$,[7] which is stabilized by two agostic interactions. In contrast, employment of the $PPh_2(2,6\text{-}Me_2C_6H_3)$ ligand with osmium led to the formation of complexes containing a tridentate *trans*-stilbene-type ligand, which results from the coupling of two *o*-methyl groups and the activation of four C–H bonds.[8] We have now found that $PR_2(2,6\text{-}Me_2C_6H_3)$ ligands (R = Ph, Cy) can be used to prepare a new class of three-coordinate 14-electron platinum(II) complexes; the crystallographic characterization of the cyclohexyl derivative is reported herein.

Treatment of [PtMeCl(cod)] (cod = cyclooctadiene) with two equivalents of $PPh_2(2,6\text{-}Me_2C_6H_3)$ in dichloromethane afforded the *trans* derivative **1** (84% yield),[9] through the substitution of cyclooctadiene. Similarly to **1**, complex **2**[9] was obtained in 85% yield from the platinum precursor and the bulky phosphane $PCy_2(2,6\text{-}Me_2C_6H_3)$ (Scheme 1).

Complexes **1** and **2** are thermally stable in solution and show NMR parameters in accordance with those of the *trans*-$[PtMeX(PR_3)_2]$ derivatives.[10] No *cis* complexes were observed during the formation of **1** and **2**, which can be attributed to the high steric requirement of the phosphanes employed.[11]

The three-coordinate complexes **3** and **4**[12] are obtained in 85 and 76% yield, respectively, by reacting **1** or **2** with $Na[BAr^f_4]$ in CH_2Cl_2 at room temperature through the cleavage of an *o*-methyl C–H bond and extrusion of methane (Scheme 1). The ^1H NMR spectrum of **3** in CD_2Cl_2 at room temperature shows a resonance at $\delta = 2.35$ ppm, with a value for J(H,Pt) (that is, the coupling constant for the metal satellite resonances) of 30.3 Hz for two methyl groups. At −95 °C this signal splits into two resonances of equal intensity at $\delta = 2.95$ and 1.75 ppm, which indicates that the rotation of the 2,6-dimethylphenyl group is frozen out. The $^{13}C\{^1H\}$ NMR spectrum at 20 °C displays a signal at $\delta = 22.7$ ppm for the $PtCH_2$ moiety with a large ^1J(C,Pt) coupling constant of 840 Hz,[10,13] consistent with a "very weak" ligand *trans* to the CH_2 group, whereas the resonance for the two methyl groups is at $\delta = 17.6$ ppm with J(C,Pt) = 94 Hz. Upon cooling at −95 °C this signal splits into two peaks at $\delta = 22.8$ and 9.4 ppm, of which the latter is attributable to the agostic methyl group.[7,14] Although the NMR data for complex **4** is similar to that for **3**, no rotation of the 2,6-dimethylphenyl group occurs at room temperature. The ^1H NMR resonance of the agostic CH_3 group appears at $\delta = 2.70$ ppm with J(H,Pt) = 64.0 Hz, whereas its $^{13}C\{^1H\}$ NMR signal is shifted to high field ($\delta = 13.6$ ppm) with a remarkably high J(C,Pt) coupling constant of 191 Hz. The NMR data of **3** and **4** clearly suggests that rotation of the 2,6-dimethylphenyl group is affected by the steric requirements of the PR_2 (R = Ph, Cy) moiety, with cyclohexyl substituents leading to a more hindered rotation than with phenyl substituents.

To establish the previous formulation with one *o*-methyl group close to the metal center, an X-ray diffraction study was carried out on a single crystal of **4**.[15] The representation of the cation of **4** with some relevant bond lengths and angles is shown in Figure 1; the $[BAr^f_4]^-$ ion is not bound directly to the platinum center.

