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Binuclear Cyclometalated Organoplatinum Complexes Containing 1,1′-Bis(diphenylphosphino)ferrocene as Spacer Ligand: Kinetics and Mechanism of MeI Oxidative Addition

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The binuclear complex [Pt$_2$Me$_2$(ppy)$_2$(μ-dppf)], **1**, in which ppy = deprotonated 2-phenylpyridyl and dppf = 1,1′-bis(diphenylphosphino)ferrocene, was synthesized by the reaction of [PtMe(SMe$_2$)(ppy)] with 0.5 equiv of dppf at room temperature. In this reaction when 1 equiv of dppf was used, the dppf chelating complex **2**, [PtMe(dppf)(ppy-$\kappa^1 C$)], was obtained. The reaction of Pt(II)−Pt(II) complex **1** with excess MeI gave the Pt(IV)−Pt(IV) complex [Pt$_2$I$_2$Me$_4$(ppy)$_2$(μ-dppf)], **3**. When the reaction was performed with 1 equiv of MeI, a mixture containing unreacted complex **1**, a mixed-valence Pt(II)−Pt(IV) complex [PtMe(ppy)(μ-dppf)PtIMe$_2$(ppy)], **4**, and complex **3** was obtained. In a comparative study, the reaction of [PtMe(SMe$_2$)(ppy)] with 1 equiv of monodentate phosphine PPh$_3$ gave [PtMe(ppy)(PPh$_3$)], **A**. MeI was reacted with **A** to give the platinum(IV) complex [PtMe$_2$I(ppy)(PPh$_3$)], **C**. All the complexes were fully characterized using multinuclear (^{1}H, ^{31}P, ^{13}C, and ^{195}Pt) NMR spectroscopy, and complex **2** was further identified by single crystal X-ray structure determination. The reaction of binuclear Pt(II)−Pt(II) complex **1** with excess MeI was monitored by low temperature ^{31}P NMR spectroscopy and further by ^{1}H NMR spectroscopy, and the kinetics of the reaction was studied by UV−vis spectroscopy. On the basis of the data, a mechanism has been suggested for the reaction which overall involved stepwise oxidative addition of MeI to the two Pt(II) centers. In this suggested mechanism, the reaction proceeded through a number of Pt(II)−Pt(IV) and Pt(IV)−Pt(IV) intermediates. Although MeI in each step was *trans* oxidatively added to one of the Pt(II) centers, further *trans* to *cis* isomerizations of Me and I groups were also identified. A comparative kinetic study of the reaction of monomeric platinum(II) complex **A** with MeI was also performed. The rate of reaction of MeI with complex **1** was some 3.5 times faster than that with complex **A**, indicating that dppf in the complex **1**, as compared with PPh$_3$ in the complex **A**, has significantly enhanced the electron richness of the platinum centers.

1. Introduction

Cyclometalated platinum complexes have recently attracted[1–4] a great deal of attention because of their potential applications in many fields, such as photocatalysts,[1e–g] metallomesogens,[2] and optoelectronic devices.[3] Square planar cyclometalated platinum complex species were also used as "building blocks" for complex systems such as self-assembly and supramolecular entities.[4]

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1,1′-bis(diphenylphosphino)ferrocene, dppf, has extensively been used as a very useful bidentate ligand in many chelating, binuclear, and cluster complexes of transition metals.[5] In the present work, a new binuclear complex was synthesized by connecting two cyclometalated organoplatinum(II) species, containing a deprotonated 2-phenylpyridyl (ppy) ligand, with dppf as a spacer ligand, combining the individual properties of these two ligands in one molecular system. The platinum(II) centers in this complex underwent oxidative addition of MeI to give the corresponding binuclear Pt(IV)−Pt(IV) complex. On the basis of low temperature ^{31}P NMR studies, we have shown that this reaction would occur via different steps involving binuclear Pt(II)−Pt(IV) and Pt(IV)−Pt(IV) intermediates in which the Pt(IV) centers performed some interesting facile *trans*−*cis* isomerizations. Although *cis-trans* isomerization of square-planar platinum(II) complexes is an interesting subject and has extensively been studied,[6] the isomerization involving Pt(IV) centers, which is expected to occur via a dissociative pathway, is not common.[7]

Oxidative addition is a fundamental reaction in many catalytically important processes.[8,9] The reactions involving addition of a variety of reagents to mononuclear square-planar organoplatinum(II) complexes have been extensively studied.[10,11] However, the reactions involving binuclear platinum(II) complexes which help in understanding the neighborhood effects of the metallic centers have not been studied much. We have recently studied the oxidative addition of MeI to a binuclear organoplatinum(II) complex and found that the bridging diphosphine ligand conveys

electronic influences among the metals.[12] It is well-known that in ferrocene complexes, when a reaction is taking place in one of the cyclopentadienyl rings, the electronic information is transferred to the second ring via the iron atom. In the present work, we have studied the kinetics of reaction of MeI with the above binuclear cyclometalated organoplatinum complex in an attempt to test the cooperative effect of the platinum(II) centers connected to each other by 1,1′-bis(diphenylphosphino)ferrocene ligand. Such studies may be useful in the quantitative assessment of electronic transformations among the cyclopentadienyl rings.

2. Experimental Section

The ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500-MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^{1}H (500 MHz, TMS), ^{13}C (125 MHz, TMS), ^{31}P (202 MHz, 85% H_3PO_4), and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). Monitoring the ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. The chemical shifts and coupling constants are in ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. 2-Phenylpyridine and 1,1′-bis(diphenylphosphino)ferrocene were purchased from commercial sources, and [PtMe$_2$(μ-SMe$_2$)]$_2$ was prepared as described previously.[13] The in situ yellow solution of [PtMe(ppy)(SMe$_2$)] in acetone was prepared as reported:[14] 2-phenylpyridine (100 μL, 0.7 mmol) was added dropwise via syringe to a solution of [PtMe$_2$(μ-SMe$_2$)]$_2$ (200 mg, 0.35 mmol) in 20 mL of acetone at room temperature in air. The solution immediately turned yellow, and small bubbles formed. This was stirred for 1.5 h and used freshly.

[Pt$_2$Me$_2$(ppy)$_2$(μ-dppf)], 1. To the above in situ solution of [PtMe(ppy)(SMe$_2$)] was added 0.5 equiv of dppf (193 mg, 0.35 mmol), and the solution was further stirred for 1 h. A bright yellow solid was precipitated which was separated and dried under vacuum. Yield: 268 mg, 68%. Anal. Calcd for C$_{58}$H$_{50}$FeN$_2$P$_2$Pt$_2$: C, 54.2; H, 3.9; N, 2.1; Found: C, 54.2; H, 4.0; N, 2.3. NMR data in CDCl$_3$: δ(^{1}H) 0.97(d, 6H, $^2J_{PtH}$ = 83.4 Hz, $^3J_{PH}$ = 7.7 Hz, 2 Me), 4.36(br s, 4H, β, β' Cp protons), 4.39(br s, 4H, α, α' Cp protons), (aromatic protons): 6.45(m, 2H, $^3J_{PtH}$ = 12.9 Hz, $^3J_{HH}$ = 1.4 Hz, CH groups adjacent to coordinated C atoms), 7.1−7.8(m, 32H, overlapping multiplets), 7.95(m, 2H, $^3J_{PtH}$ = 45.9, 2 CH groups adjacent to coordinated N atoms); δ(^{13}C) −13.5 (d, 2C, $^1J_{PtC}$ = 732 Hz, $^2J_{PC}$ = 6 Hz, 2 Me), 73.9(d, 4C, $^3J_{PC}$ = 8 Hz, β, β' Cp Cs), 75.7(d, 4C, $^2J_{PC}$ = 11 Hz, α, α' Cp Cs), 76.7 (d, 2C, $^1J_{PC}$ = 47 Hz, $^2J_{PtC}$ = 33 Hz, *ipso* Cp Cs), 118.7(s, $J_{PC} \approx$ 12 Hz), 121.6(s), 123.6(d, J_{PC} = 5 Hz, $J_{PtC} \approx$ 38 Hz), 124.2(s), 128.1(d, J_{PC} = 9.5 Hz), 129.7(d, J_{PC} = 7 Hz, J_{PtC} = 63 Hz), 130(d, J_{PC} = 1 Hz), 132.2 (s, J_{PtC} = 90 Hz), 134(s), 134.3 (d, J_{PC} = 12 Hz), 136.9(s), 147.7(s, $J_{PtC} \approx$ 6 Hz), 150.6 (d, $J_{PtC} \approx$ 12 Hz, J_{PC} = 5 Hz), 164.5(d, 2C, $^1J_{PtC}$ = 942 Hz, $^2J_{PC}$ = 123 Hz, C atoms of the ppy ligands connected to Pt atoms), 167.0(d, J_{PtC} = 70 Hz, J_{PC} = 6 Hz; δ(^{31}P) 24.1 ($^1J_{PtP}$ = 2092 Hz, 2P of dppf); δ(^{195}Pt) −537 (d, $^1J_{PtP}$ = 2090 Hz, 2Pt).

