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Syn−*Anti* Isomerization by Intramolecular Alkene Rotation: Study of the Dynamics of the Bicyclo[2.2.1]hept-2-ene Ligands in a Diplatinum(I) Complex and Its Lewis Acid Adducts

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Intramolecular exchange by alkene rotation observed for the first time in a dinuclear d^9-Pt(I) olefin complex was evidenced for $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1**) (dppm = bis(diphenylphosphino)methane). The dynamic behavior leads to the occurrence of two diastereomers in solution with relative *syn* and *anti* orientation of the two in-plane coordinated bicyclo[2.2.1]hept-2-ene ligands. The low activation energy $\Delta G^{\ddagger}_{rot}$ of 43 kJ/mol found for this exchange process was attributed (a) to a favorable geometry due to the ample P−Pt−P angle of the phosphorus ligands in mutual *trans* position promoting flexibility and reducing steric hindrance in the intermediate or transition state with upright alkene orientation and (b) to the positive charge of the complex cation, which reduces the ability of platinum for metal-to-ligand π-back-donation compared to neutral or anionic complexes. Intramolecular alkene rotation was also observed for the Lewis acid adducts at the Pt−Pt bond of **1** with Ag^+, $[Pt_2(\mu\text{-Ag})(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)_2$ (**2**), and H^+, $[Pt_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)_2$ (**3**), respectively. The solid state structure of **2** was determined by single-crystal X-ray diffraction and reveals that the core geometry of the $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2]$ framework remains substantially unchanged compared with the parent compound **1** upon Ag^+ coordination at the Pt−Pt bond. No A-frame structure is formed as usually observed in di-Pt(I) complexes. Complex **3**, containing a bridging hydride ligand across both platinum centers, displays—besides alkene rotation—an additional, unique intramolecular fluxionality by tunneling of hydrogen through the Pt−Pt bond.

Introduction

There has been considerable interest in the chemistry of platinum complexes containing π-coordinated unsaturated ligands.[1] Especially alkene complexes have been investigated extensively with respect to structure and bonding, and complexes in which the platinum atom is formally in the zerovalent oxidation state differ substantially from those in which it is formally in the divalent oxidation state.[2] In most of the 16 VE d^8-platinum(II) complexes the olefinic double bond lies approximately perpendicular to the square plane of ligands surrounding the platinum atom ("upright" coordination mode; see Figure 1); by contrast, in 16 VE d^{10}-platinum(0) complexes the olefinic double bond lies essentially coplanar with the trigonal plane containing platinum, the mid point of the olefinic double bond, and the other two ligands ("in-plane" coordination mode; see Figure 1). There exist only a few examples for 16 VE d^8-Pt(II) complexes with "in-plane" or intermediate alkene orientation, which were attributed to the geometry and steric demands of the olefin.[3] There are no reports on 16 VE d^{10}-Pt(0) complexes with "upright" alkene orientation.

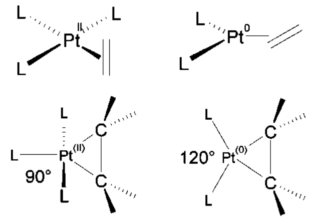

Figure 1. Observed alkene orientations in 16 VE d^8-Pt(II) complexes ("upright") and 16 VE d^{10}-Pt(0) complexes ("in plane"). Upper images: View along the planar Pt coordination environment. Lower images: View perpendicular to the Pt−C=C plane.

The experimentally observed structures of platinum alkene complexes were qualitatively described by Dewar[4] and Chatt and Duncanson[5] with a σ-donation/π-back-donation molecular orbital model, which could be confirmed by further theoretical studies.[6]

In zerovalent platinum complexes the π-back-donation from the electron-rich metal center is the most important contribution

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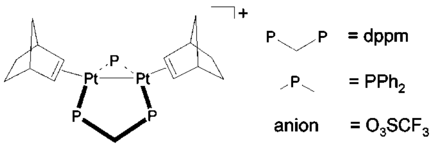

Figure 2. Structure of the cation of **1**.

for the metal−alkene bond, whereas this contribution is usually much smaller for divalent platinum complexes,[7] leading to different dynamic properties of the coordinated alkene ligand: It was observed that the energy barrier to rotation of the olefin about the platinum−alkene bond is generally low for Pt(II) (40–65 kJ/mol), whereas in Pt(0) complexes the olefin appears to be rigidly bound;[2] for example, activation energies for alkene rotation in Pt(0) maleic anhydride complexes were estimated by Elsevier et al. to be >72 kJ/mol on the basis of NMR spectroscopy.[7] There is only one literature example for Pt(0) bis(ethylene)-phosphine complexes, where intramolecular alkene rotation could be detected via NMR spectroscopy: The relatively low energy barriers of 41–54 kJ/mol lying in the range of Pt(II) alkene complexes were explained by the presence of two olefin ligands at one platinum(0) center so that the electron density for $d_\pi-\pi^*$ bonding has to be divided between these two olefin ligands.[8]

In a former publication we described the synthesis of the dinuclear platinum compound $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1**) (dppm = bis(diphenylphosphino)methane) containing platinum in a formal d^9 electronic configuration with an oxidation state of +1 (see Figure 2).[9] Compound **1**, which is a 30 VE complex with a Pt−Pt single bond leading to a 16 VE environment for each platinum center, was one of the rare structurally characterized Pt(I) olefin complexes reported in the literature.[10] The complex cation contains two Pt-bound bicyclo[2.2.1]hept-2-ene ligands exhibiting a C═C orientation essentially coplanar with the other ligands coordinated to the Pt atoms.[9] The "in-plane" orientation for the alkene ligands in **1** was attributed to a favorable geometry within the $Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)$ framework, leading to distorted square-planar platinum coordination environments due to the ample P−Pt−P angle of the phosphorus ligands in mutual *trans* position (see Figure 2).

As **1** is one of the first 16 VE platinum alkene complexes exhibiting a d^9 electron configuration intermediate between the well-studied d^8- and d^{10}-complexes, we were particularly interested in the dynamic properties of the platinum-bound bicyclo[2.2.1]hept-2-ene ligands, giving information on the contribution of π-back-donation to metal−alkene bonding within the diplatinum(I) system. Another interesting feature of complex **1** is the seldom found "in-plane" orientation of the alkene ligands in a quasi square-planar platinum coordination environment: The dynamic properties of such systems have not been investigated so far. In order to get deeper insight into the dynamics and bonding, we examined compound **1** and its adducts with the Lewis acids Ag^+ and H^+ by multinuclear variable-temperature NMR spectroscopy.

