

A Tetramethylplatinum(IV) Complex with 1,1'-Bis(diphenylphosphanyl)-ferrocene Ligands: Reaction with Trifluoroacetic Acid

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A new tetramethylplatinum(IV) complex [PtMe₄(dppf)] (**2**; dppf = 1,1'-bis(diphenylphosphanyl)ferrocene), as the first platinum(IV) complex to contain a chelating dppf ligand, was prepared by the reaction of the known dimeric tetramethylplatinum(IV) complex *cis,cis*-[Me₄Pt(μ-SMe₂)₂PtMe₄] (**1**) with the biphosphane ligand dppf (2 equiv.) at room temperature by replacement of the SMe₂ ligands with the P ligating atoms of dppf. The single-crystal X-ray structure of complex **2** revealed that the dppf chelating ligand is arranged close to the "synperiplanar-eclipsed" conformation, with a Cp(centroid)⋯Fe⋯Cp(centroid) twist angle of 17.6° and a dppf bite angle, P1–Pt1–P2, of 95.77(3)°. This is in contrast to the usually preferred "synclinal-staggered" conformation, in which the Cp(centroid)⋯Fe⋯Cp(centroid) twist angle is close to 36° as found in Pt^{II} complexes with chelating dppf ligands,

like for example [PtMe₂(dppf)] exhibiting a dppf bite angle close to 100°. When complex **2** was treated with the strong acid CF₃COOH (1 equiv.) first evolution of methane was observed, followed by a C–C coupling reaction to give ethane and the methylplatinum(II) complex [PtMe(OCOCF₃)(dppf)] (**3**). The reaction of complex **2** with the nucleophile HgCl₂ (1 equiv.) similarly gave MeHgCl, ethane, and the methylplatinum(II) complex [PtMeCl(dppf)] (**11**). The structure of complex **3** was also determined by X-ray crystallography. The geometry around the platinum center is best described as distorted square-planar and the dppf is arranged in the usually preferred "synclinal-staggered" conformation.

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Introduction

Ever since the serendipitous synthesis of the binuclear tetramethylplatinum(IV) complex *cis,cis*-[Me₄Pt(μ-SMe₂)₂PtMe₄] by the reaction of *cis*-[PtCl₂(SMe₂)₂] with a mixture of MeLi/MeI,^[1] several related tetramethylplatinum(IV) complexes have been prepared by displacement of the labile SMe₂ ligands in this useful synthon with several phosphorus and nitrogen donor ligands, and some of their reactions have been studied.^[2] In these complexes, two Me groups are forced into the *trans* position to each other, and as a result of the high *trans* influence of the Me ligand, the Pt–Me bonds become rather weak, as suggested by a comparatively low Pt–C coupling constant;^[3] interesting reactions and properties are thus observed.^[2] The only reported X-ray crystal structures having a Pt(Me)₄ moiety are [(dppe)-PtMe₄] [dppe = Ph₂P(CH₂)₂PPh₂] and [(dppbz)PtMe₄] [dppbz = *o*-PPh₂(C₆H₄)PPh₂], in which the Pt–Me bond lengths vary only slightly with respect to the *trans* ligand.^[4]

Although several platinum(II) complexes containing the biphosphane ligand dppf [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene] have been reported,^[5,6] the related platinum(IV) complexes are not common. We recently reported a binuclear Pt^{IV} complex with dppf as a spacer ligand and characterized its structure by using multinuclear studies,^[6] but there are no reports for a Pt^{IV} complex bearing a chelating dppf ligand.^[5] The P–M–P bite angle of dppf has been shown to be important in carbon–carbon coupling reactions, and it seems to be influenced by several factors.^[5b]

Reductive elimination involving C–C bond formation is of fundamental importance in homogeneous catalysis by d⁶ and d⁸ transition-metal complexes.^[7] The mechanistic evidence obtained for the processes involving Pt^{IV} complexes supported that either prior dissociation of a ligand or formation of a cationic five-coordinated intermediate are responsible for the C–C coupling.^[4,8]

In this study, a new tetramethylplatinum(IV) complex [PtMe₄(dppf)] (**2**) was synthesized and characterized by multinuclear NMR studies and its single-crystal structure was determined by X-ray crystallography. The reaction of the complex with CF₃COOH was also investigated. Our results indicate that the steric demand imposed by dppf has an interesting effect on the related chemistry, and especially on C–C bond formation.