[PtMe(dppf)(ppy-κ^1C)], 2. To the above in situ solution of [PtMe(ppy)(SMe$_2$)] was added 1 equiv of dppf (386 mg, 0.7 mmol),

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and the solution was further stirred for 1 h. A bright yellow solution was formed, then the solvent was removed under reduced pressure and the residue was triturated with ether (2 × 3 mL). The product as a yellow solid was dried under vacuum. Yield: 508 mg, 79%. Anal. Calcd for $C_{46}H_{39}FeNP_2Pt$: C, 60.1; H, 4.3; N, 1.5; Found: C, 60.3; H, 4.5; N, 1.7. NMR data in $CDCl_3$: $\delta(^1H)$ 0.27(dd, 3H, $^2J_{PtH}$ = 66.5 Hz, $^3J_{PH}$ = 6.7 Hz, Me), 3.54, 3.68, 4.04(each a br s, 1H, 1H, 2H, respectively, β, β' Cp protons), 4.35, 4.38, 4.42, 4.65(each a br s, 4H, α, α' Cp protons), (aromatic protons): 6.72 (m, 2H, $^3J_{PtH}$ = 14.1 Hz, different CH groups adjacent to coordinated C atoms), 6.9−7.9(overlapping multiplets), 8.5(m, 2H, CH groups adjacent to coordinated N atoms); $\delta(^{13}C)$ 5.4(dd, 1C, $^1J_{PtC}$ = 610 Hz, $^2J_{PC}$ = 7 and 92 Hz, Me ligand), 70.9, 71.1, 72.4, 72.7(each a doublet, 4C, with $^3J_{PC}$ = 5 Hz, β, β' Cp Cs), [74.0(d, 1C, $^2J_{PC}$ = 8 Hz), 74.2(d, 1C, $^2J_{PC}$ = 8 Hz), 75.2(d, 1C, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 12 Hz), 75.8(d, 1C, $^2J_{PC}$ = 11 Hz, $^3J_{PtC}$ = 18 Hz), α, α' Cp Cs], [78.1(dd, 1C, $^1J_{PC}$ = 48 Hz, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 45 Hz), 80.0 (dd, 1C, $^1J_{PC}$ = 47 Hz, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 50 Hz), *ipso* Cp Cs], 166.9(dd, 1C, $^2J_{PC}$ = 11 Hz, $^2J_{PC}$ = 120 Hz, $^1J_{PtC}$ = 892 Hz, C atom of the ppy ligand connected to Pt atom), other aromatic Cs were not assigned; $\delta(^{31}P)$ 20.5(d, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 1888 Hz, 1P *trans* to Me), 23.9(d, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 1995 Hz, 1P *trans* to ppy); $\delta(^{195}Pt)$ −2890(dd, $^1J_{PtP}$ = 1883 Hz and 1990, Pt).

[Pt$_2$I$_2$Me$_4$(ppy)$_2$(μ-dppf)], 3. An excess of MeI (50 μL) was added to a solution of complex **1** (100 mg in 20 mL of chloroform) at room temperature. The mixture was stirred at this condition for 1 h, then the solvent was removed under reduced pressure, the residue was triturated with ether (2 × 3 mL), and the product as an orange solid was dried under vacuum. Yield: 73 mg, 60%. Anal. Calcd for $C_{60}H_{56}I_2FeN_2P_2Pt_2$: C, 45.8; H, 3.6; N, 1.8; Found: C, 45.3; H, 3.7; N, 1.8. NMR data in $CDCl_3$: $\delta(^1H)$ 1.07(d, 6H, $^2J_{PtH}$ = 61.0 Hz, $^3J_{PH}$ = 7.6 Hz, 2 Me groups *trans* to P), 1.44(d, 3H, $^2J_{PtH}$ = 70.8 Hz, $^3J_{PH}$ = 7.8 Hz, 1 Me group *trans* to N), 1.46 (d, 3H, $^2J_{PtH}$ = 70.9 Hz, $^3J_{PH}$ = 7.9 Hz, 1 Me group *trans* to N), 3.01, 3.10, 3.18, 3.25(each a br s, 4H, β, β' Cp protons), 3.58, 3.62, 3.63(each a br s, 1H, 2H, 1H, respectively, α, α' Cp protons), (aromatic protons): 6.66(d, 1H, $^3J_{PtH}$ = 42.8 Hz, $^3J_{HH}$ = 7.8, CH group adjacent to coordinated C atom), 6.71(d, 1H, $^3J_{PtH}$ = 43.0 Hz, $^3J_{HH}$ = 7.8, CH group adjacent to coordinated C atom), 6.8−7.7(overlapping multiplets), 9.39 (d, 1H, J_{HH} = 5.1 Hz, $^3J_{PtH}$ ≈ 7 Hz, CH group adjacent to coordinated N atom), 9.43(d, 1H, J_{HH} = 5.2 Hz, $^3J_{PtH}$ ≈ 7 Hz, CH group adjacent to coordinated N atom); $\delta(^{13}C)$ −6.3(d, 1C, $^1J_{PtC}$ = 637 Hz, $^2J_{PC}$ = 3 Hz, Me *trans* to N), −6.2(d, 1C, $^1J_{PtC}$ = 637 Hz, $^2J_{PC}$ = 3 Hz, Me *trans* to N), 6.1(d, 1C, $^1J_{PtC}$ = 491 Hz, $^2J_{PC}$ = 112 Hz, Me *trans* to P), 6.2(d, $^1J_{PtC}$ = 492 Hz, $^2J_{PC}$ = 112 Hz, Me *trans* to P), 71.8, 72.1, 72.6, 73.0(each a doublet, 4C, with $^3J_{PC}$ = 8 Hz, β, β' Cp Cs) 74.0, 74.1, 74.8(each a doublet, 1C, 1C, 2C, respectively, with $^2J_{PC}$ = 11 Hz, $^3J_{PtC}$ ≈ 6 Hz, α, α' Cp Cs), 75.6, 75.9(each a doublet, 2C, with $^1J_{PC}$ = 18 Hz, $^2J_{PtC}$ = 27 Hz, *ipso* Cp Cs), 147.7, 147.8(each a doublet, 2C, with $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 880 Hz, C atoms of the ppy ligands connected to Pt atoms), other aromatic Cs were not assigned; $\delta(^{31}P)$ −13.3(s, $^1J_{PtP}$ = 990 Hz, 1P), −13.4(s, $^1J_{PtP}$ = 990 Hz, 1P); $\delta(^{195}Pt)$ 316 and 317(2 overlapping d, each with $^1J_{PtP}$ = 990 Hz, 2 Pt).

This reaction was also monitored by ^{31}P and ^1H NMR spectroscopy at low and room temperature, respectively, in an NMR tube as follows: a small sample (10 mg) of **1** was dissolved in $CDCl_3$ (0.75 mL) in a sealed NMR tube, and while the tube was cooled by liquid N_2 (when necessary), an excess of MeI was added. The NMR spectra were recorded several times over about 4 h until the mixture was gradually converted to complex **3** in solution.