Results and Discussion

Compound **1** was characterized by single-crystal X-ray diffraction and by multinuclear NMR spectroscopy in solution at room temperature.[9] The complex cation displays a quasi-C_s-symmetry in the solid state (see Figure 2), since both bridging methylene groups of the bicyclo[2.2.1]hept-2-ene ligands point to the same side perpendicular to the platinum coordination plane (*syn* orientation). Both bicyclo[2.2.1]hept-2-ene ligands are bound to Pt via the *exo* face of the C═C double bond, which is the preferred coordination mode of this ligand: All X-ray crystal structures of transition metal complexes contained in the Cambridge Structural Database (CSD) display *exo* coordination of the respective bicyclo[2.2.1]hept-2-ene ligands without exception, which indicates that an *endo* coordination is generally largely disfavored and does not seem to play a significant role in transition metal complexes of this ligand.[9,11]

A careful examination of the room-temperature ^1H and ^{13}C NMR spectra of **1** shows that these do not reflect the C_s-symmetry found in the crystal; for example, only *one* signal is observed for the hydrogens at the bicyclo[2.2.1]hept-2-ene sp^2-carbon atoms and only *one* resonance is detected for the dppm-methylene hydrogens, whereas in both cases an AB system would be expected if a rigid structure, as found in the solid state, was present in solution. This observation reveals that a fluxional process of the bicyclo[2.2.1]hept-2-ene ligands is taking place in solution, which can in principle be described either as (a) an *inter*molecular exchange or (b) an *intra*molecular scrambling of the two bicyclo[2.2.1]hept-2-ene ligands or (c) an *intra*molecular rotation of each single bicyclo[2.2.1]hept-2-ene ligand, respectively. An intermolecular exchange (possibility *a*) via dissociation of the bicyclo[2.2.1]hept-2-ene ligands can be excluded due to the observation of $^{195}Pt-^{13}C$ and $^{195}Pt-^{1}H$ coupling to bicyclo[2.2.1]hept-2-ene.[9] Intramolecular scrambling of both alkenes between the two platinum centers (possibility b) can be excluded as well, since both, $^1J(Pt-C)$ of 145 Hz *and* $^2J(Pt-C)$ of 24 Hz[9] Pt couplings toward the olefinic C atoms of the bicyclo[2.2.1]hept-2-ene ligands are resolved, which would coalesce into one single averaged coupling in the case of an intramolecular scrambling process. Therefore we assumed that the fluxional behavior in **1** must take place with retention of the bicyclo[2.2.1]hept-2-ene ligands at their respective platinum atoms by an intramolecular rotation about the

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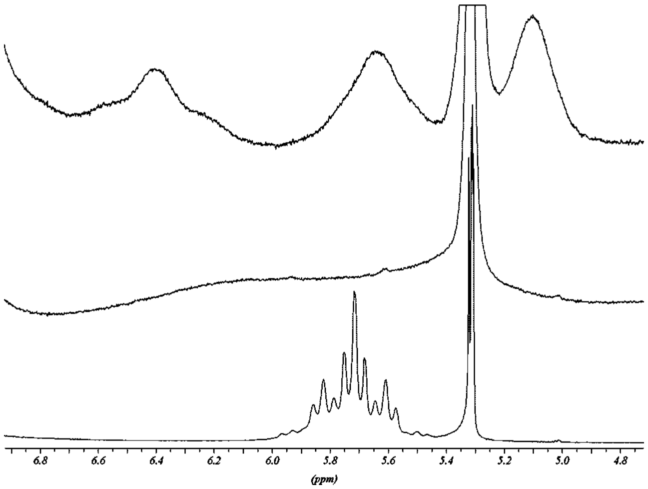
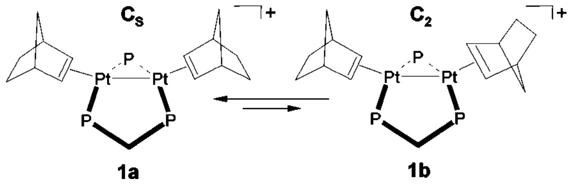


Figure 3. ^{1}H NMR spectrum of **1** (dppm-CH$_2$ region) at 298 K (lower trace; fast exchange), 223 K (middle trace; intermediate exchange/coalescence), and 188 K (upper trace; slow exchange); the large signals at ca. 5.31 ppm are due to residual CH$_2$Cl$_2$ and CHDCl$_2$ in the solvent CD$_2$Cl$_2$.

Scheme 1. Exchange for 1 in Solution



platinum alkene bond (possibility c), which leads to the appearance of a virtually higher symmetry in solution at room temperature.

By lowering the temperature of a solution of **1** in CD$_2$Cl$_2$ the ^{1}H spectrum shows a typical line-broadening pattern expected for intermediate exchange in the range of the NMR time scale. At very low temperatures line splitting and sharpening of the resonances is observed, consistent with a slow exchange on the respective NMR time scale. All ^{1}H resonances show this behavior, but due to the complex ^{1}H−^{1}H coupling pattern within the bicyclo[2.2.1]hept-2-ene ligands or the phenyl groups of dppm and PPh$_2$, respectively, only the splitting of the dppm-CH$_2$ group was found to be sufficiently resolved for a qualitative interpretation of the dynamic process (see Figure 3): At 188 K a splitting of the room-temperature signal (at 5.72 ppm) into *three* discrete resonances of approximate relative intensities of 1:1:1 is observed (6.40; 5.64; 5.10 ppm); no ^{31}P−^{1}H or ^{1}H−^{1}H coupling is resolved at this temperature. This result cannot be explained by assuming one single structure of C_s-symmetry as found in the solid state, which would lead to the appearance of only *two* ^{1}H resonance frequencies with equal intensities for the dppm methylene group.

Due to this observation, the presence of a second isomer had to be suggested, which could in turn be verified by a subsequent ^{31}P NMR experiment: At 178 K all ^{31}P resonances are doubled, with relative intensities of approximately 2:1. This proves that two diastereomeric structures are present in solution, which are in a dynamic equilibrium.