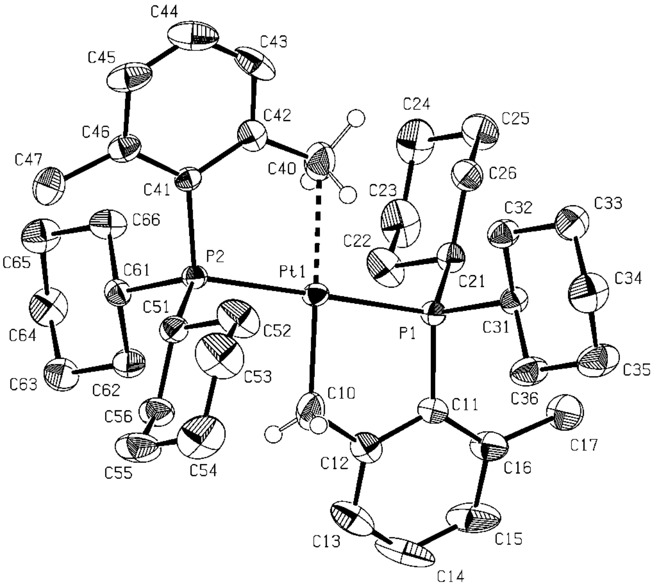
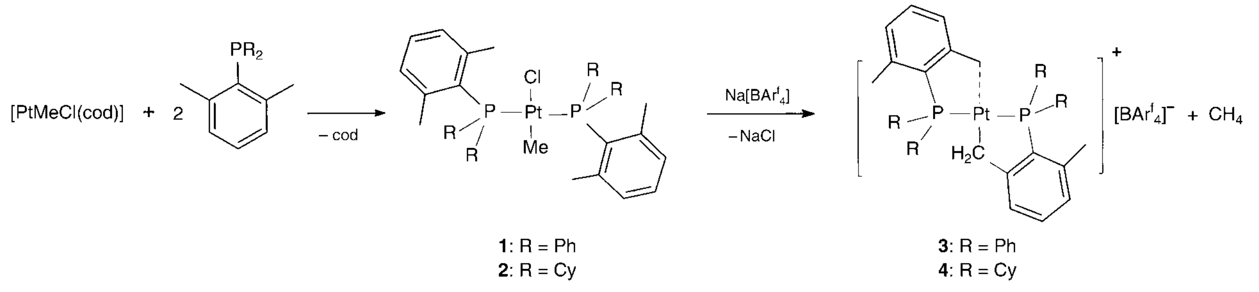


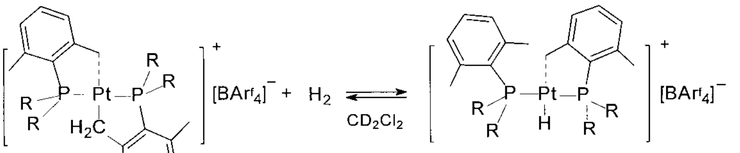
Figure 1. ORTEP-style drawing of the Pt-centered cation in the solid-state structure of $4\cdot0.25\,CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.3088(9), Pt1–P2 2.3279(9), Pt1–C10 2.088(7), Pt1···C40 2.432(6); P1-Pt1-P2 177.71(3), P1-Pt1-C10 81.91(14), P1-Pt1···C40 101.41(12), P2-Pt1-C10 97.28(14), P2-Pt1···C40 79.63(12), C10-Pt1···C40 172.94(18), Pt1-P2-C41 107.21(11).



Scheme 1. Synthesis of **1**–**4**.