[PtMe(ppy)(μ-dppf)PtIMe$_2$(ppy)], 4. In the above procedure, used to prepare complex **3**, when complex **1** (100 mg in 20 mL of chloroform) was reacted with 1 equiv of MeI (4.8 μL, 0.078 mmol), then complex **4** was obtained as a mixture with **3** and the starting complex **1**, in approximately 1:1:1 mol ratio, and the components of the mixture were not isolable. NMR data for complex **4** in $CDCl_3$: $\delta(^1H)$ 0.84[d, 3H, $^2J_{PtH}$ = 88.5 Hz, $^3J_{PH}$ = 7.7 Hz, Me ligand on Pt(II) center], 1.09[d, 3H, $^2J_{PtH}$ = 61.0 Hz, $^3J_{PH}$ = 7.6 Hz, Me ligand *trans* to P on Pt(IV) center], 1.53[d, 3H, $^2J_{PtH}$ = 71.1 Hz, $^3J_{PH}$ = 7.8 Hz, Me ligand *trans* to N on Pt(IV) center], 3.35, 3.52[each a br s, 2H, β, β' Cp protons in the Pt(IV) site], 3.74, 3.86(each a br s, 2H, α, α' Cp protons in the Pt(IV) site], 3.90, 4.04[each a br s, 2H, β, β' Cp protons in the Pt(II) site], 4.08, 4.14[each a br s, 2H, α, α' Cp protons in the Pt(II) site], (aromatic protons): mostly overlapped with the aromatic protons of complexes **1** and **3**, 7.8[m, 1H, CH group adjacent to coordinated N atom, on Pt(II) site], 9.35[d, 1H, J_{HH} = 5.3 Hz, $^3J_{PtH}$ ≈ 12 Hz, CH group adjacent to coordinated N atom, on Pt(IV) site]; 6.43(m, 1H, $^3J_{PtH}$ = 12.0 Hz, CH group adjacent to coordinated C atom on Pt(II) site), 6.69[m, 1H, CH group adjacent to coordinated C atom on Pt(IV) site]; $\delta(^{31}P)$ −13.2[s, $^1J_{PtP}$ = 990 Hz, 1P of dppf on Pt(IV) site], 23.9[s, $^1J_{PtP}$ = 2090 Hz, 1P of dppf on Pt(II) site]; $\delta(^{195}Pt)$ −538 [d, $^1J_{PtP}$ = 2088 Hz, Pt(II)], 315[d, $^1J_{PtP}$ = 985 Hz, Pt(IV)].

[PtMe(ppy)(PPh$_3$)], A. To the above in situ solution of [PtMe-(ppy)(SMe$_2$)] was added 1 equiv of PPh$_3$ (183.5 mg, 0.7 mmol) and the solution was further stirred for 1 h. A yellow solution was formed, and then the solvent was removed under reduced pressure. The residue was triturated with ether (2 × 3 mL), and the product as a yellow solid was dried under vacuum. Yield: 352 mg, 80%. Anal. Calcd for $C_{30}H_{26}NPPt$: C, 57.5; H, 4.2; N, 2.2; Found: C, 57.2; H, 4.1; N, 2.5. NMR data in $CDCl_3$: $\delta(^1H)$ 0.78 (d, 3H, $^2J_{PtH}$ = 83.0 Hz, $^3J_{PH}$ = 8.0 Hz, Me ligand), (aromatic protons): 6.49 (m, 1H, $^3J_{PtH}$ = 11.3 Hz, $^4J_{PH}$ = 1.5 Hz CH group adjacent to coordinated C atom), 7.1−7.8 (overlapping multiplets), 8.1 (m, 1H, CH group adjacent to coordinated N atom); $\delta(^{31}P)$ 33.2 [s, $^1J_{PtP}$ = 2105 Hz, 1P of PPh$_3$].

[PtMe$_2$I(ppy)(PPh$_3$)], C. An excess of MeI (100 μL) was added to a solution of complex [PtMe(ppy)(PPh$_3$)], **A**, (100 mg, 0.16 mmol in 20 mL of acetone) at room temperature. The mixture was allowed to stand at this condition for 1 h, and then the solvent was removed under reduced pressure. The residue was washed twice with ether, and the product was dried under vacuum. Yield: 103 mg, 84%. Anal. Calcd for $C_{31}H_{29}INPPt$: C, 48.4; H, 3.8; N, 1.8; Found: C, 48.6; H, 3.7; N, 1.9. NMR data in $CDCl_3$: $\delta(^1H)$ 1.28(d, 3H, $^2J_{PtH}$ = 60.7 Hz, $^3J_{PH}$ = 7.5 Hz, Me ligand *trans* to P), 1.65 (d, 3H, $^2J_{PtH}$ = 70.8 Hz, $^3J_{PH}$ = 7.7 Hz, Me ligand *trans* to N), (aromatic protons): 6.7−7.7 (overlapping multiplets), 9.7 (d, 1H, J_{HH} = 5.3 Hz, $^3J_{PtH}$ ≈ 10 Hz, CH group adjacent to coordinated N atom); $\delta(^{31}P)$ −9.2 [s, $^1J_{PtP}$ = 961 Hz, 1P of PPh$_3$].

Kinetic Study. In a typical experiment, a solution of complex **1** in CHCl$_3$ (3 mL, 1.5 × 10^{-4} M) in a cuvette was thermostatted at 25 °C, and a known excess of MeI was added using a microsyringe. After rapid stirring, the absorbance at λ = 360 nm was monitored with time.

X-ray Structure Determination. Single crystals of [PtMe(dp-pf)(ppy-κ^1C)], **2**, were grown from a concentrated chloroform solution by slow diffusion of hexane. A yellow needle of approximate 0.15 × 0.08 × 0.05 mm in size was mounted on a glass fiber. All measurements were made on a STOE IPDSII diffractometer with graphite monochromator using Mo Kα radiation. The data were collected and integrated using the Stoe X-AREA[15] software package. Crystal data, data collection, and structure refinement details are listed in Table 1. A numerical absorption

Table 1. Crystal Data, Data Collection and Structure Refinement Details for Complex **2**

formula	$C_{46}H_{39}FeNP_2Pt$
formula weight	918.65
temperature/K	293(2)
wavelength/Å	0.71073
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a/Å	10.6124(9)
b/Å	11.7917(13)
c/Å	30.138(3)
vol/Å^3	3771.5(6)
Z	4
D(calc)/Mg m^{-3}	1.618
Abs coeff/mm^{-1}	4.209
abs. correction	numerical
T_{min}/T_{max}	0.674/0.810
F(000)	1824
no. of reflns	20966
no. of independent reflns	8835[R(int) = 0.0292]
no. of observed reflns [$I > 2\sigma(I)$]	8371
GooF (F^2)	1.114
R1, wR2 [$I > 2\sigma(I)$]	0.0231, 0.0442
R1, wR2 (all data)	0.0265, 0.0452

correction was applied using the X-RED[16] and X-SHAPE[17] software programs. The data were corrected for Lorentz and polarization effects. No decay correction was applied. The structure was solved by direct methods.[18] All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in ideal positions except C37−C46 hydrogens that placed in the different Fourier map. Molecular graphics were performed using the ORTEP3[19] and WinGX[20] crystallographic software programs.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 687007. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, CB2 1EZ, U.K. (http://www.ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Synthesis of the Complexes. The routes to prepare the cyclometalated organoplatinum complexes are described in Scheme 1. The reaction of a yellow solution of [PtMe-(SMe$_2$)(ppy)], prepared in situ by reaction of [PtMe$_2$(μ-SMe$_2$)]$_2$ with 2 equiv of 2-phenylpyridine in acetone,[14] with 0.5 equiv of dppf at room temperature gave in good yield the binuclear complex [Pt$_2$Me$_2$(ppy)$_2$(μ-dppf)], **1**, in which ppy = deprotonated 2-phenylpyridyl and dppf = 1,1'-bis(diphenylphosphino)ferrocene, by replacement of SMe$_2$ ligands with the P ligating atoms of dppf. Complex **1** is an air-stable yellow solid that has green luminescence both in solution and solid state. The observations suggest that the Pt−ppy subunits are "separated" at these conditions and so no Pt−Pt or $\pi-\pi$ interaction of any kind between ppy ligands is expected in this complex.[3b] Complex **1** is stable in acetone or chloroform solutions for several hours.