Taking into account the observed ^{1}H and ^{31}P NMR pattern, this dynamic equilibrium can be explained by intramolecular alkene rotation as follows (see Scheme 1): The major isomer **1a** displays overall C_s-symmetry and exhibits a geometry of the bicyclo[2.2.1]hept-2-ene ligands similar to that found in the crystal structure. The orientation of the C=C double bonds is in plane with respect to the other ligands coordinated to the Pt atoms, and both bridging methylene groups of the bicyclo[2.2.1]hept-2-ene ligands are situated in a *syn* orientation pointing to the same side perpendicular to the platinum coordination plane. Assignment of the dppm-CH$_2$ ^{1}H resonances was made by assuming a rigid envelope conformation for the Pt$_2$−P−C−P five-membered ring in **1a** with the carbon atom at the flap. This conformation was also observed in the solid state structure and is most probably induced by the orientation of the bicyclo[2.2.1]-hept-2-ene ligands, which in turn direct the dppm ligand into a rigid envelope conformation via the sterically demanding phenyl groups. The axial and equatorial methylene protons were assigned to the ^{1}H signals at 5.10 and 6.40 ppm, respectively, which show significantly different ^{195}Pt−^{1}H coupling constants of 0 and 100 Hz. This phenomenon has been observed in various dppm-bridged and related metal complexes:[12] Due to the dihedral angular dependence of vicinal coupling constants (Karplus−Conroy relationship), the value of ^{3}J(Pt−P−C−H) is expected to be ca. 0 Hz for a hydrogen atom in an axial position (φ ca. 90°), whereas a hydrogen atom in an equatorial position (φ ca. 180°) should exhibit a significantly higher value (see Figure 4). The remarkably large chemical shift difference $\Delta\delta$ of 1.50 ppm is a further hint for a rigid envelope conformation of the Pt$_2$−P−C−P five-membered ring in **1a**.[12]

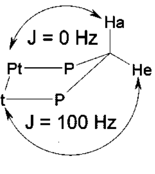


Figure 4. Envelope conformation of the Pt$_2$−P−C−P five-membered ring: The axial (H$_a$) and equatorial (H$_e$) methylene protons show significantly different vicinal coupling constants toward Pt due to the Karplus−Conroy relationship; for a detailed explanation, see text.

The minor compound **1b** is proposed to exhibit overall C_2-symmetry (see Scheme 1). In compound **1b**, which could only be detected in solution, probably due to unfavorable crystallization kinetics, the relative conformation of the C=C double bonds is in-plane with respect to the other ligands coordinated to the Pt atoms as in **1a**, but the respective bridging methylene groups of the bicyclo[2.2.1]hept-2-ene ligands are situated in an *anti* orientation, pointing to the opposite sides perpendicular to the platinum coordination plane. The formation of two diastereomers due to metal−alkene coordination differing by formal rotation of the alkene by 180° about its metal bond axis was observed for asymmetric Pt(0) complexes with "in-plane" coordinated maleic anhydride ligands.[7] The C_2-symmetry of **1b** is in accordance with one single dppm-methylene ^{1}H resonance, which was assigned to the signal at 5.64 ppm. The dppm-CH$_2$ ^{1}H resonance frequency as well as the ^{195}Pt−^{1}H coupling constant of 52 Hz are approximately intermediate between the two respective methylene proton chemical shifts and coupling constants detected for isomer **1a**. This accounts for either a static structure of the Pt$_2$−P−C−P five-membered ring in **1b** with a

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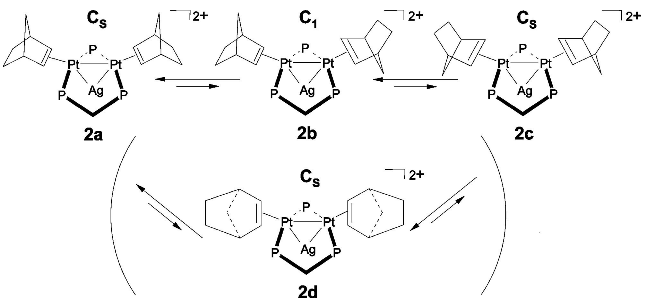
planar or twist conformation or a dynamic structure, where the $Pt_2-P-C-P$ five-membered ring exhibits an envelope conformation that shows a fast exchange via methylene flips on the ^{1}H NMR time scale down to the temperature limit of the solvent.

From the ^{1}H NMR spectrum of **1** at the coalescence temperature an estimation of the activation energy for the exchange process depicted in Scheme 1 was attempted: Presuming that the thermodynamic equilibrium between the two diastereomers (2:1 ratio of **1a** and **1b** found at 188 K) is not significantly shifted with temperature, the activation energy at coalescence temperature was calculated by the formula $\Delta G^{\ddagger}_{\mathrm{rot}} = RT_{\mathrm{c}}\,[22.96 + \ln(T_{\mathrm{c}}/\Delta\nu)]$.[13] Since the signal at 5.64 ppm assigned to **1b** may exchange with the resonance at 6.40 ppm ($\Delta\delta = 0.76$ ppm; $\Delta\nu = 228$ Hz at 300 MHz) and at 5.10 ppm ($\Delta\delta = 0.54$ ppm; $\Delta\nu = 162$ Hz at 300 MHz), the activation energy $\Delta G^{\ddagger}_{\mathrm{rot}}$ was roughly estimated to be ca. 42.5−43.2 kJ/mol at the coalescence temperature $T_{\mathrm{c}} = 223$ K.

The activation energy for alkene rotation in **1** is rather low and compares to that found in Pt(II) alkene complexes and not to Pt(0) complexes. This is also in accordance with the relatively small ^{13}C coordination chemical shift of $\Delta\delta = -56$ ppm ($\delta_{C=C} = 135.5$ ppm in bicyclo[2.2.1]hept-2-ene;[13] $\delta_{C=C} = 79.5$ ppm for bicyclo[2.2.1]hept-2-ene in **1**) found for the olefinic bicyclo[2.2.1]hept-2-ene carbon atoms. The ^{13}C shifts are considered to give an estimate of the electronic density around the olefinic carbon nuclei and thus of the extent of metal-to-ligand π-back-donation.[14] The example of compound **1** clearly shows that an in-plane orientation of the olefin in a square-planar Pt environment does not necessarily account for higher rotation barriers than an upright orientation. This means that metal-to-ligand π-back-donation does not depend significantly on the relative alkene orientation in platinum complexes but on other intrinsic properties of these respective complexes that have to be interpreted carefully on a case by case basis. The low activation energy found for alkene rotation in **1** is therefore mainly attributed to the following: (a) the ample P−Pt−P angle of the phosphorus ligands in mutual *trans* position, which promotes flexibility and reduces steric hindrance for possible transition states of the fluxional process in the quasi quadratic-planar ligand environment, and (b) the positive charge (+1) of the complex, which reduces the ability of platinum for metal-to-ligand π-back-donation compared to neutral or anionic complexes.