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Results and Discussion

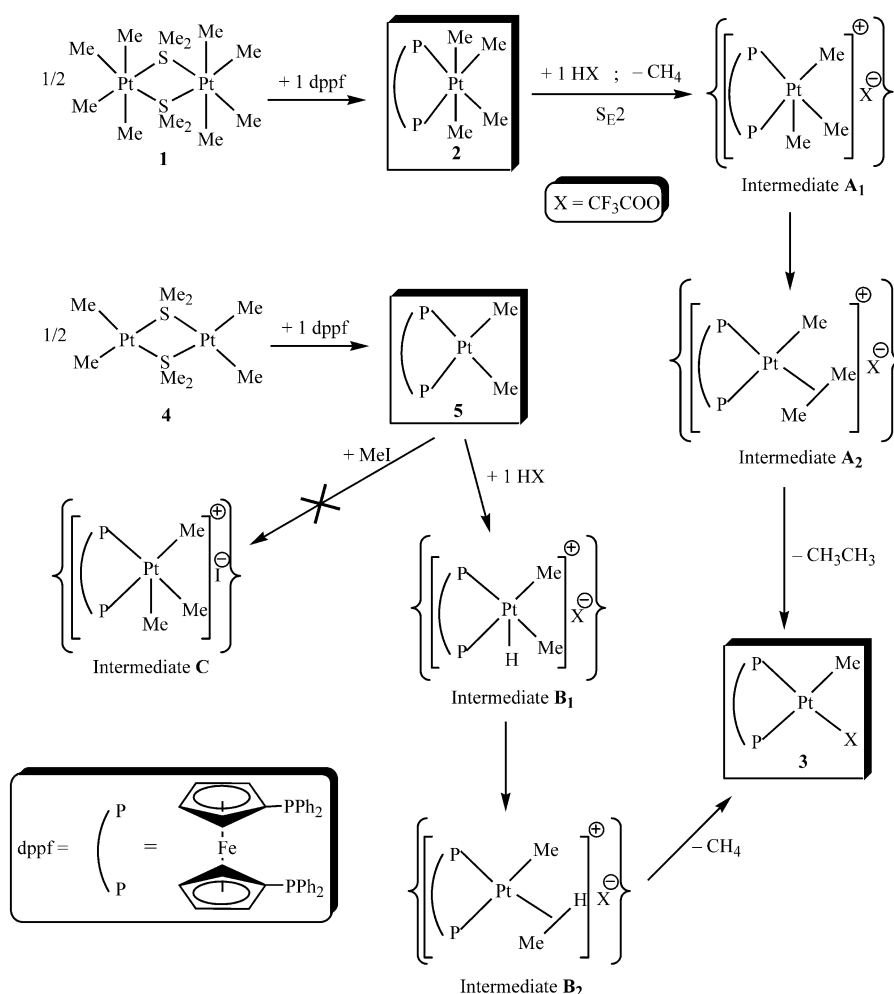
The routes to prepare complexes **2**, **3**, and **5** from starting complexes **1** and **4** are indicated in Scheme 1; the suggested intermediates are shown by letters A–C.

Syntheses and Reactions

The reaction of the known dimeric tetramethylplatinum(IV) complex *cis,cis*-[Me₄Pt(μ-SMe₂)₂PtMe₄] (**1**) with the biphosphane ligand dppf (2 equiv.) at room temperature gave in good yield the monomeric tetramethylplatinum(IV) complex [PtMe₄(dppf)] (**2**) by replacement of the SMe₂ ligands with the P ligating atoms of dppf. Complex **2** was very rapidly treated with the strong acid CF₃COOH (1 equiv.) to give methane, ethane, and the methylplatinum(II) complex [PtMe(OCOCF₃)(dppf)] (**3**). We suggest that in this reaction, the initial protonation of the Pt–C bond of one of the mutually *trans* methyl groups proceeds through an S_E2 (open) mechanism to give CH₄ and the very unstable cationic five-coordinate intermediate [PtMe₃-(dppf)]⁺(OCOCF₃)[−] (**A**₁). The high reactivity of mutually

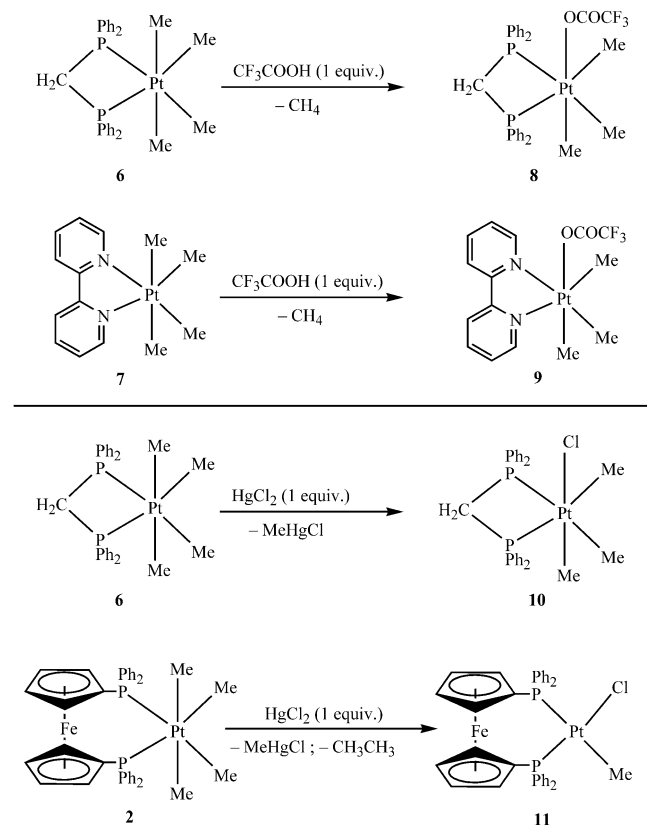
trans methyl groups is attributed to the high *trans* influence of the methyl group *trans* to a Pt–C bond being cleaved.^[2,3] Subsequently, intermediate **A**₁ very rapidly undergoes reductive elimination of ethane, through intermediate **A**₂, to yield Pt^{II} complex **3**. We attribute the latter reductive elimination of the C–C bond (forming ethane) to a large steric demand imposed by dppf on the square base of the square pyramidal intermediate **A**₁.