The crystal structure consists of discrete monomeric units with the platinum center in a nearly square environment, coordinated to two *trans* phosphane groups and an alkyl group. The coordination sphere is completed by one methyl group of the 2,6-dimethylphenyl moiety. The Pt1-P2-C41 angle for the 2,6-dimethylphenyl group of **4** is 107.21(11)° and is smaller than the equivalent angles for the cyclohexyl substituents Pt1-P2-C51 (114.57(13)°) and Pt1-P2-C61 (115.11(12)°).[7] The five atoms Pt1, P1, P2, C10, and C40 are almost coplanar, and lie less than ± 0.10 Å from the mean plane, whereas the 2,6-dimethylphenyl group is bent back from this plane and is hinged about the P2–C40 axis at an angle of 8.4(2)° (as defined by the P2-Pt1-C40 and P2-C41-C42-C40 planes). The Pt1···C40 separation (2.432(6) Å) is a relatively short nonbonding distance, and is longer than the length reported for β-agostic complexes.[4a–b] It is noteworthy that the hydrogen atoms bonded to C40, which have been located and refined, are "tilted" away from the metal, a phenomenon that has been observed in $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$[7] and in some lanthanoid derivatives that contain the $CH(SiMe_3)_2$ ligand.[16] This may indicate an agostic interaction with the carbon atom providing a strong contribution.

As a result of the high coordinative unsaturation of **3** and **4**, these complexes react with dihydrogen in an equilibrium reaction in which the hydrido derivatives **5** and **6** are readily formed by heterolytic dihydrogen splitting and Pt–C bond cleavage [Eq. (1)].[17]



(1)

3: R = Ph
4: R = Cy

5: R = Ph
6: R = Cy

When a solution of **3** (CD_2Cl_2, 20 °C) is treated with dihydrogen (1 atm), the $^{31}P\{^1H\}$ NMR spectrum exhibits one sharp resonance at $\delta = 29.0$ ppm with $^1J(P,Pt) = 2717$ Hz for **5**, in addition to signals for **3** (**5**:**3** molar ratio = 1:4). The ^1H NMR spectrum reveals one signal at $\delta = 2.22$ ppm with $J(H,Pt) = 11.3$ Hz for the four *o*-methyl groups and one broad signal at $\delta = -20.83$ for the hydrido ligand with a remarkably high $^1J(H,Pt)$ coupling constant of 2052 Hz.[18] Similarly to **3**, the reaction of **4** with H_2 leads to the formation of complex **6** ($\delta(^{31}P) = 54.5$; $^1J(P,Pt) = 2631$ Hz), where **6** and **4** are recovered in a molar ratio of 2:1, which indicates that for the Cy derivative the equilibrium is more shifted to the right. The ^1H NMR spectrum of **6** exhibits one signal at $\delta = 2.74$ ppm with $J(H,Pt) = 15.0$ Hz for the *o*-methyl groups and one triplet at $\delta = -19.74$ ppm ($^2J(H,P) = 10.0$ Hz) with a $^1J(H,Pt)$ coupling constant of 2074 Hz. The data is similar to that of the three-coordinate derivatives $[PtH(P^tBu_3)_2]X$ ($X = BF_4$, PF_6, ClO_4, CF_3SO_3)[5] but differs from that of the related cyclohexyl species $[PtH(PCy_3)_2(L)][BAr^f_4]$ ($L = CD_2Cl_2$ and H_2)[6a] indicating that **5** and **6** are not solvato or dihydrogen[19] complexes of platinum(II), but are actually three-coordinate complexes with time-averaged agostic interactions of the four *o*-methyl groups. When the solutions containing either **5** or **6** are gently heated (40 °C) under Ar for a few minutes, the equilibrium completely shifts to the left as a result of the deprotonation of an agostic *o*-methyl group and associated H_2 extrusion. In the reversible Pt–C hydrogenolysis, H_2 probably replaces the agostic *o*-methyl group, which leads to a transient cationic dihydrogen-cyclometalated platinum(II) complex that may be in equilibrium with the 16-electron platinum(IV) dihydrido species.[1j,19] Interestingly, Milstein and co-workers have recently reported the opening of a platinum(II) metallacycle complex by reaction with dihydrogen, but under harsher conditions.[20]

In conclusion, the accessibility of 14-electron platinum(II) complexes relies on the use of the bulky ligands $PR_2(2,6\text{-}Me_2C_6H_3)$ (R = Ph, Cy) which allow protection against solvent coordination. Complexes **3** and **4** represent rare examples of three-coordinate platinum(II) complexes, characterized both in solution and in the solid state, that undergo a reversible and facile platinum–carbon hydrogenolysis through loss of the weakly bound *o*-methyl group. These complexes may be suitable precursors for new investigations of the relatively unexplored chemistry of 14-electron platinum(II) complexes.