Although the exchange mechanism depicted in Scheme 1 looks chemically meaningful and highly probable, there remained still some residual doubt concerning the relative orientation of the bicyclo[2.2.1]hept-2-ene ligands in isomer **1b**: A structure with a symmetric upright coordination of the bicyclo[2.2.1]hept-2-ene ligands in a C_{2v}-symmetry seems—at least theoretically—possible by synchronous rotation of the bicyclo[2.2.1]hept-2-ene ligands in **1a** about 90° and would as well be in accordance with the observed NMR pattern of **1b**. In this case there would exist local energy minima for in-plane and upright orientation in one complex. In order to corroborate (or reject) the dynamic mechanism depicted in Scheme 1, a chemical derivatization of **1** with AgO_3SCF_3 was attempted by preparation and characterization of the compound $[Pt_2(\mu\text{-}Ag)(\mu\text{-}dppm)(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)_2$ (**2**). The idea behind was to observe three different diastereomeric structures (**2a**, **2b**, **2c**) in solution by NMR spectroscopy due to coordination of the Lewis acid Ag^+ at the Pt−Pt bond perpendicular to the roughly planar ligand environment as depicted in Scheme 2. Three possible diastereomers with C_s-, C_1-, and C_s-symmetry may be constructed by successive rotation of the in-plane-coordinated bicyclo[2.2.1]hept-2-ene ligands by 180° about the Pt−alkene axis, whereas a C_s-symmetry instead of C_1 would be expected in the case of a symmetric upright coordination of the bicyclo[2.2.1]hept-2-ene ligands (isomer **2d**; synchronous rotation of both bicyclo[2.2.1]hept-2-ene ligands by 90° about the Pt−alkene axis). The reactivity of the Pt−Pt bond in diplatinum(I) complexes toward various electrophiles has been extensively studied and is well described in the literature, e.g., by Braunstein et al.[15] and Anderson and Puddephatt et al.[16]

Scheme 2. Possible Exchange Pathways for 2 in Solution



Addition of 1 equiv of AgO_3SCF_3 to a solution of **1** in CD_2Cl_2/MeOH (10:1) leads to a significant upfield shift of the ^{31}P phosphido signal (222.1 ppm; $\Delta\delta = -6.9$ ppm) and a slight downfield shift of the ^{31}P dppm signal (2.8 ppm; $\Delta\delta = +2.0$ ppm) at room temperature. The P−P and Pt−P couplings are affected as well ($^{2}J(PP) = 192.6$, $^{1}J(PtP)_{\mathrm{dppm}} = 2840$, $^{1}J(PtP)_{\mathrm{phosphido}} = 2328$ Hz). Attempts to record a ^{195}Pt spectrum at room temperature failed as well as crystallization trials from MeOH, CD_2Cl_2, or MeOH/CD_2Cl_2 mixtures, which yielded only crystals of pure compound **1**. All these observations indicated the presence of a thermodynamically labile Ag^+ adduct of **1** in solution.[17]

Crystals of compound **2** suitable for X-ray diffraction could be obtained from benzene solution at room temperature as a solvate containing three benzene molecules (see Figure 5). The relative bicyclo[2.2.1]hept-2-ene orientation in the solid state corresponds to isomer **2a** in Scheme 2. In comparison with the crystal structure of the parent compound **1** only small geometric variations are observed within the $[Pt_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2]$ framework. Both bridging methylene groups of the *exo*-coordinated bicyclo[2.2.1]hept-2-ene ligands as well as the methylene carbon atom of the dppm ligand point to the same side perpendicular to the platinum coordination plane; the silver atom is situated on the opposite side and is bound to the two platinum atoms. Furthermore the coordination sphere of Ag involves two oxygen atoms of both trifluoromethanesulfonate moieties. The overall coordination geometry around the silver atom may be best described as distorted square-planar. The slight twist angle between the Ag(1)−Pt(1)−Pt(2) and the Ag(1)−O(1)−O(4) planes amounts to 16.2(3)°, and the *transoid* Pt and O atoms, respectively, display pairwise a short

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(13) Günther, H. *NMR Spektroskopie*; G. Thieme Verlag: Stuttgart, 1992.

(14) Cavallo, L.; Macchioni, A.; Zuccaccia, C.; Zuccaccia, D.; Orabona, I.; Ruffo, F. *Organometallics* **2004**, *23*, 2137., and references therein.

(15) Archambault, C.; Bender, R.; Braunstein, P.; Dusausoy, Y. *J. Chem. Soc., Dalton Trans.* **2002**, 4084.

(16) (a) Anderson, G. K. *Adv. Organomet. Chem.* **1993**, *35*, 1., and references therein. (b) McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1986**, 811.

(17) A partial reaction of **1** with 2 equiv of Ag^+, theoretically present in thermodynamic equilibrium, was excluded, since the spectral pattern of solutions of **2** does not change upon addition of a second equivalent of AgO_3SCF_3.

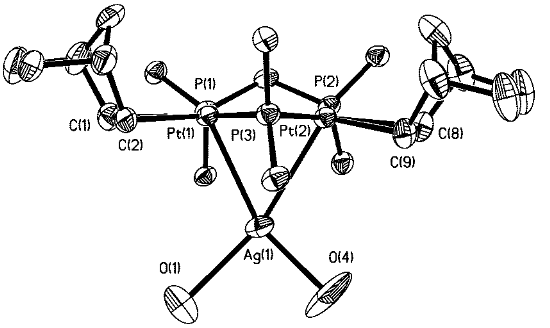

Figure 5. Molecular structure of **2** × 3 C_6H_6 (projection into the plane formed by the diplatinum-phosphido triangle). The *ipso* C atoms of the phenyl groups and the Ag-bound O atoms of the two (O_3SCF_3) moieties are shown. The solvate molecules are omitted for clarity.