(15) *X-AREA Program for the acquisition and analysis of data*, version 1.30. Stoe & Cie GmbH: Darmstadt, Germany, 2005.
(16) *X-RED Program for data reduction and absorption correction*, version 1.28b. Stoe & Cie GmbH. Darmstadt, Germany, 2005.
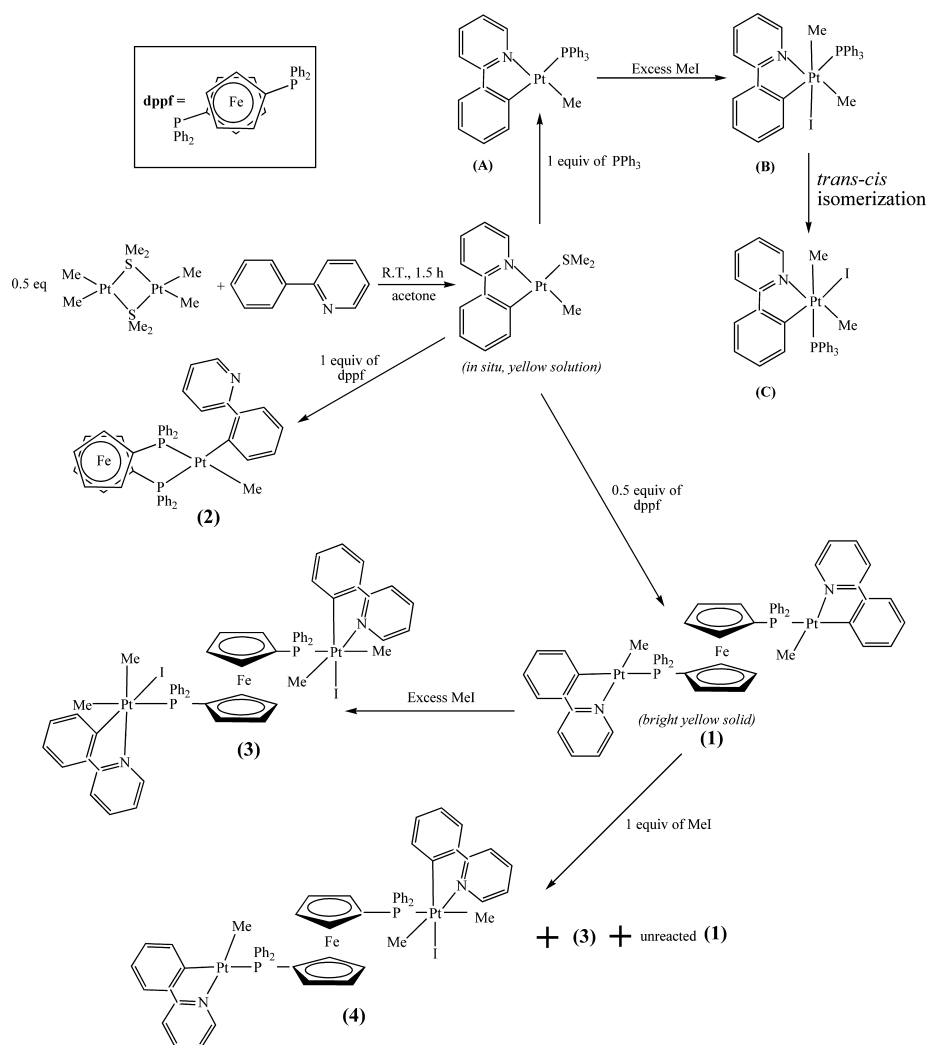(17) *X-SHAPE Program for crystal optimization for numerical absorption correction*, version 2.05. Stoe & Cie GmbH: Darmstadt, Germany, 2004.
(18) G. M. Sheldrick,. *SHELX97 Program for crystal structure solution and refinement*; University of Göttingen: Göttingen, Germany, 1997.
(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(20) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

When the above solution of [PtMe(SMe$_2$)(ppy)] was reacted with 1 equiv of dppf, the monomeric complex [PtMe(dppf)(ppy-κ^1C)], **2**, was obtained. The strong chelating ability of dppf has forced the Pt−N bonding of the cyclo-metalated part to break up and form the unusual monodentate Pt(ppy-κ^1C) complex **2**. This complex did not react with MeI probably because the bulky *ortho* substitution on the aryl ligand, which is an aromatic group, prevented the reaction to occur.

When 1 equiv of PPh$_3$ was reacted with the in situ solution of [PtMe(SMe$_2$)(ppy)] in acetone, a yellow solid product was obtained which was identified as [PtMe(ppy)(PPh$_3$)], **A**.

Reaction of the Pt(II)−Pt(II) binuclear complex **1** with excess methyl iodide at room temperature led to formation of the binuclear Pt(IV)−Pt(IV) complex **3** as the only product. The reported platinum complexes containing dppf ligand are usually square-planar Pt(II) complexes,[5a] and therefore the binuclear Pt(IV)−Pt(IV) complex **3** is an interesting example of dppf complexes. When complex **1** was reacted with 1 equiv of MeI, the mixed-valence Pt(II)−Pt(IV) complex **4** was formed as a mixture with the Pt(IV)−Pt(IV) complex **3** along with some unreacted starting complex **1**. This indicates that MeI has been oxidatively added to one of the Pt(II) centers of the Pt(II)−Pt(II) starting complex **1** to give the Pt(II)−Pt(IV) complex **4** and in parallel has been added to the Pt(II) center of complex **4** to give the final product Pt(IV)−Pt(IV) complex **3**. Because the amount of MeI has not been enough for completing the process, some starting complex **1** has remained unreacted. As mentioned above, when excess MeI was used, only the final product complex **3** was obtained.

MeI oxidatively added to the mononuclear Pt(II) complex **A** and the expected Pt(IV) product **B** with the Me and I ligands in *trans* position to each other was most probably formed first and very quickly isomerized to the final Pt(IV) product **C** with Me and I ligands in *cis* position to each other.

3.2. Characterization of the Complexes. The complexes were fully characterized by multinuclear (^{1}H, ^{31}P, ^{13}C, and ^{195}Pt) NMR spectroscopy. The data are collected in the Experimental Section, and the structures are shown in Schemes 1 and 2.

In the ^{31}P NMR spectrum of complex **1**, the two equivalent P atoms appeared as a singlet signal at δ 24.1 which were coupled to Pt atoms to give satellites with $^1J_{PtP}$ = 2092 Hz. Consistent with this, in the ^{195}Pt NMR spectrum of **1**, a doublet at δ −537 with $^1J_{PtP}$ = 2090 Hz was observed. The equivalency of the P atoms suggests that dppf is acting as a spacer ligand between the two PtMe(ppy) moieties, and each P atom is coordinated to a Pt atom in a *trans* disposition to the coordinating C atom of the phenyl ring of the ppy ligand. Each Me ligand is thus located *trans* to the coordinated N atom of the ppy ligand. In the ^{1}H NMR spectrum of complex **1**, the two equivalent methyl ligands resonated at δ 0.74 with a rather large value of $^2J_{PtH}$ = 84.5 Hz, confirming that the methyl ligands are located *trans* to imine N atoms than to P atoms. The four equivalent α and four equivalent β protons of the cyclopentadienyl rings appeared as two broad singlets at δ 4.2 and 4.1, respectively.

Scheme 1

In the ^{13}C NMR spectrum of **1**, the methyl ligands appeared as a doublet at δ −13.5 with $^{1}J_{PtC}$ = 732 Hz and $^{2}J_{PC}$ = 6 Hz. The low value of the latter coupling confirms that the methyl groups are in *cis* position to the P atoms. The parameters of the doublet at δ 164.5 with $^{1}J_{PtC}$ = 942 Hz and $^{2}J_{PC}$ = 123 Hz observed for C atoms of the ppy ligands connected to Pt atoms are comparable with previously reported data for N,C(sp^2) cyclometalated Pt(II) complexes,[21] and the relatively large value of $^{2}J_{PC}$ is consistent with the C atom being *trans* to the P atom.

In the ^{31}P NMR spectrum of the dppf chelating complex **2**, two signals appeared at δ 23.9 ($^{1}J_{PtP}$ = 1995 Hz) and δ 20.5($^{1}J_{PtP}$ = 1888 Hz). As will be discussed later, the Pt−P bond *trans* to the Me ligand is rather longer than that of the Pt−P bond *trans* to C atom of ppy-κ^1C ligand. We therefore assume that the *trans* influence of the Me ligand is higher than that of the ppy-κ^1C ligand and therefore assign the first signal to the P atom *trans* to the ppy-κ^1C ligand and the second one to the P atom *trans* to the Me ligand. In fact, one might have expected the reverse, as it has been shown

that Ph and p-MeC$_6$H$_4$ ligands exert higher *trans* influence than the Me ligand.[22] The considerably lower value of $^{1}J_{PtP}$ = 1995 Hz for the P atom *trans* to the C atom of ppy, as compared with the value of $^{1}J_{PtP}$ = 2092 Hz observed for the similar P atom in complex **1**, described above, is probably due to the dppf ligand being more strained in chelating form in complex **2** than in complex **1**, acting as a spacer ligand. Consistently, a doublet of doublets at δ −2890 with $^{1}J_{PtP}$ = 1883 and 1990 Hz was observed in the ^{195}Pt NMR spectrum of **2**. In the ^{1}H NMR spectrum of complex **2**, the methyl ligand, which is *trans* to the P atom, was resonated at δ 0.27 and as expected its $^{2}J_{PtH}$ value of 66.5 Hz was significantly lower than the value of $^{2}J_{PtH}$ = 84.5 Hz, observed for the methyl ligands located *trans* to imine N atoms in complex **1**. The observation of eight different peaks at δ 3.54−4.65 indicated that all eight α and β protons of the cyclopentadienyl rings are different, showing that the staggered conformation of the dppf ring is rigid. In line with this, in

(21) (a) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A. *Organometallics* **2003**, *22*, 4770. (b) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.