Experimental Section

3: $Na[BAr^f_4]$ (298 mg, 0.36 mmol) was added to **1** (300 mg, 0.36 mmol) dissolved in dichloromethane (20 mL), which afforded the evolution of methane and a precipitate of NaCl. After filtration of the NaCl, the solution was evaporated to dryness. The white solid was washed with cold pentane, filtered, and dried under reduced pressure. Yield 501 mg (85 %). The derivative **4** was prepared by an analogous method (76 % yield).

Received: August 26, 2002 [Z50047]

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[12] **3**: ^{1}H NMR (299.9 MHz, CD_2Cl_2, 20C, TMS): $\delta = 7.78$–7.00 (m, 38H; aromatic protons), 3.91 (d, J(P,H) = 4.6 Hz, ^{2}J(Pt,H) = 109 Hz, 2H; $PtCH_2$), 2.35 (s, J(Pt,H) = 30.3 Hz, 6H; agostic CH_3), 1.96 ppm (s, 3H; CH_3); ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20C, TMS): $\delta = 162.2$ (q, ^{1}J(C,B) = 50 Hz; *ipso* aromatic carbons), 144.5–143.7 (*ipso* aromatic carbons), 135.2–125.8 (aromatic carbons), 125.0 (q, ^{1}J(C,F) = 272 Hz; CF_3), 117.9 (aromatic carbons), 22.7 (s, ^{1}J(C,Pt) = 840 Hz; $PtCH_2$), 21.6 (d, ^{3}J(C,P) = 3.0 Hz; CH_3), 17.6 ppm (s, J(C,Pt) = 94 Hz; agostic CH_3); ^{31}P{^{1}H} NMR (122.4 MHz, CD_2Cl_2, 20 C, H_3PO_4): $\delta = 51.3$ (d, ^{2}J(P,P) = 351 Hz, ^{1}J(Pt,P) = 2866 Hz), 39.5 ppm (d, ^{2}J(P,P) = 351 Hz, ^{1}J(Pt,P) = 2751 Hz); elemental analysis (%) calcd for $C_{72}H_{49}BF_{24}P_2Pt$: C 52.80, H 3.02; found: C 52.84, H 3.08. **4**: ^{1}H NMR (299.9 MHz, CD_2Cl_2, 20C, TMS): $\delta = 7.68$–7.09 (m, 18H; aromatic protons), 4.22 (d, J(P,H) = 4.6 Hz, ^{2}J(Pt,H) = 107 Hz, 2H; $PtCH_2$), 2.70 (s, J(Pt,H) = 64.0 Hz, 3H; agostic CH_3), 2.54 (s, 3H; CH_3), 2.50 (s, 3H; CH_3), 2.38–1.12 ppm (m, 44H; Cy); ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 C, TMS): $\delta = 162.1$ (q, ^{1}J(C,B) = 50 Hz; *ipso* aromatic carbons), 143.7–141.5 (*ipso* aromatic carbons), 135.1–125.3 (aromatic carbons), 124.9 (q, ^{1}J(C,F) = 272 Hz; CF_3), 124.1 and 117.8 (aromatic carbons), 38.7 (d, ^{1}J(C,P) = 26.5 Hz; PCH of Cy), 38.0 (d, ^{1} J(C,P) = 27.5 Hz; PCH of Cy), 31.9 (d, ^{2}J(C,P) = 104.0 Hz; CH_2 of Cy), 30.9 (d, ^{2}J(C,P) = 63.5 Hz, ^{3}J(C,Pt) = 12.0 Hz; CH_2 of Cy), 27.4–26.8 (s, CH_2 of Cy), 26.1 (s; CH of Cy), 23.4 and 22.1 (s; CH_3), 17.8 (d, ^{2}J(C,P) = 3.0 Hz, ^{1}J(C,Pt) = 806 Hz; $PtCH_2$), 13.6 ppm (d, J(C,P) = 7.7 Hz, J(C,Pt) = 191 Hz; agostic CH_3); ^{31}P{^{1}H} NMR (122.4 MHz, CD_2Cl_2, 20C, H_3PO_4): $\delta = 73.3$ (d, ^{2}J(P,P) = 316 Hz, ^{1}J(Pt,P) = 2776 Hz), 54.9 ppm (d, ^{2}J(P,P) = 316 Hz, ^{1}J(Pt,P) = 2677 Hz); elemental analysis (%) calcd for $C_{72}H_{73}BF_{24}P_2Pt$: C 52.03, H 4.43; found: C 52.65, H 4.47.