or a long distance to Ag. In contrast to many literature examples of dppm-bridged Pt(I) reaction products with electrophiles, no A-frame structure is formed in compound **2**, where the bicyclo[2.2.1]hept-2-ene ligands would be shifted into a mutual *trans* position with respect to the coordinating electrophile. This is attributed to the presence of the bridging phosphido ligand preventing major conformational and angular changes of the platinum ligand environment due to its rigid three-membered Pt−Pt−P ring structure. A similar effect was recently observed by Braunstein et al. in a related Pt(I)-phosphido-copper adduct.[15] Although some other Pt_2Ag clusters were reported in the literature,[15,18] compound **2** seems to be the first diplatinum(I)−silver adduct, which was structurally characterized by X-ray diffraction. There exist crystal structure determinations of Pt−Ag d^8−d^{10} compounds,[19] one Pt_3Ag cluster, which has been reported by Braunstein et al.,[20a] and one trimetallic Pt_3AgAu cluster.[20b,c] The Pt−Ag distances in **2** (293.17(8), 282.48(8) pm) are in the range of those found in other bimetallic complexes of silver and platinum (263.7–304.9 pm) (for selected bond lengths and angles in **2** see Table 1).

The thermodynamic lability of **2** in CD_2Cl_2/MeOH (10:1) is overcome by cooling a solution of equimolar amounts of AgO_3SCF_3 and **1** to 193 K.[21] At this temperature alkene rotation is frozen out on the ^{31}P NMR time scale for compound **2**, and three distinct spin systems are observed in the ^{31}P NMR spectrum. Two A_2X systems were assigned to the isomers **2a** (33% relative intensity) and **2c** (10% relative intensity), which both display a C_s-symmetry (see Scheme 2). The assignments of major and minor compound were made by assuming an increased steric hindrance of bicyclo[2.2.1]hept-2-ene ligands, dppm-phenyl groups, and the Ag center in **2c**, which should be therefore energetically less favored. The AMX system (47% relative intensity) was assigned to the dissymmetric isomer **2b**. The detection of isomer **2b**, formally synthesized by reaction of **1b** with Ag^+ and showing no intrinsic symmetry according to ^{31}P NMR spectroscopy, is the final proof for the in-plane *anti* orientation of the two bicyclo[2.2.1]hept-2-ene ligands proposed for **1b** in Scheme 1. An upright coordination of bicyclo[2.2.1]hept-2-ene ligands is therefore not considered to play a significant role as an energetically stable rotamer but to form an intermediate or transition state for interconversion of the *syn* and *anti* isomers **1a** and **1b**.

Table 1. Selected Bond Lengths (pm) and Angles (deg) in 2·3C_6H_6

Pt(1)−Pt(2)	271.44 (5)	P(3)−Pt(1)−Pt(2)	53.16 (4)
Pt(1)−P(1)	232.7 (2)	P(3)−Pt(2)−Pt(1)	53.08 (5)
Pt(1)−P(3)	226.1 (2)	Pt(1)−P(3)−Pt(2)	73.75 (5)
Pt(2)−P(2)	231.9 (2)	P(1)−Pt(1)−Pt(2)	91.94 (5)
Pt(2)−P(3)	226.3 (2)	P(2)−Pt(2)−Pt(1)	96.26 (5)
Pt(1)−C(1)	224.2 (7)	P(1)−Pt(1)−P(3)	144.84 (6)
Pt(1)−C(2)	222.6 (7)	P(2)−Pt(2)−P(3)	148.30 (6)
Pt(2)−C(8)	223.2 (7)	P(2)−C(15)−P(1)	112.4 (3)
Pt(2)−C(9)	220.0 (7)	C(1)−Pt(1)−C(2)	35.8 (3)
C(1)−C(2)	137.4 (10)	C(8)−Pt(2)−C(9)	36.9 (3)
C(8)−C(9)	140.2 (10)	Pt(1)−Ag(1)−Pt(2)	56.23 (2)
Pt(1)−Ag(1)	282.48 (8)	Pt(2)−Pt(1)−Ag(1)	63.88 (2)
Pt(2)−Ag(1)	293.17 (8)	Pt(1)−Pt(2)−Ag(1)	59.89 (2)
Ag(1)−O(1)	255.1 (5)	O(1)−Ag(1)−Pt(2)	159.1 (2)
Ag(1)−O(4)	223.0 (6)	O(4)−Ag(1)−Pt(1)	157.8 (3)
		O(1)−Ag(1)−O(4)	90.8 (3)
C(8)−Pt(2)−Ag(1)	115.7 (2)	C(2)−Pt(1)−Pt(2)	142.4 (2)
C(9)−Pt(2)−Ag(1)	106.6 (2)	C(1)−Pt(1)−Pt(2)	177.74 (19)
C(1)−Pt(1)−Ag(1)	114.7 (2)	C(9)−Pt(2)−Pt(1)	139.36 (19)
C(2)−Pt(1)−Ag(1)	109.2 (2)	C(8)−Pt(2)−Pt(1)	174.5 (2)

In contrast to the thermodynamically labile Ag^+ adduct **2**, the reaction of **1** with an excess of 100% HO_3SCF_3 in CD_2Cl_2 leads to quantitative formation of compound $[Pt_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)_2$ (**3**) at room temperature according to ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR. The ^1H and ^{195}Pt spectra indicate that a formal hydride ligand is coordinated to both Pt centers: The relative intensity of a signal in the ^1H NMR spectrum with a chemical shift of −8.60 ppm typical for platinum hydrides[16,22] is consistent with the presence of one single hydride ligand. The proton-coupled ^{195}Pt spectrum exhibits only one chemical shift for both Pt atoms, and the splitting pattern clearly proves the presence of a single hydride directly bound to both Pt centers ($^1J(PtH) = 530$ Hz). The ensemble of multinuclear NMR parameters of **3** as well as geometrical constraints within the complex clearly support a structure with a hydride ligand symmetrically bridging both platinum centers perpendicular to the metal coordination plane, analogously to the isolobal Ag^+ in **2**. The chemical shift of the phosphido resonance in the ^{31}P spectrum of **1** remains nearly unchanged by coordination of H^+ and clearly reveals the presence of the Pt−Pt bond in **3**, since chemical shifts of phosphido ligands bridging two metal centers are very sensitive toward even slight changes of the M−P−M angle.[23] By contrast, other NMR parameters, especially coupling constants, are significantly affected by coordination of H^+; for example, all $^1J(PtP)$ couplings are largely reduced with respect to the parent compound **1**.