(22) (a) Rashidi, M.; Jamali, S.; Hashemi, M. *J. Organomet. Chem.* **2001**, *633*, 105. (b) Hashemi, M.; Rashidi, M. *J. Organomet. Chem.* **2005**, *690*, 982. (c) Nilsson, P.; Plamper, F.; Windt, O. F. *Organometallics* **2003**, *22*, 5235. (d) Appleton, T. G.; Bennett, M. A.; Tomkines, B. *J. Chem. Soc., Dalton Trans.* **1976**, 439. (e) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

Scheme 2

Excess MeI
k_2

trans-cis isomerization of the Pt(IV) center
Fast

(1)

(5)

k_1
+ N

(2)

(4)

Fast

(M)   + 1/2   **(N)**

MeI

(3)

trans-cis isomerization of the second Pt(IV) center
Fast

(6)
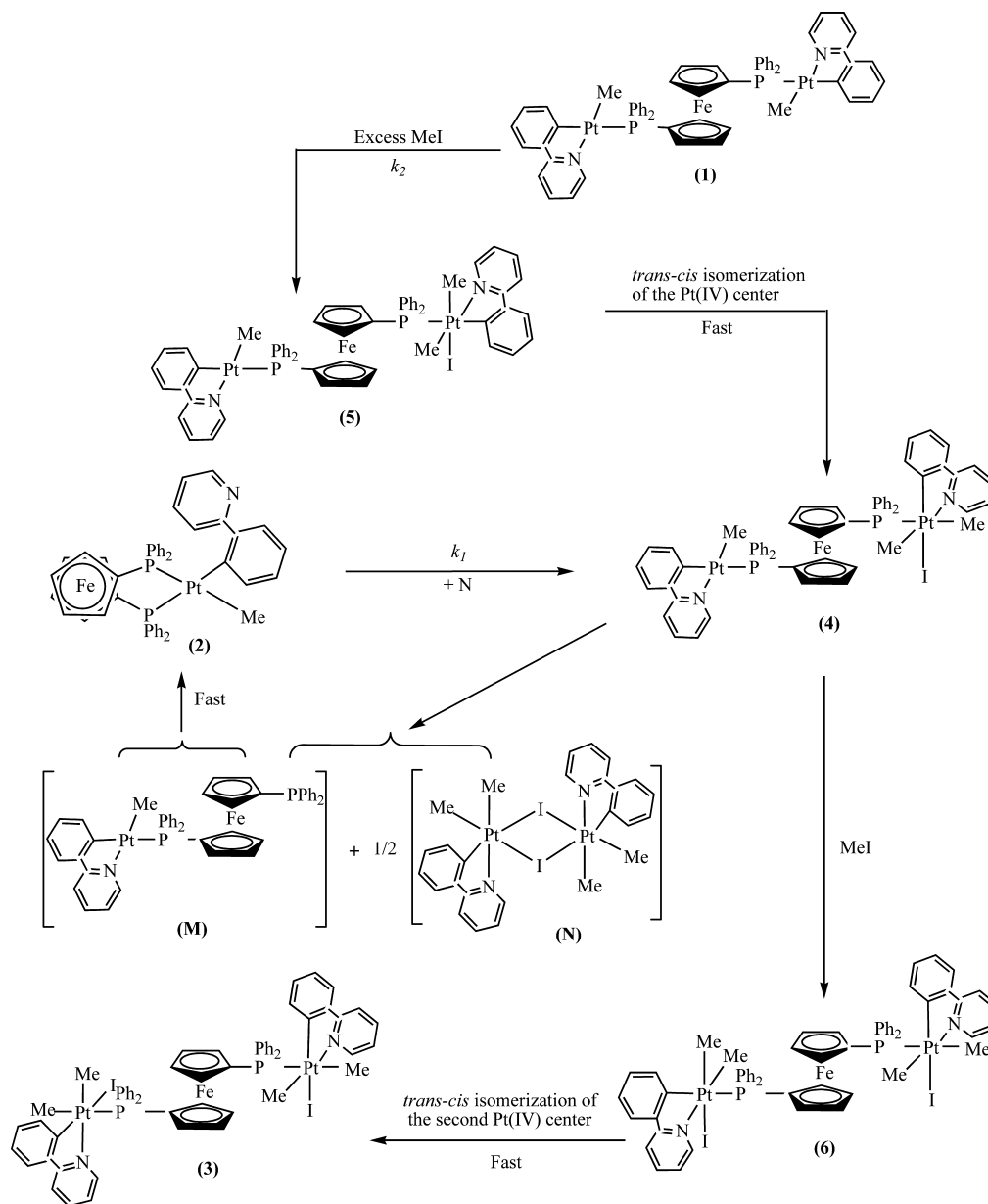
the ^{13}C NMR spectrum of complex **2**, eight different doublet signals at δ 70.9−75.8 have been observed for the α and β C atoms of the Cp ligands. The corresponding *ipso* Cs of Cp ligands appeared at δ 78.1 (with $^3J_{PtC} = 45$ Hz) for the CPPt *trans* to the Me ligand and at δ 80.0 (with a higher value of $^3J_{PtC} = 50$ Hz) for the CPPt *trans* to the ppy ligand, having a lower *trans* influence that the Me ligand.

In the ^{1}H NMR spectrum of complex **3**, the relative intensity of Me ligand protons to dppf protons is exactly 12:8, confirming that the complex is a dimer. However, on the basis of both ^{1}H and ^{13}C NMR spectra, which are shown in Figure 1, two different Me groups being *trans* to P and two different Me groups locating *trans* to N ligating atoms were assigned. Thus, in the ^{13}C NMR spectrum of **3**, in the Me region (see Figure 1B), two closely located doublets appeared at δ 6.1 and 6.2 each with a $^2J_{PC}$ value of 112 Hz for the Me groups *trans* to P; each doublet further coupled

to platinum to give a $^1J_{PtC}$ value close to 490 Hz. Two other doublets appeared further high field at δ −6.3 and −6.2 each with a $^2J_{PC}$ value of 3 Hz, indicating that they are located *cis* to the P atom and thus must be *trans* to the N atom; the $^1J_{PtC}$ value of 637 Hz for each of the signals is also significantly higher than the value of 490 Hz found for Me groups *trans* to P atoms. Consistently, in the ^{1}H NMR spectrum of complex **3**, the Me groups *trans* to P were observed at δ 1.07 as overlapping doublets with, $^2J_{PtH} = 61.0$ Hz, while Me groups locating *trans* to N ligating atoms appeared at δ 1.44 and 1.46, with a considerably higher $^2J_{PtH}$ values close to 71 Hz because of the lower *trans* influence of a N atom as compared with that of a P atom[22d,e] (see Figure 1A). In the ^{31}P NMR spectrum of the Pt(IV)−Pt(IV) complex **3**, two different P signals at δ −13.3 and −13.4 (each with $^1J_{PtP} = 990$ Hz, a value much smaller than the values of around 2000 Hz observed in the spectra of the Pt(II)

(B)

(A)
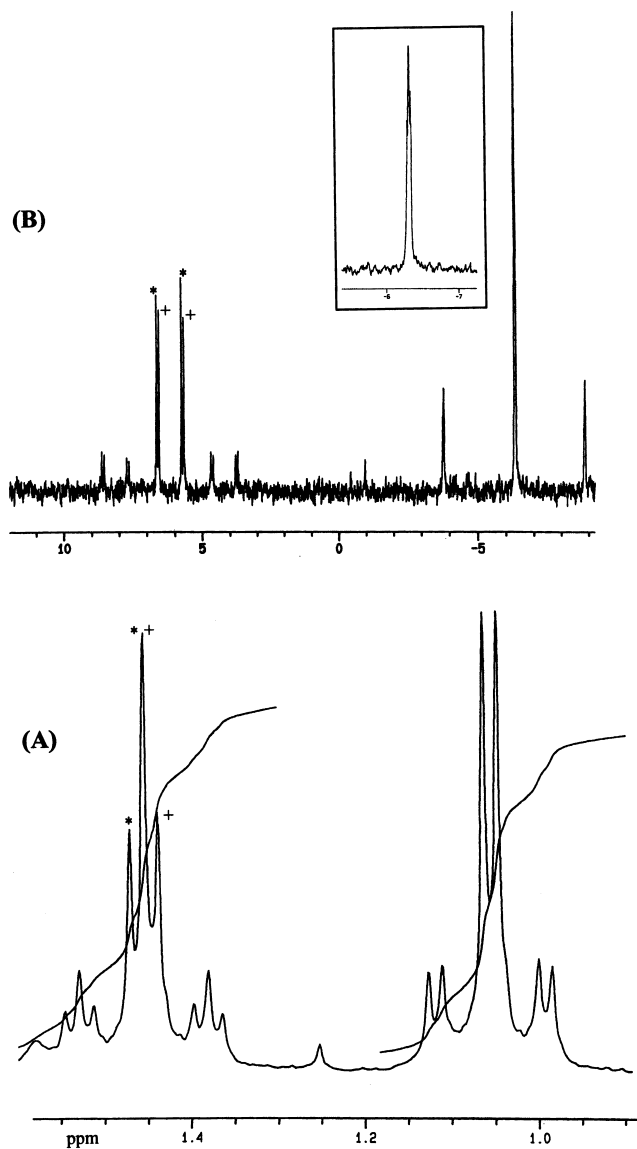
Figure 1. NMR spectra of complex **3** in the Me region. (A) ^{1}H and (B) ^{13}C, with the expansion of the central peaks due to Me ligands observed at higher field (shown in inset).