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[15] a) Crystal structure analysis of **4**$\cdot 0.25\,CH_2Cl_2$: $4(C_{72}H_{73}BF_{24}P_2Pt)\cdot CH_2Cl_2$, $M_r = 6733.46$, triclinic, space group $P\bar{1}$, $a = 13.8101(1)$, $b = 19.2354(2)$, $c = 29.6683(3)$ Å, $\alpha = 101.466(1)$, $\beta = 93.333(1)$, $\gamma = 109.049(1)°$, $V = 7236.26(13)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.545$ g cm^{-3}, $F_{000} = 3378$, $\mu = 2.105$ mm^{-1}. A suitable single crystal for the X-ray diffraction study was obtained from a CH_2Cl_2/toluene solution at 4 °C. The selected crystal was coated with perfluorinated ether, fixed in a capillary, and transferred to the diffractometer and the cold nitrogen flow (Oxford Cryosystems). Preliminary examinations and data collection were carried out on a kappa-CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data collection was performed at 123 K within the Θ range of $1.20 < \Theta < 25.35°$. A total of 81323 reflections were integrated and corrected for Lorentz and polarization effects. A correction for absorption effects was applied with the DIFABS algorithm ($C_{min/max}$ 0.632/0.892). After merging ($R_{int} = 0.0338$), 26468 (21745: $I_o > 2\sigma(I_o)$) independent reflections remained and all were used to refine 2187 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All nonhydrogen atoms were refined anisotropically. All 61 hydrogen atom positions for the Pt1 cation were found in the difference Fourier map calculated from the model containing all nonhydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. All of the other 104 hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.95$, 0.98, 0.99, 1.00 Å). Isotropic displacement parameters were calculated from the parent carbon atom ($U_H = 1.2/1.5 \cdot U_C$). The hydrogen atoms were included in the structure factor calculations but not refined. Full-matrix least-squares refinements in 4 blocks were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0348$ ($I_o > 2\sigma(I_o)$), $wR2 = 0.0825$ (all data), GOF = 1.012 and shift/error < 0.001. The asymmetric unit cell contains three crystallographically independent Pt cations. Two of them ($Pt2^+$ and $Pt3^+$) are located around a center of inversion and therefore show a disorder (in each of two positions, 50:50) which could be clearly resolved. The two anions and the CH_2Cl_2 solvent molecule are well-ordered. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the nonhydrogen atoms were taken from *International Tables for Crystallography.* Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-191944 (**4**$\cdot$0.25 CH_2Cl_2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk); b) Data Collection Software for Nonius kappa-CCD devices, Delft (The Netherlands), **1997**; c) Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307ff; d) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435; e) *International Tables for Crystallography*, Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2 (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht (The Netherlands), **1992**; f) A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, **2000**; g) G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen (Germany), **1998**.

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