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(18) (a) Bender, R.; Bouaoud, S.-E.; Braunstein, P.; Dusausoy, Y.; Merabet, N.; Raya, J.; Rouag, D. *J. Chem. Soc., Dalton Trans.* **1999**, 735. (b) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556. (c) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1987**, *26*, 3482.

(19) (a) Xu, C.; Anderson, G. K.; Brammer, L.; Braddock-Wilking, J.; Rath, N. P. *Organometallics* **1996**, *19*, 3972. (b) Casas, J. M.; Fornies, J.; Martin, A.; Rueda, A. J. *Organometallics* **2002**, *21*, 4560. (c) Casas, J. M.; Falvello, L. R.; Fornies, J.; Martin, A. *Inorg. Chem.* **1996**, *35*, 7867. (d) Albano, V. G.; Di Serio, M.; Monari, M.; Orabona, I.; Panunzi, A.; Ruffo, F. *Inorg. Chem.* **2002**, *41*, 2672. (e) Yam, V. W.-W.; Yeung, P. K.-Y.; Cheung, K.-K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 739.

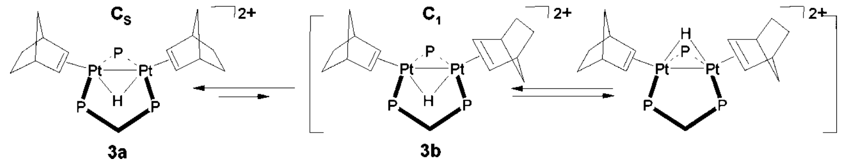
(20) (a) Archambault, C.; Bender, R.; Braunstein, P.; DeCian, A.; Fischer, J. *Chem. Commun.* **1996**, 2729. (b) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L.; Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4516. (c) Douglas, G.; Jennings, M. C.; Muir, K. W.; Manojlovic-Muir, L.; Puddephatt, R. J. *Inorg. Chem.* **1989**, *28*, 3086.

(21) Weak ^{31}P signals in the phosphido region indicate the presence of only small amounts of compound **1** being in equilibrium with **2** (ca. 10%).

(22) (a) Schuh, W.; Wachtler, H.; Laschober, G.; Kopacka, H.; Wurst, K.; Peringer, P. *Chem. Commun.* **2000**, 1181. (b) Alonso, E.; Fornies, J.; Fortuno, C.; Martin, A.; Orpen, A. G. *Organometallics* **2001**, *20*, 850.

(23) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1987; Chapter 16.

Scheme 3. Exchange Pathways for 3 in Solution



A possible coordination of the hydride ligand via the platinum−phosphido bonds as seldom found, for example, in $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PHBu^t_2)(PHBu^t_2)_2]^+$ or the adduct of $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ with 2 equiv of the electrophile $Au(PPh_3)^+$ can be excluded due to the lack of any large coupling of the hydride ligand toward the phosphorus nuclei.[24,25] Unfortunately compound **3** could not be isolated analytically pure in the solid state, and no single-crystal X-ray structure could be determined.

Compound **3** shows a remarkable feature in the ^1H NMR spectrum at room temperature: There is only one single resonance observed for the dppm-methylene hydrogens (as well as for the hydrogens at the bicyclo[2.2.1]hept-2-ene sp^2-carbon atoms, etc.), whereas two resonances (AB system) would be expected, due to the suggested position of the hydride ligand perpendicular to the platinum coordination plane. This extraordinary feature may be interpreted by the unique physical characteristics of hydride ligands: It is well-known that hydride ligands may display fluxionality in platinum clusters.[26] Even in bimetallic complexes chemical exchange of bridging hydrides is observed, for example, in the A-frame complexes $Pt_2(dppm)_2(\mu\text{-}H)L_2^+$ (L = H, Cl, . . .), where inversion of the bridging hydride was shown to proceed fast at room temperature.[27] Therefore a fast intramolecular inversion of the hydride ligand is anticipated for complex **3** as well.

At low temperatures the ^1H (188 K) and ^{31}P (213 K) spectra of **3** show the presence of only two diastereomers in solution in a ratio of 2:1. All phosphorus signals in the ^{31}P NMR spectrum as well as the hydride signal in the ^1H NMR spectrum are doubled (all other ^1H signals show crucial overlapping and are not sufficiently resolved for a qualitative interpretation). The two diastereomers detected in solution are assigned to the structures **3a** and **3b**, analogously to compound **1** (see Scheme 3). One A_2X system found in the ^{31}P NMR is in accordance with structure **3a**.[28] However a fast intramolecular inversion of the hydride ligand through the Pt−Pt bond (flip motion) has to be assumed for **3b** in order to comply with the observed A_2X system in the ^{31}P NMR spectrum. A sort of tunneling process may account for the fast inversion through the platinum−platinum bond in **3**, which is anticipated to have a considerably lower activation barrier compared to $Pt_2(dppm)_2(\mu\text{-}H)H_2^+$ (46.5 kJ/mol).[27a] Taking into consideration the solid state structure of **2**, no A-frame structure is assumed to be present for the isolobal compound **3**, which should facilitate a hydrogen flip through the Pt−Pt bond, since no substantial motion of other ligands would be mandatory for this unique intramolecular fluxionality with unpecedentedly low activation barrier.

Conclusion

The appearance of two diastereomeric structures for $[Pt_2(\mu\text{-}dppm)(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1**) was traced back to relative *syn*/*anti* orientation of the bicyclo[2.2.1]hept-2-ene ligands via an intramolecular alkene rotation process. The low energy barrier for the rotation of the in-plane-coordinated bicyclo[2.2.1]hept-2-ene ligands was attributed to a favorable electronic and steric environment in **1**. Reaction of **1** with the Lewis acids Ag^+ and H^+, respectively, at the Pt−Pt bond leaves the $[Pt_2(\mu\text{-}dppm)(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2]$ framework substantially unchanged, as evidenced by the X-ray crystal structure of the Ag^+ adduct **2**. Both reaction products display alkene rotation like the parent compound **1**; the H^+ adduct **3** exhibits an additional, unique fluxionality by hydrogen tunneling through the Pt−Pt bond, indicating an unprecedentedly low energy barrier, since no substantial motion of other ligands is mandatory for this exchange process.

Experimental Section

General Information. Compound **1** was prepared by the literature method.[9] All other reagents were purchased from commercial suppliers and used without further purification. The solvents were dried using standard procedures. All operations were carried out under standard Schlenck conditions.