It is interesting to note that, in contrast to the above routes observed for the reaction of **2** with CF₃COOH (Scheme 2), when either of the analogous tetramethylplatinum(IV) complexes [PtMe₄(dppm)] [**6**; dppm = bis(diphenylphosphanyl)methane = Ph₂PCH₂PPh₂] or [PtMe₄(bpy)] [**7**; bpy = 2,2'-bipyridine] is similarly treated with CF₃COOH (1 equiv.), only methane is formed along with the corresponding *fac*-trimethylplatinum(IV) complexes [PtMe₃(OCOCF₃)(dppm)] (**8**)^[2e] or [PtMe₃(OCOCF₃)(bpy)] (**9**), respectively. This indicates that after initial protonation of Pt–C by an S_E2 mechanism to give CH₄ and the related intermediates, either [PtMe₃(dppm)]⁺(OCOCF₃)[−] or [PtMe₃(bpy)]⁺(OCOCF₃)[−], rather than reductive elimination of the C–C bond to give ethane, is



Scheme 1.

formed first and then the counteranion OCOCF_3^- is attached to the metallic center to form stable Pt^{IV} complexes **8** and **9**.



Scheme 2.

A similar behavior is also observed when in the above reactions, HgCl_2 is used instead of CF_3COOH as the nucleophile. Thus, as described in Scheme 2, complex **6** was treated with HgCl_2 to give methane and the Pt^{IV} product complex $[\text{PtMe}_2\text{Cl}(\text{dppm})]$ (**10**), whereas a similar reaction using dppf analog **2** gave methane, ethane, and $[\text{PtMeCl}(\text{dppf})]$ (**11**).

Nolan, et al.^[9] prepared the complex $[\text{PtMe}_2(\text{dppf})]$ (**5**) by reaction of $[\text{PtMe}_2(\text{cod})]$ ($\text{cod} = \eta^4\text{-1,5-cyclooctadiene}$) with dppf. We, however, successfully made complex **5** by reaction of $\text{cis,cis-}[\text{Me}_2\text{Pt}(\mu\text{-SMe}_2)\text{PtMe}_2]$ (**4**) with dppf (2 equiv.) in high yields. Although the reaction of complex **5** with HBF_4 is reported to lead to decomposition,^[10] we found that the use of a stoichiometric equivalent of CF_3COOH , with CF_3COO^- having a much higher coordinating ability than that of BF_4^- , complex **3** could successfully be prepared in good yield (see Scheme 1).

It is known that MeI oxidatively adds to the dimethylplatinum(II) complex through the pentacoordinate intermediate $[\text{PtMe}_3(\text{dppm})]^+\text{I}^-$ to give the Pt^{IV} product $[\text{PtMe}_3\text{I}(\text{dppm})]$.^[11] In contrast, we found that in a similar reaction, MeI failed to react with the dppf analogous complex **5** (see Scheme 1). This observation confirms the suggested large steric demand imposed by dppf (vide supra), preventing the formation of the corresponding intermediate $[\text{PtMe}_3(\text{dppf})]^+\text{I}^-$ (**C**).

Characterization of the Complexes

The complexes were fully characterized by their spectroscopic data, which are listed in the Experimental section. The molecular and crystal structures of complexes **2** and **3** were further determined by single-crystal X-ray structure determination.

In the ^{31}P NMR spectrum of the complex **2** a singlet is observed at $\delta = -17.6$ ppm accompanied by platinum satellites with $^1J_{\text{Pt,P}} = 1119$ Hz. This coupling is more than 16% greater than the corresponding value of $^1J_{\text{Pt,P}} = 936$ Hz observed for dppm complex **6**. This discrepancy can be attributed to a rather large strain existing in the PCPpt ring of dppm in forming chelate complexes with the metallic center. In the ^1H NMR spectrum of **2**, the two equivalent Me groups *trans* to P atoms appeared as a triplet at $\delta = 0.46$ ppm with $^3J_{\text{P,H}} = 6.0$ Hz and $^2J_{\text{Pt,H}} = 59.4$ Hz. The two equivalent Me groups *trans* to each other appeared as a triplet at $\delta = 0.00$ ppm with $^3J_{\text{P,H}} = 6.0$ Hz, but with a significantly smaller $^2J_{\text{Pt,H}}$ value of 44.0 Hz as a result of the high *trans* influence of the Me group as compared to that of the chelating P atoms. The α and β protons of dppf each appeared as a broad singlet at $\delta = 4.24$ ppm and $\delta = 4.14$, respectively.