complexes **1** and **2**) were observed, and these are consistent with the observation of two signals in the ^{195}Pt NMR spectrum of complex **3** at δ 316 and 317 (two almost overlapping doublets each with $^1J_{PtP}$ = 990 Hz). Although the data would well establish the relative disposition of the different ligands on each Pt center as indicated in Scheme 2 (with chirality at each Pt center), it is impossible to use the present data to actually propose any "frozen" conformer(s) for complex **3** resulting from rotation around one or two of the Pt—P bonds. As twice the "expected" number of signals was observed in the NMR spectra of complex **3**, the formation of a statistical 1:1:2 mixture of three stereoisomers (the first two being enantiomers that are not distinguishable by NMR spectroscopy) may be a reasonable explanation. A NOE experiment was also carried out for complex **3** to further investigate the geometry around the platinum centers. As would be expected for the suggested arrangement around each Pt center, the NOE effect was observed between Me

ligands *trans* to P and C—H groups adjacent to the coordinated N atoms of the ppy ligands, while no effect was observed for Me groups that are located *trans* to N atoms of the ppy ligands. Also, Me ligands *trans* to P indicated NOE effect with α, α' Cp protons (and not with β, β' Cp protons), while the Me groups *trans* to N atom indicated NOE effects with both α and β Cp protons.

As mentioned above, the Pt(II)−Pt(IV) complex **4**, was obtained as a mixture with complexes **1** and **3**. By subtracting the peaks due to complexes **1** and **3** from the spectra obtained for the mixture, we determined the structure of complex **4**. Thus, in the ^{31}P NMR spectrum, a singlet at δ −13.2 with $^1J_{PtP}$ = 990 Hz, the values very close to those obtained for the Pt(IV)−Pt(IV) complex **3**, and another singlet at δ 23.9 with $^1J_{PtP}$ = 2090 Hz, the values very close to those obtained for the Pt(II)−Pt(II) complex **1**, were assigned to the Pt(IV) and Pt(II) centers of complex **4**, respectively. In line with this, two doublets at δ −538 ($^1J_{PtP}$ = 2088 Hz) and 315 ($^1J_{PtP}$ = 985 Hz) in the ^{195}Pt NMR spectrum of complex **4** were observed in the Pt(IV) and Pt(II) regions, respectively. The ^{1}H NMR spectrum was very useful in the structure determination of complex **4**. A doublet at δ 0.84 (with $^2J_{PtH}$ = 88.5 Hz and $^3J_{PH}$ = 7.7 Hz) was clearly assigned to the Me ligand on the Pt(II) center which is *trans* to the N ligating atom. For the Me ligands on the Pt(IV) center, two doublets at δ 1.09 (for the Me ligand *trans* to P with $^2J_{PtH}$ = 61.0 Hz and $^3J_{PH}$ = 7.6 Hz) and 1.53 (for the Me ligand *trans* to N with $^2J_{PtH}$ = 71.1 Hz and $^3J_{PH}$ = 7.8 Hz) were observed.

In the ^{31}P NMR spectrum of the mononuclear complex **A**, as expected, a singlet signal at δ 33.2 was observed with $^1J_{PtP}$ = 2105 Hz. In the ^{1}H NMR spectrum of the complex, the Me ligand that is *trans* to N atom was observed at δ 0.78 with a typical value of $^2J_{PtH}$ = 83.0 Hz and $^3J_{PH}$ = 8.0 Hz. In the ^{31}P NMR spectrum of the corresponding Pt(IV) complex **C**, the phosphorus signal, as is expected when compared to the same signal in the Pt(II) complex **A**, appeared at a higher field of δ −9.2 with a much lower value of $^1J_{PtP}$ = 961 Hz. The ^{1}H NMR spectrum of complex **C** was useful in determining its stereochemistry. Observation of a doublet at δ 1.28($^3J_{PH}$ = 7.5 Hz) with $^2J_{PtH}$ = 60.7 Hz confirmed that the Me ligand is located *trans* to P;[22d,e] the value is similar to the value of $^2J_{PtH}$ = 61.0 Hz observed for the Me ligand *trans* to the P in the Pt(IV) complex **3**. The second doublet signal at 1.65($^3J_{PH}$ = 7.7 Hz) was assigned to the Me ligand *trans* to N; this has a value of $^2J_{PtH}$ = 70.8 Hz, the same value obtained for the Me ligand *trans* to N in complex **3**. This confirms that MeI is oxidatively added to complex **A** to give the expected Pt(IV) complex intermediate **B** with Me and I ligands *trans* to each other, and a further *trans* to *cis* isomerization occurs to yield the final Pt(IV) complex **C** with Me and I ligands *cis* to each other.

The structure of complex [PtMe(dppf)(ppy-κ^1C)], **2**, was determined by X-ray crystallography and is shown in Figure 2; selected bond parameters are listed in Table 2. H atoms were treated by a mixture of independent and constrained refinement. The complex contains a square planar platinum(II) center with the Me group, the *ortho* C of the ppy ligand, and two P atoms of the dppf. The angles around the Pt center
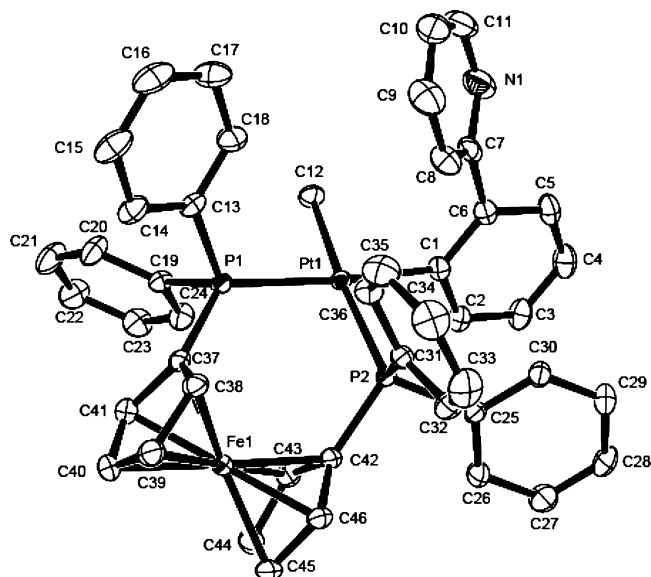
Figure 2. Molecular structure of complex [PtMe(dppf)(ppy-$\kappa^1 C$)], **2**, (50% probability ellipsoids, H atoms omitted for clarity).
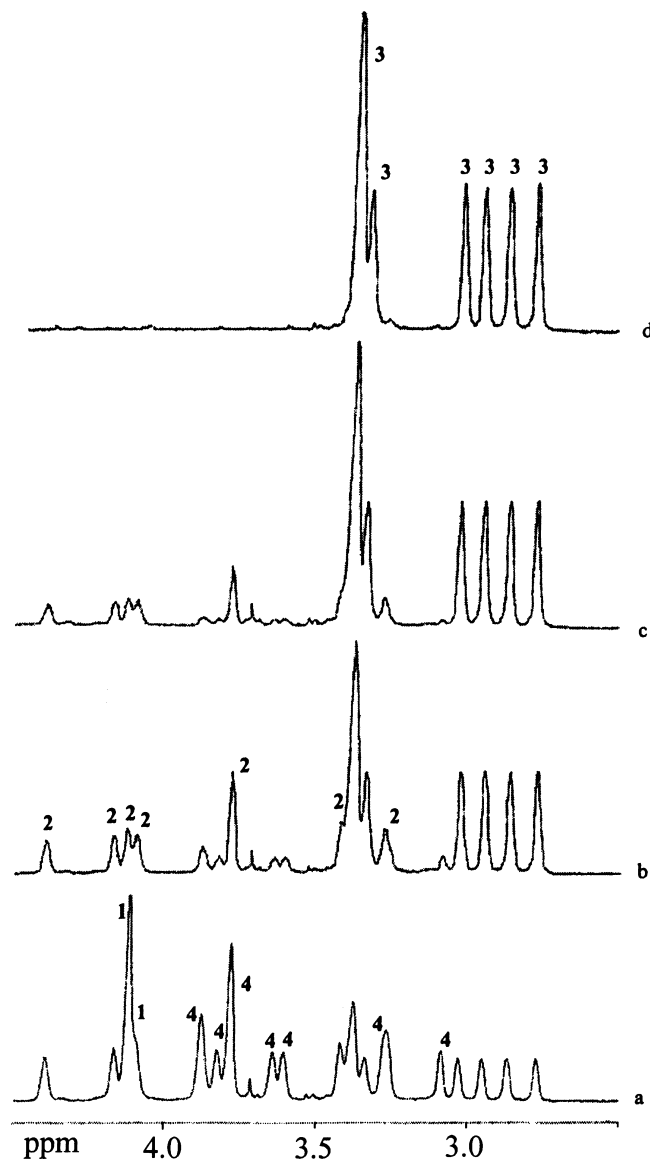
Table 2. Selected Bond Distances (Å) and Angles (°) for Complex **2**