^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra were recorded on Bruker DPX 300 or Bruker DRX 500 NMR spectrometers using standard Bruker pulse sequences; they were referenced against TMS, 85% H_3PO_4 or 1 mol/L Na_2PtCl_6, respectively. Chemical shifts are reported in ppm; coupling constants in hertz. The low-temperature ^{31}P NMR spectra of **1**, **2**, and **3** as well as the low-temperature ^1H NMR spectrum of **1** (dppm-CH_2 part) were simulated by WIN-DAISY.[29] Connectivities of the dppm and phosphido ^{31}P resonances of the three isomers **2a**, **2b**, and **2c** have been established unambiguously by selectively homonuclear decoupled ^{31}P NMR experiments (irradiation at 215 and 210 ppm, respectively).

Preparation of solutions of **1** for NMR spectroscopy: $[Pt_2(\mu\text{-}dppm)(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1**) (69.9 mg, 0.05 mmol) was dissolved in 0.5 mL of CD_2Cl_2. The resulting pale yellow solution was transferred into a NMR tube. The room-temperature ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR data of **1** were reported elsewhere.[9]

1a: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 178 K): 229.9 (t, $^2J(PP) = 180.1$, $^1J(PtP) = 2610$, PPh_2, line width 48 Hz), 0.8 (d, $^2J(PCP) = 53$, $^1J(PtP) = 2967$, $^2J(PtP) = -50$, dppm, line width 38 Hz). ^1H NMR (CD_2Cl_2, 188 K): 6.40 ($^3J(PtH) = 100$, H^a PCH_2P), 5.10 ($^3J(PtH)$ ca. 0, H^e PCH_2P).

1b: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 178 K): 229.7 (t, $^2J(PP) = 179.7$, $^1J(PtP) = 2586$, PPh_2, line width 24 Hz), 0.6 (d, $^2J(PCP) = 55$,

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[24] Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1993**, *12*, 1702.

[25] Bender, R.; Braunstein, P.; Dedieu, A.; Dusausoy, Y. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 923.

[26] Lloyd, B. R.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 7785.

[27] (a) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642. (b) Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1015.

[28] Structure **3a** might theoretically be in a rapid equilibrium with a structure related to **2c** by fast intramolecular hydride exchange through the Pt−Pt bond; however there is no analytical proof for this suggestion.

[29] (a) Weber, U.; Spiske, R.; Höffken, H.-W.; Hägele, G.; Thiele, H. *Manual and Program System, Bruker Manual*; 1993. (b) Hägele, G.; Reinemer, P.; Grzonka, M. *Workshop,,Computer in der Chemie Softwareentwicklung in der Chemie* **1988**, *2*, 241.

^1J(PtP) = 2989, ^2J(PtP) = −53, dppm, line width 11 Hz). ^{1}H NMR (CD_2Cl_2, 188 K): 5.64 (^3J(PtH) = 52, PCH_2P).

Synthesis of **2**·$3C_6H_6$: [Pt_2(*μ*-dppm)(*μ*-PPh_2)(η^2-bicyclo[2.2.1]hept-2-ene)$_2$](O_3SCF_3) (**1**) (129.7 mg, 0.1 mmol) and AgO_3SCF_3 (25.7 mg, 0.1 mmol) were dissolved under slight stirring in 2 mL of benzene. After complete dissolution, the resulting yellow solution was left for crystallization under exclusion of light at room temperature. After 2 weeks prismatic yellow crystals of **2**·$3C_6H_6$ were obtained, which lose benzene of crystallization upon standing. Yield: 84 mg (47%). Anal. Calcd for $C_{53}H_{52}AgF_6O_6P_3Pt_2S_2 \cdot C_6H_6$: C, 43.42; H, 3.58. Found: C, 42.98; H, 3.35.

Preparation of solutions of **2** for NMR spectroscopy: [Pt_2(*μ*-dppm)(*μ*-PPh_2)(η^2-bicyclo[2.2.1]hept-2-ene)$_2$](O_3SCF_3) (**1**) (69.9 mg, 0.05 mmol) and AgO_3SCF_3 (12.9 mg, 0.05 mmol) were dissolved in 0.55 mL of CD_2Cl_2/MeOH (10:1). The resulting yellow solution was transferred into a NMR tube.

2a: ^{31}P{^{1}H} NMR (CD_2Cl_2/MeOH, 10:1, 193 K): 219.5 (br, ^2J(PP) = 199.7, ^1J(PtP) ca. 1600, PPh_2),[30] 4.1 (d, ^2J(PCP) = 56, ^1J(PtP) = 2636, ^2J(PtP) = −50, dppm).

2b: ^{31}P{^{1}H} NMR (CD_2Cl_2/MeOH, 10:1, 193 K): 210.4 (dd, ^2J(PP) = 205.4, ^2J(PP′) = 200.8, ^1J(PtP) = 2024, ^1J(Pt'P) = 1938, PPh_2), 7.2 (dd, ^2J(PCP′) = 59, ^1J(PtP) = 2588, ^2J(Pt′P) = −58, dppm-P), 2.4 (dd, ^2J(PtP′) = −58, ^1J(Pt′P′) = 2673, dppm-P′).

2c: ^{31}P{^{1}H} NMR (CD_2Cl_2/MeOH, 10:1, 193 K): 211.9 (t, ^2J(PP) = 201.6, ^1J(PtP) = 1931, PPh_2), 5.5 (d, ^2J(PCP) = 56, ^1J(PtP) = 2613, ^2J(PtP) = −57, dppm).

Preparation of solutions of **3** for NMR spectroscopy: [Pt_2(*μ*-dppm)(*μ*-PPh_2)(η^2-bicyclo[2.2.1]hept-2-ene)$_2$](O_3SCF_3) (**1**) (69.9 mg, 0.05 mmol) was dissolved in 0.5 mL of CD_2Cl_2, and 3 drops of 100% HO_3SCF_3 were added. The resulting biphasic system was stirred for 2 min. After complete separation of the two liquid phases the yellow organic phase was transferred into a NMR tube.