In the ^{31}P NMR spectrum of complex **3** shown in Figure 1; the P atom *trans* to the CF_3COO ligand appeared at $\delta = 12.8$ ppm with $^1J_{\text{Pt,P}} = 4773$ Hz, whereas the P atom *trans* to the Me group is observed at $\delta = 32.4$ ppm with a much smaller $^1J_{\text{Pt,P}}$ value of 1995 Hz as a result of the *trans* influence of the Me ligand being far greater than that of the CF_3COO ligand. It is interesting to note that probably due to a rather large PP bite angle of dppf, which is found to be $101.848(18)^\circ$ (vide infra), the two inequivalent P atoms of dppf in this complex are coupled to each other through the Pt atom and so each signal appears as a doublet with $^2J_{\text{P,P}} = 13$ Hz. This kind of P,P coupling between the two inequivalent P atoms in a *cis* (or chelate) platinum complex is usually not observed. In the ^{195}Pt NMR spectrum of complex **3**, a doublet of doublets at $\delta = -2773$ ppm with $^1J_{\text{Pt,P}}$ values of 4774 and 1990 Hz, close to the values obtained from the ^{31}P NMR spectrum, is observed.

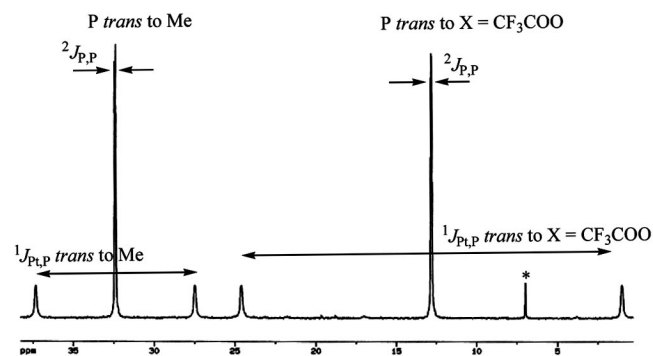


Figure 1. ^{31}P NMR spectrum of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$ (**3**). The trace impurity is shown by *.

In the ^1H NMR spectrum of complex **9** the two equivalent Me ligands *trans* to the N atoms appear as a singlet at $\delta = 1.27$ ppm with $^2J_{\text{Pt,H}} = 67.6$ Hz. The Me ligand *trans* to the O atom appeared as a singlet at $\delta = 0.48$ ppm with a larger $^2J_{\text{Pt,H}}$ value of 77.7 Hz as a result of the lower *trans* influence of the O donor atom as compared to that of the N chelating atoms. Consistently, the structure of complex **9** was confirmed by its ^{13}C NMR spectrum. Thus, the two equivalent C atoms of the Me ligands *trans* to the N atoms appear as a singlet at $\delta = -4.0$ ppm with $^1J_{\text{Pt,C}} = 670$ Hz, whereas the C atom of the Me ligand *trans* to O appeared as a singlet at $\delta = -13.9$ ppm with a larger value of $^1J_{\text{Pt,C}} = 735$ Hz. The remaining signals appeared at expected chemical shifts.

The molecular and crystal structure of complex **2** was determined by X-ray crystallography and is shown in Figure 2, with selected bond parameters listed in Table 1. The geometry around the platinum center is somewhat distorted from octahedral. Thus, as compared to the ideal angle of 90° , the dppf bite angle, P1–Pt1–P2, is increased to $95.77(3)^\circ$, whereas the angle formed by the Me ligands *trans* to P, C37–Pt1–C35, is reduced to $81.86(12)^\circ$. The angle formed by the two *trans* Me ligands with the platinum center, C38–Pt1–C36, is $168.98(11)^\circ$, and these Me ligands lean towards the Me ligands *trans* to P; one of the angles formed by two of the different Me ligands and the platinum center, C35–Pt1–C38, is $83.37(11)^\circ$, and the other C–Pt–C angles are also more or less smaller than 90° . This indicates that the axial Me ligands are significantly under pressure by the steric demands of the Ph groups on the phosphorus ligating atoms. Besides, although Goldberg et al. have reported that for the complex [PtMe₄(dppe)], the Pt–Me bond lengths vary only slightly with respect to the *trans* ligands (average for Pt–C bond *trans* to P is 2.11 ± 0.01 Å, and for those *trans* to Me is 2.13 ± 0.02 Å) for complex **2**, we found that the difference is rather significant (average for Pt–C bond

trans to P is 2.102 ± 0.004 Å, whereas for those *trans* to Me is 2.153 ± 0.004 Å). The dppf bite angle, P1–Pt1–P2, which is $95.77(3)^\circ$, can be compared with the PP bite angle for the dppa [bis(diphenylphosphanyl)amine] ligand in the complex [PtMe₃I(η^2 -dppa)], in which the corresponding angle P1–Pt1–P2 $68.93(5)^\circ$ is much smaller than the ideal angle of 90° .^[12]

Table 1. Selected bond lengths [Å] and angles [$^\circ$] for complex [PtMe₄(dppf)] (**2**).