Pt(1)−C(1)	2.075(4)	P(2)−Pt(1)−P(1)	97.61(3)
Pt(1)−C(12)	2.117(4)	C(1)−Pt(1)−C(12)	84.39(15)
Pt(1)−P(1)	2.3024(9)	C(1)−Pt(1)−P(2)	89.96(10)
Pt(1)−P(2)	2.3186(9)	C(12)−Pt(1)−P(1)	88.03(10)
P(1)−C(37)	1.824(4)	C(1)−Pt(1)−P(1)	172.24(10)
P(2)−C(42)	1.801(3)	C(12)−Pt(1)−P(2)	174.35(12)

are rather close to the ideal angle of 90°, and this could be contrasted with the strain observed in, for example, organoplatinum complexes containing bis(diphenylphosphino)amine, dppa, as chelating ligand. Thus, in complex [PtMe$_3$I(η^2-dppa)], dppa = bis(diphenylphosphino)amine, the angle P(1)−Pt(1)−P(2) = 68.93(5)° is much less than the ideal angle of 90°.[23] The imine N is not coordinated and is positioned opposite to the platinum center, and this is in contrast to the usual preference of the ppy ligand to form cyclometalated complexes. The dppf is arranged in the usually preferred "synclinal-staggered" conformation.[5a] The Pt−P(2) distance of 2.3186(9) Å is rather significantly longer than the Pt(1)−P(1) distance of 2.3024(9) Å, indicating that the Me ligand probably exerts a higher *trans* influence than the ppy-$\kappa^1 C$ ligand.

3.3. Kinetic and Mechanism of the Reaction of Complex 1 with MeI. On the basis of the NMR and UV−vis spectroscopic studies, described below, a mechanism for reaction of complex **1** with MeI is suggested as shown in Scheme 2.

(i) Monitoring the Reaction by ^{1}H NMR Spectroscopy. The reaction of complex **1** with a 25 fold excess MeI was monitored by using ^{1}H NMR spectroscopy in CDCl$_3$ in an NMR tube at 27 °C, and the resulting spectra are shown in Figure 3. As can be seen, 8 min after the addition of MeI, complex **4**, which is supposed to be the result of S$_N$2 addition of MeI to one of the Pt(II) centers of the starting complex **1** followed by a rapid *trans-cis* isomerization of the resulting
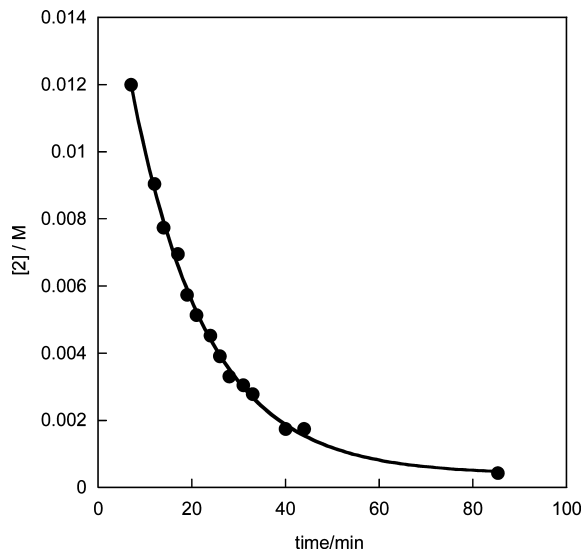
(23) Hoseini, S. J.; Mohamadikish, M.; Kamali, K.; Heinemann, F. W.; Rashidi, M. *Dalton Trans.* **2007**, 1697.

Figure 3. ^{1}H NMR spectra of reaction of complex **1** with a 25 fold excess of MeI at 27 °C; (a) 8 min after addition, (b) 13 min after addition (c), 20 min after addition, and (d) 2 h after addition.

Pt(IV) center, largely appeared along with a significant amount of both the monomeric complex **2** and the final Pt(IV)−Pt(IV) complex **3**. Five minutes later, the Pt(II)−Pt(IV) complex **4** was largely diminished while complexes **2** and **3** were appearing and the starting complex **1** had almost completely disappeared. The conversion of complex **2** to the final complex **3** was rather slow (see spectrum c obtained after 20 min). Two hours after the addition of MeI at this condition, as shown in Figure 3d, all complexes **1**, **2**, and **4**, disappeared, and the final Pt(IV)−Pt(IV) complex **3** was almost the only species present. Attempts to follow the reaction at low temperatures by ^{1}H NMR spectroscopy to gain insight about the other intermediates in the reaction sequence were not successful as extensive overlapping of the peaks prevented any useful conclusions. As can be seen, after addition of MeI to the first Pt(II) center, complex **2** is rapidly formed, and its disappearance to give complex **3** was very slow. We measured the rate constant, k_1, for this "very slow intermediate step" in CDCl$_3$ at 27 °C using the above
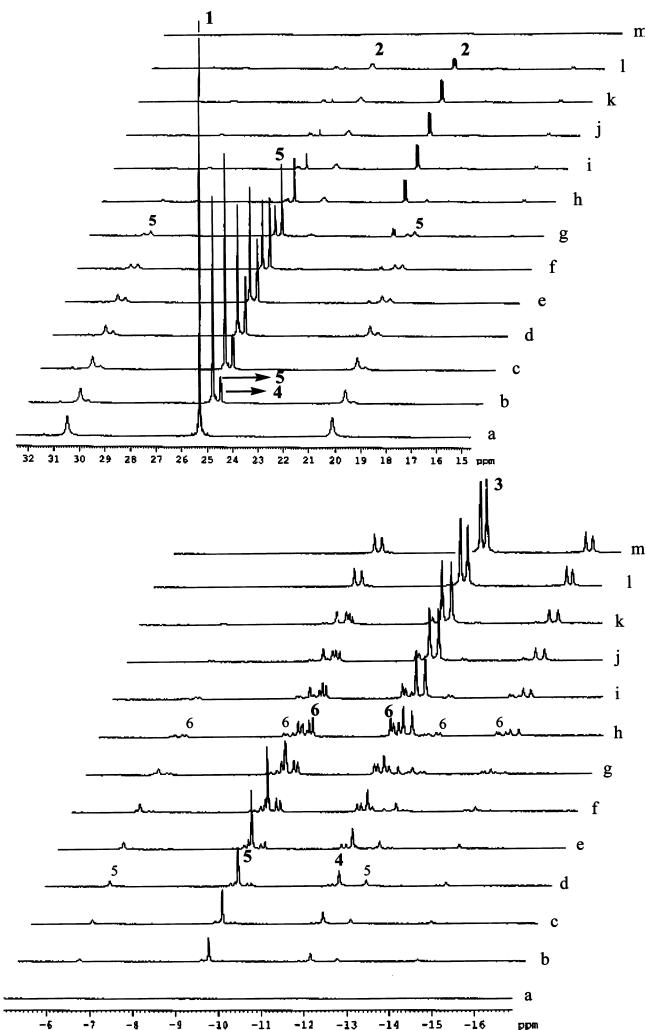
Figure 4. Concentration-time curve for the disappearance of the intermediate complex **2**, in reaction of complex **1** with MeI in CDCl$_3$ at 27 °C, using ^{1}H NMR spectroscopy.