3: ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): 229.1 (t, ^2J(PP) = 209.3, ^1J(PtP) = 1528, PPh_2), 13.7 (d, ^2J(PCP) = 56.7, ^1J(PtP) = 2304, ^2J(PtP) = −17, dppm). ^{195}Pt{^{1}H} NMR (CD_2Cl_2, 293 K): −5832 (td, ^1J(PtPt) = 467, Pt). ^{1}H NMR (CD_2Cl_2, 293 K): bicyclo[2.2.1]hept-2-ene δ 4.27 (s, 4H, ^2J(PtH) = 70, HC=CH), 2.38 (s, 4H, CH), 1.49 (d, 4H, ^2J(HH) = 8.5, CH_2), 0.93 (d, 4H, ^2J(HH) = 8.5, CH_2), 0.46 (d, 2H, ^2J(HH) = 10, CH_2 bridge), 0.38 (d, 2H, ^2J(HH) = 10, CH_2 bridge), dppm/PPh_2 δ 7.85 – 7.30 (m, ca. 30H, Ph), 3.77 (t, 2H, ^2J(PH) = 11, ^3J(PtH) = 40, PCH_2P), hydride δ −8.60 (dt, 1H, ^2J(PH) 11, ^2J(PH) 11, ^1J(PtH) 530, PtHPt). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): bicyclo[2.2.1]hept-2-ene δ 93.0 (^1J(PtC) = 88, HC=CH), 44.4 (^2J(PtC) = 8, CH), 26.1 (^3J(PtC) = 27, CH_2), 42.8 (^3J(PtC) = 18, CH_2 bridge), dppm δ 125.0 (^1J(PC) = 60, ^2J(PtC) = 20, C_{ipso}), 133.2 (^2J(PC) = 12, C_{ortho}), 130.6 (^3J(PC) = 12, C_{meta}), 134.3 (C_{para}), 34.3 (^1J(PC) = 33, PCH_2P), PPh_2 δ 128.8 (^1J(PC) = 44, ^2J(PtC) = 26, C_{ipso}), 133.3 (^2J(PC) = 13, C_{ortho}), 130.9 (^3J(PC) = 12, C_{meta}), 135.3 (C_{para}), trifluoromethanesulfonate δ 118.8 (^1J(FC) = 317, CF_3).

3a: ^{31}P{^{1}H} NMR (CD_2Cl_2, 213 K): 228.0 (t, ^2J(PP) = 206.4, ^1J(PtP) = 1517, PPh_2), 12.6 (d, ^2J(PCP) = 52, ^1J(PtP)) = 2311, ^2J(PtP) = −15, dppm). ^{1}H NMR (CD_2Cl_2, 188 K): −8.53 (^1J(PtH) = 530, PtHPt).

3b: ^{31}P{^{1}H} NMR (CD_2Cl_2, 213 K): 230.5 (t, ^2J(PP) = 208.2, ^1J(PtP)) = 1539, PPh_2), 13.3 (d, ^2J(PCP) = 52, ^1J(PtP) = 2280, ^2J(PtP) = −15, dppm). ^{1}H NMR (CD_2Cl_2, 188 K): −8.77 (^1J(PtH) = 530, PtHPt).

Table 2. Crystal Data and Structure Refinement of 2·$3C_6H_6$

molecular formula	$C_{53}H_{52}AgF_6O_6P_3Pt_2S_2$ x 3 C_6H_6
fw	1788.35
cryst syst	monoclinic
space group	$P2_1/n$ (No.14)
unit cell dimens	a = 1119.4(2) pm, α = 90°
	b = 2348.8(4) pm, β = 96.52(2)°
	c = 2619.0(4) pm, γ = 90°
volume	6.842(2) nm^3
Z	4
temperature	213(2) K
density (calcd)	1.736 g/cm^3
absorp coeff	4.561 mm^{-1}
F(000)	3512
color, habit	yellow prism
cryst size	0.6 × 0.4 × 0.3 mm
θ range for data collection	2.5 to 23.0°
index ranges	$0 < h < 11$, $0 < k < 25$, $-28 < l < 28$
no. of reflns collected	9459
no. of indep reflns	8902 (R_{int} = 0.0288)
no. of reflns with $I > 2\ \sigma(I)$	7323
max. and min. transmn	1.000 and 0.787
no. of data/restraints/params	8902/10/852
goodness-of-fit on F^2	1.030
final R indices [$I > 2\sigma(I)$]	R1 = 0.0334, wR2 = 0.0694
R indices (all data)	R1 = 0.0487, wR2 = 0.0735
extinction coeff	0.00042(3)
largest diff peak and hole	1217 and −1133 e nm^{-3}
weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 28.4P]$ where $P = (F_o^2 + 2F_c^2)/3$

X-ray Structure Determination. A crystal of **2**·$3C_6H_6$ was mounted on a glass fiber, and X-ray data were collected on a Bruker P4 diffractometer using Mo Kα radiation (monochromator: highly oriented graphite crystal, *ω*-scan). Unit cell parameters were determined and refined from 41 randomly selected reflections by the P4 automatic routine. Every 97 reflections, three standard reflections were measured. Data were corrected for Lorentz−polarization and absorption effects (*ψ*-scans). The structure was solved by direct methods and subsequent Fourier techniques (SHELXS-86).[31] Refinement on F^2 with all measured reflections was carried out by the full-matrix least-squares technique (SHELXL-97).[32]

All non-hydrogen atoms were refined with anisotropic displacement parameters except the disordered carbon atoms C40A, C42A−43A, and C45A of the minor disordered part of a benzene molecule. The hydrogens at C1, C2, C8, and C9 were found and refined isotropically. All other hydrogen atoms were placed at calculated ideal positions (riding model). One benzene molecule shows a 2:1 disorder (C40−C45, C40A−C45A), such that C41 and C41A as well as C44 and C44A were refined using the same parameters.

Crystal data and details of the structure determination and refinement are collected in Table 2.

Supporting Information Available: Positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates of **2**·$3C_6H_6$. Low-temperature ^{31}P and ^{1}H NMR spectra of **1** and low-temperature ^{31}P NMR spectra of **2** and **3**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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(30) Values of chemical shift and ^1J(PtP) couplings of PPh_2 in **2a** are derived from WIN-DAISY simulation. According to homonuclear ^{31}P decoupling experiments the chemical shift of PPh_2 in **2a** is at ca. 215 ppm; therefore the parameters for this nucleus gained from simulation of this broad and mostly structureless signal are considered not to be very precise.

(31) Sheldrick, G. M. *SHELXS-86*: program for crystal structure solutions; University of Göttingen, 1986.

(32) Sheldrick, G. M. *SHELXL-97*: program for refinement of crystal structures; University of Göttingen, 1997.