Pt1–C37	2.098(3)	Pt1–C36	2.154(3)
Pt1–C35	2.106(3)	Pt1–P1	2.3658(7)
Pt1–C38	2.153(3)	Pt1–P2	2.3726(7)
C37–Pt1–C35	81.86(12)	C38–Pt1–P1	92.34(8)
C37–Pt1–C38	90.06(11)	C36–Pt1–P1	89.41(8)
C35–Pt1–C38	83.37(11)	C37–Pt1–P2	90.53(8)
C37–Pt1–C36	87.04(11)	C35–Pt1–P2	170.92(8)
C35–Pt1–C36	85.69(11)	C38–Pt1–P2	91.75(8)
C38–Pt1–C36	168.98(11)	C36–Pt1–P2	98.90(8)
C37–Pt1–P1	173.19(8)	P1–Pt1–P2	95.77(3)
C35–Pt1–P1	92.09(9)		

The dppf ligand is arranged close to the “synperiplanar–eclipsed” conformation,^[5a] as defined by the Cp(centroid)⋯Fe⋯Cp(centroid) twist angle of 17.6° [the angle was determined as the torsion angle C1⋯Cp(centroid)1⋯Cp(centroid)2⋯C6]. This is in contrast to the usually preferred “synclinal–staggered” conformation found in Pt^{II} complexes with chelating dppf ligands, like for example [PtMe₂(dppf)],^[9] [PtMeCl(dppf)],^[10] **3** (see below), and [PtMe(dppf)(ppy- $\kappa^1\text{C}$)] (ppy = deprotonated 2-phenylpyridyl)^[6] as defined by a Cp(centroid)⋯Fe⋯Cp(centroid) twist angle close to 36° .^[5a]

The molecular and crystal structure of complex **3** was also determined by X-ray crystallography and is shown in Figure 3, with selected bond parameters listed in Table 2. The geometry is best described as distorted square-planar and the bond angles around the Pt center range from 83 to 101° . The different *trans* influences implemented by the strong σ -donor Me ligand and the trifluoroacetate

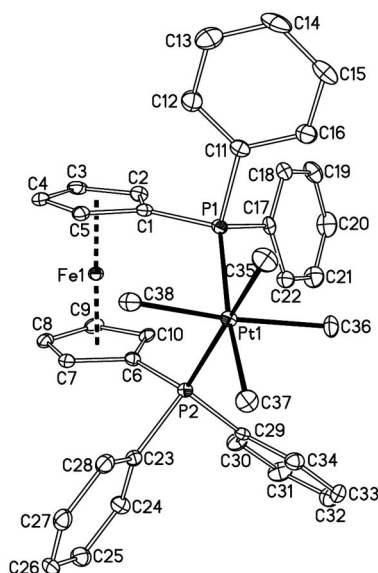


Figure 2. Molecular structure of complex [PtMe₄(dppf)] (**2**; 50% probability ellipsoids, H atoms omitted for clarity).

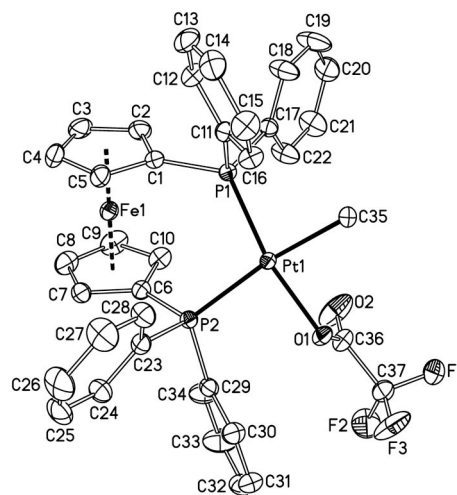


Figure 3. Molecular structure of complex [PtMe(OCOCF₃)(dppf)] (**3**; 50% probability ellipsoids, H atoms omitted for clarity).

(CF₃COO[−]) ligand is reflected by the bond length of the *trans* Pt–P bonds; the distance of the Pt1–P1 bond *trans* to the trifluoroacetate ligand is 2.1995(5) Å, whereas the distance of the Pt1–P2 bond *trans* to the Me ligand is 2.3266(5) Å. The dppf bite angle, P1–Pt1–P2, amounts to 101.85(2)° and is close to those obtained for the Pt^{II} complexes with dppf as a chelating ligand, for example **5**,^[9] with a corresponding bite angle of 100.77(3)°, but is significantly different from that obtained for complex **2**, which is 95.77(3)°. The dppf ligand is arranged in the usually preferred “synclinal–staggered” conformation,^[5a] as defined by the Cp(centroid)⋯Fe⋯Cp(centroid) twist angle of 32.0° [the angle has been determined as the torsion angle C1⋯Cp(centroid)1⋯Cp(centroid)2⋯C6].

Table 2. Selected bond lengths [Å] and angles [°] for complex [PtMe(OCOCF₃)(dppf)] (**3**).

Pt1–C35	2.104(2)	Pt1–P1	2.1995(5)
Pt1–O1	2.108(2)	Pt1–P2	2.3266(5)
C35–Pt1–O1	83.54(7)	C35–Pt1–P2	172.34(6)
C35–Pt1–P1	85.57(6)	O1–Pt1–P2	89.20(4)
O1–Pt1–P1	168.31(4)	P1–Pt1–P2	101.85(2)

Conclusions

The tetramethylplatinum(IV) complex [PtMe₄(dppf)] (**2**) synthesized in the present study is the first Pt^{IV} complex with a chelating dppf ligand reported so far. The dppf bite angle amounts to 95.77(3)°, which is significantly smaller than that of related Pt^{II} complex **5**,^[9] with a corresponding bite angle of 100.77(3)°. This probably caused the dppf ligand to arrange close to the “synperiplanar–eclipsed” conformation,^[5a] as defined by the Cp(centroid)⋯Fe⋯Cp(centroid) twist angle of 17.6°, and this is in contrast to the usually preferred “synclinal–staggered” conformation found in Pt^{II} complexes with chelating dppf ligands, like for example [PtMe₂(dppf)],^[9] [PtMeCl(dppf)],^[10] and [PtMe(OCOCF₃)(dppf)] (**3**; reported in the present communication), as defined by a Cp(centroid)⋯Fe⋯Cp(centroid) twist angle of close to 36°.^[5a]

Thus, it can be seen that the two Me ligands situated in *trans* to each other are actually under significant steric pressure imposed by the Ph groups of the dppf ligand. We believe that this steric effect is responsible for the fact that Pt^{IV} complexes with dppf as chelating ligand cannot be formed easily, with complex **2** being an exception. We have confirmed this by the observation that the related Pt^{II} complex **5**^[9] failed to react with MeI to give the expected Pt^{IV} complex [PtMe₃I(dppf)]. Consistently, we have found that when complex **2** was treated with either of the electrophiles H⁺ (using CF₃COOH) or HgCl⁺ (using HgCl₂), methane or MeHgCl, respectively, was formed first and the steric pressure expected to be imposed by the Ph groups of the dppf ligand on the two *trans* ligands of the resulting Pt^{IV} intermediate forced its two *cis* Me ligands to rapidly undergo reductive elimination of ethane by a C–C coupling reaction. The latter has not been observed in similar reac-

tions involving several tetramethylplatinum(IV) complexes with other nitrogen or phosphorus bidentate ligands. For example, when complex [PtMe₄(dppm)] (**6**) or [PtMe₄(bpy)] (**7**) was treated with CF₃COOH, only methane was formed along with the corresponding *fac*-trimethylplatinum(IV) complex [PtMe₃(OCOCF₃)(dppm)] (**8**)^[2e] or [PtMe₃(OCOCF₃)(bpy)] (**9**), respectively. Similarly, reaction of complex **6** with HgCl₂ gave only MeHgCl along with [PtMe₃Cl(dppm)] (**10**).

Experimental Section

General: ¹H and ¹³C NMR spectra were recorded with a Bruker Avance DPX 250 MHz spectrometer, and ¹⁹F, ³¹P, and ¹⁹⁵Pt NMR spectra were recorded with a Bruker Avance DRX 500 MHz spectrometer. Microanalyses were performed with a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. 1,1'-Bis(diphenylphosphanyl)ferrocene was purchased from Aldrich. The known precursor complexes *cis,cis*-[Me₂Pt(μ-SMe₂)₂PtMe₂] (**4**),^[13] *cis,cis*-[Me₄Pt(μ-SMe₂)₂PtMe₄] (**1**),^[1] [PtMe₄(dppm)] (**6**),^[1] and [PtMe₄(bpy)] (**7**)^[1] were prepared according to literature methods. The stock solution of CF₃CO₂H was prepared by adding CF₃CO₂H (920 μL) to dichloromethane (10 mL).

[PtMe₄(dppf)] (2**):** To a solution of complex **1** (200 mg, 0.315 mmol), in acetone (30 mL) was added dppf (350 mg, 0.630 mmol, 2 equiv.), and the solution was stirred for 1 h. A yellow solid precipitated, which was separated and dried under vacuum. Yield: 450 mg, 82%; m.p. 177–180 °C (decomp.). C₃₈H₄₀FeP₂Pt (809.58); calcd. C 56.4, H 5.0; found C 56.1, H 4.8. ¹H NMR (250 MHz, CDCl₃, TMS): δ = 0.00 (t, ²J_{Pt,H} = 44.0 Hz, ³J_{Pt,H} = 6.0 Hz, Me ligands *trans* to Me, 6 H), δ = 0.46 (t, ²J_{Pt,H} = 59.4 Hz, ³J_{Pt,H} = 6.0 Hz, 6 H, Me ligands *trans* to P), 4.14 (br. s, 4 H, β,β' Cp protons), 4.24 (br. s, 4 H, α, α' Cp protons), 7.04–7.40 (aromatic protons) ppm. ³¹P NMR (202 MHz, CDCl₃, 85% H₃PO₄): δ = −17.6 (s, ¹J_{Pt,P} = 1119 Hz, 2 P) ppm.

[PtMe(OCOCF₃)(dppf)] (3**):** To a solution of complex **2** (100 mg, 0.124 mmol) in dichloromethane (30 mL) was added the stock solution of CF₃CO₂H (100 μL, 0.124 mmol), and the solution was stirred for 1 h. A bright-yellow solution was formed, then the solvent was removed under reduced pressure, and the residue was triturated with *n*-hexane (2 × 3 mL). The product as a bright yellow solid was dried under vacuum. Yield: 87 mg, 76%; m.p. 255–258 °C (decomp.). C₃₇H₃₁F₃FeO₂P₂Pt (877.50); calcd. C 50.6, H 3.6; found C 50.1, H 3.4. ¹H NMR (250 MHz, CDCl₃, TMS): δ = 0.50 (dd, ²J_{Pt,H} = 48.6 Hz, ³J_{Pt,H} = 7.2, 3.0 Hz, 3 H, Me ligand), 3.70 (br. m, ³J_{Pt,H} = 1.8 Hz, 2 H, α Cp protons), 4.14 (br. m, 2 H, β Cp protons), 4.45 (br. m, 2 H, β' Cp protons), 4.70 (br. m, ³J_{Pt,H} = 1.8 Hz, 2 H, α' Cp protons), 7.26–7.85 (aromatic protons) ppm. ¹⁹F NMR (470 MHz, CDCl₃, CFCl₃): δ = −74.9 (s, 3 F) ppm. ³¹P NMR (202 MHz, CDCl₃, 85% H₃PO₄): δ = 12.8 (d, ²J_{Pt,P} = 13 Hz, ¹J_{Pt,P} = 4773 Hz, 1 P, P *trans* to O), 32.4 (d, ²J_{Pt,P} = 13 Hz, ¹J_{Pt,P} = 1995 Hz, 1 P, P *trans* to Me) ppm. ¹⁹⁵Pt NMR (107 MHz, CDCl₃, aqueous Na₂PtCl₄): δ = −2773.0 (dd, ¹J_{Pt,P} = 4774, 1990 Hz, 1 Pt) ppm.

The reaction was followed by ¹H NMR spectroscopy in an NMR tube. To a small sample of complex **2** (10 mg, 0.012 mmol) dissolved in CD₂Cl₂ in a sealed NMR tube was added the stock solution of CF₃CO₂H (10 μL, 0.012 mmol). The ¹H NMR spectrum

was recorded after a few minutes and the observation of two singlet signals at $\delta = 0.17$ and 0.81 ppm confirmed the formation of methane and ethane, respectively.

This complex was also synthesized similarly by the reaction of complex **5** (100 mg, 0.128 mmol) with the stock solution of $\text{CF}_3\text{CO}_2\text{H}$ (110 μL , 0.128 mmol).

[PtMe₂(dppf)] (5): To a solution of complex **4** (200 mg, 0.348 mmol) in ethyl ether (30 mL) was added dppf (386 mg, 0.696 mmol, 2 equiv.), and the solution was stirred for 1 h. A light-yellow solid precipitated, which was separated and dried under vacuum. Yield: 463 mg, 79%; m.p. 266–270 °C (decomp.). $\text{C}_{36}\text{H}_{34}\text{FeP}_2\text{Pt}$ (779.55): calcd. C 55.5, H 4.4; found C 55.1, H 4.4. ^1H NMR (250 MHz, CDCl_3 , TMS): $\delta = 0.11$ (t, $^2J_{\text{Pt,H}} = 68.8$ Hz, $^3J_{\text{Pt,H}} = 6.4$ Hz, 6 H, Me ligands), 3.87 (br. s, 4 H, β, β' Cp protons), 4.05 (br. s, 4 H, α, α' Cp protons), 7.00–7.48 (aromatic protons) ppm. ^{31}P NMR (202 MHz, CDCl_3 , 85% H_3PO_4): $\delta = 24.8$ (s, $^1J_{\text{Pt,P}} = 1903$ Hz, 2 P) ppm. ^{195}Pt NMR (107 MHz, CDCl_3 , aqueous Na_2PtCl_4): $\delta = -3004$ (t, $^1J_{\text{Pt,P}} = 1905$ Hz, 1 Pt) ppm.

[PtMe₂(OCOCF₃)(bipy)] (9): To a solution of complex **7** (100 mg, 0.243 mmol) in dichloromethane (30 mL) was added the stock solution of $\text{CF}_3\text{CO}_2\text{H}$ (200 μL , 0.243 mmol), and the solution was stirred for 1 h. A colorless solution was formed, then the solvent was removed under reduced pressure, and the residue was triturated with *n*-hexane (2×3 mL). The product as a white solid was dried under vacuum. Yield: 93 mg, 73%; m.p. 230–233 °C (decomp.). $\text{C}_{15}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2\text{Pt}$ (509.40): calcd. C 35.4, H 3.4, N 5.5; found C 35.1, H 3.4, N 5.3. ^1H NMR (250 MHz, CDCl_3 , TMS): $\delta = 0.48$ (s, $^2J_{\text{Pt,H}} = 77.7$ Hz, Me ligand *trans* to O, 3 H), 1.27 (s, $^2J_{\text{Pt,H}} = 67.6$ Hz, 6 H, 2 Me ligands *trans* to N), 7.65 (m, $^3J_{\text{H}_5, \text{H}_6} = 5.6$ Hz, 2 H₅ of bipy), 8.09 (m, $^3J_{\text{H}_4, \text{H}_3} = 8.0$ Hz, 2 H₄ of bipy), 8.19 (d, $^3J_{\text{H}_3, \text{H}_4} = 8.0$ Hz, 2 H₃ of bipy), 8.99 (d, $^3J_{\text{Pt, H}_6} = 11.2$ Hz, $^3J_{\text{H}_6, \text{H}_5} = 5.6$ Hz, 2 H₆ of bipy) ppm. ^{13}C NMR (69 MHz, CDCl_3 , TMS): $\delta = -13.9$ (s, $^1J_{\text{Pt,C}} = 735$ Hz, C *trans* to O, 1 C atom of Me ligand), -4.0 (s, $^1J_{\text{Pt,C}} = 670$ Hz, C *trans* to N, 2 C atoms of Me ligands), 122.8 (s, $^3J_{\text{Pt,C}_3} = 8$ Hz, 2 C₃ of bipy), 126.5 (s, $^1J_{\text{Pt,C}_5} = 13$ Hz, 2 C₅ of bipy), 139.0 (s, 2 C₄ of bipy), 147.2 (s, $^2J_{\text{Pt,C}_6} = 15$ Hz, 2 C₆ of bipy), 155.3 (s, 2 C₂ of bipy) ppm.

[PtMeCl(dppf)] (11): To a solution of complex **2** (100 mg, 0.124 mmol) in dichloromethane (30 mL) was added HgCl_2 (34 mg, 0.124 mmol), and the solution was stirred for 1 h. A bright-yellow solution was formed, then the solvent was removed under reduced pressure, and the residue was triturated with *n*-hexane (2×3 mL). The product as a dark-yellow solid was dried under vacuum and identified as the known complex [PtMeCl(dppf)] by its NMR spectroscopic data.^[10]

Attempted Reaction of MeI with Complex [PtMe₂(dppf)] (5): To a solution of [PtMe₂(dppf)] (10 mg, 0.013 mmol) in dichloromethane (5 mL) was added an excess amount of MeI (3 mL), and the solution was stirred for 1 h. No reaction was detected, as confirmed by ^1H NMR spectroscopic investigation.

X-ray Crystal-Structure Determination: Single crystals of [PtMe₂(dppf)] (**2**) and [PtMe(OCOCF₃)(dppf)] (**3**) were grown from a concentrated dichloromethane solution by slow diffusion of *n*-hexane. For **2**, a yellowish block approximately $0.13 \times 0.11 \times 0.10$ mm³ in size and in the case of **3** a yellow prism approximately $0.25 \times 0.19 \times 0.09$ mm³ in size was coated with protective perfluoro polyalkylether oil and mounted on a glass fiber. Data were collected at 150 K for **2** and 200 K for **3** with a Bruker-Nonius KappaCCD diffractometer using Mo- K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The data were corrected for Lorentz and polarization effects, a semiempirical absorption correction based on multiple scans was carried out using SADABS.^[14] The structures were solved by direct methods and refined using full-matrix least-squares procedures on F^2 with SHELXTL NT 6.12 software.^[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. Crystal data, data collection, and structure refinement details are listed in Table 3.

CCDC-731082 (for **2**) and -731083 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data, data collection, and structure refinement details for **2** and **3**.

	Complex 2	Complex 3
Formula	$\text{C}_{38}\text{H}_{40}\text{FeP}_2\text{Pt}$	$\text{C}_{37}\text{H}_{31}\text{F}_3\text{FeO}_2\text{P}_2\text{Pt}$
Formula weight	809.58	877.50
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	16.6052(8)	9.4727(6)
b [Å]	14.1992(14)	12.6990(4)
c [Å]	26.448(2)	15.2806(6)
α [°]	90	109.977(3)
β [°]	93.532(5)	91.668(5)
γ [°]	90	106.728(3)
vol. [Å ³]	6224.1(8)	1637.8(2)
Z	8	2
$D_{\text{calcd.}}$ [Mg m ⁻³]	1.728	1.779
Abs. coeff. [mm ⁻¹]	5.086	4.857
$F(000)$	3216	860
No. of collected reflection	56282	70738
No. of independent reflections	7414 [$R(\text{int}) = 0.0498$]	8286 [$R(\text{int}) = 0.0327$]
No. of observed reflections, [$I > 2\sigma(I)$]	6106	7460
$T_{\text{min}}, T_{\text{max}}$	0.510, 0.600	0.366, 0.650
Largest diff. peak, hole [e Å ⁻³]	0.547, -0.524	0.457, -0.601
Goof (F^2)	0.926	1.097
R_1, wR_2 [$I > 2\sigma(I)$]	0.0233, 0.0436	0.0160, 0.0346
R_1, wR_2 (all data)	0.0376, 0.0470	0.0222, 0.0362

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