mentioned ^{1}H NMR technique. The peaks for complex **2** appeared rather quickly, and the disappearance of the signal at $\delta = 4.64$ (due to one of the CH groups of dppf in complex **2**) was used to monitor the reaction. The process followed good first-order kinetics (Figure 4) and by fitting of [**2**]/time data with a first order equation (eq 1), the k_1 value for the disappearance of complex **2** was found to be $1.04(\pm 0.04) \times 10^{-3}$ s^{-1}. By using eq 2, it was also possible to calculate k_1 by an alternative method.[24] Thus, substituting the value of k_2 (in CHCl$_3$ at 27 °C), the rate constant for the first addition of MeI to complex **1** to form complex **4** as obtained easily by UV−vis spectroscopy (calculated from the data in Table 2, see below), in eq 2, $k_1 = 1.03(\pm 0.09) \times 10^{-3}$ s^{-1} is obtained. As can be seen, the values resulted by the two methods are almost identical.

$$A_t = (A_0 - A_\infty)[\exp(-k_{obs}t)] + A_\infty \quad (1)$$

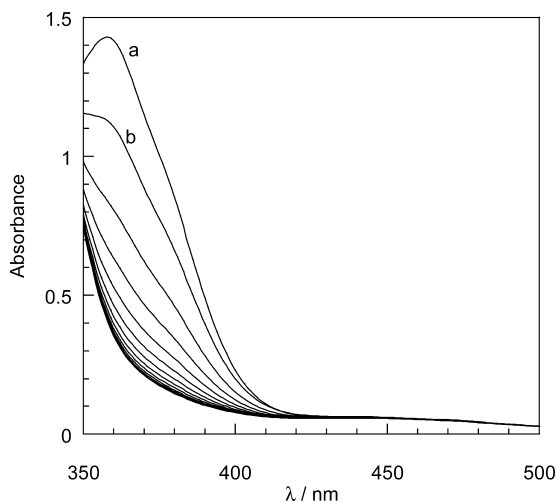$$[\mathbf{2}]_t = \frac{k_2[\text{MeI}][A_0]}{k_1 - k_2[\text{MeI}]}[\exp(-k_2[\text{MeI}]t) - \exp(-k_1 t)] \quad (2)$$

(ii) Monitoring the Reaction By ^{31}P NMR Spectroscopy. To investigate the details of mechanism, the reaction of complex **1** with excess methyl iodide was monitored by ^{31}P NMR spectroscopy at low temperatures, as shown in Figure 5. On the basis of the results, the complexes and intermediates suggested for the reaction sequence described in Scheme 2 were assigned. Note that complexes **1**, **2**, **3**, and **4** appeared in the suggested sequence, all characterized as described in the Characterization of the Complexes section, and so their characteristic ^{31}P NMR data were used to indicate the complexes. Also, by using ^{31}P NMR parameters of these complexes, good support for the structures of the suggested intermediates **5** and **6** (see below) was obtained. Thus, immediately after the addition of MeI at −20 °C, apart from complex **1**, a Pt(II)−Pt(IV) species assigned as intermediate **5** was detected. Two singlet signals, one at

(24) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995.

Figure 5. Reaction of complex **1** with excess methyl iodide as monitored by ^{31}P NMR spectroscopy at low temperatures. Top view: Pt(II) region. Down view: Pt(IV) region. (a) Pure **1** (253 K), (b) immediately after addition of excess MeI (253 K), (c) 10 min after addition of excess MeI (253 K), (d−k) successive runs each after 10 min and 2−3 K temperature raise, (l) after 100 min and temperature of 278 K, (m) 1 h after the temperature was raised up to room temperature. Peak assignments are shown; platinum satellites are observed for all involved species but are shown only for intermediates **5** and **6**.

δ 25.0 (with $^1J_{PtP} = 2072$ Hz), which is located in the Pt(II) region and its $^1J_{PtP}$ value is close to that of the Pt(II)−Pt(II) starting complex **1**, and another one at δ −9.8, located in the Pt(IV) region with $^1J_{PtP} = 1205$ Hz, were observed. The latter value is typical for Pt(IV)−P coupling but is significantly higher than the corresponding value found for Pt(IV)−Pt(IV) complex **3**; as we indicated above, this is probably due to higher *trans* influence of Me as compared to that of the ppy-κ^1C ligand. Although the data provide a reasonable support for the relative disposition of the different ligands on both Pt(II) and Pt(IV) centers as indicated in Scheme 2 for **5**, because of the limited available data it is not possible to suggest any specific conformation for the intermediate **5**. As the time was passing and the temperature was rising, the signals due to the starting material **1** were disappearing while those due to the intermediate **5** were growing and then later started fading away. Meanwhile, comparatively weak signals due to complex **4** were also
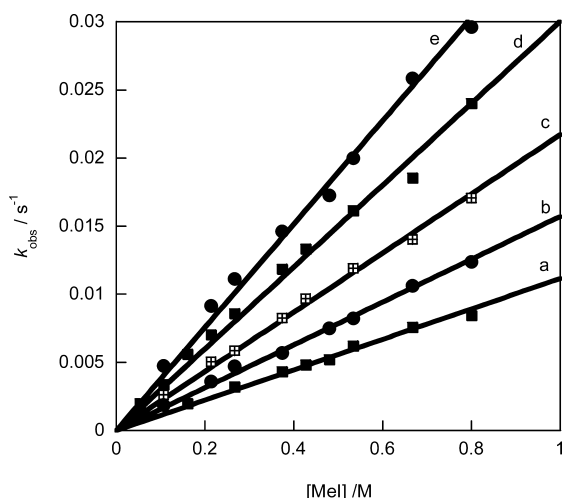
Figure 6. Changes in the UV−vis spectrum during the reaction of complex **1** (1.5×10^{-4} M) with MeI (0.533 M) in CHCl$_3$ at T = 25 °C: (a) initial spectrum (before adding MeI); (b) spectrum at t = 0 s. Successive spectra were recorded at intervals of 30 s.
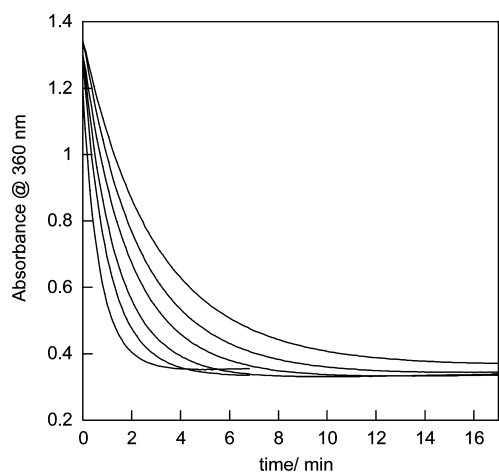
Figure 7. Absorbance-time curves for the reaction of complex **1** with MeI (0.16−0.8 M; [MeI] increases reading downward) in CHCl$_3$ at 25 °C.

Figure 8. Plots of first-order rate constants for the reaction of complex **1** with MeI at different temperatures (a, 10 °C; b, 15 °C; c, 20 °C; d, 25 °C; d, 30 °C) versus the concentration of MeI in CHCl$_3$.

observed in the first stages. In the meantime, the suggested intermediate **6** along with complex **2** started to show up. As the reaction progressed, the Pt(IV)−Pt(IV) intermediate **6**

was quickly disappearing while the concentration of complex **2** was rather rapidly increasing and the final Pt(IV)−Pt(IV) complex **3** started to appear. Around this time on, complex **2** was slowly disappearing while the signals due to the final product **3** were being slowly increased. Although the slow conversion of **2** to **3** is suggested as occurring via intermediates **4** and **6**, the latter intermediate could not be seen at these stages as its conversion to **3** was relatively fast. Note that for the suggested intermediate **6**, a set of two singlets are predicted, one for Pt(IV)−P *trans* to the Me ligand, which is expected to be located close to the corresponding signal for complex **4** (or close to the signals for complex **3**), and another one for Pt(IV)−P *trans* to the ppy-$\kappa^1 C$ ligand, which is expected to be located close to the corresponding signal for intermediate **5**. In fact, we observed two sets of such signals in the expected regions with expected $^1J_{\text{PtP}}$ values (one set at δ −11.7, with $^1J_{\text{PtP}}$ = 1012 Hz, and δ −9.7, with $^1J_{\text{PtP}}$ = 1214 Hz, and another set at δ −11.8, with $^1J_{\text{PtP}}$ = 1012 Hz, and δ −9.8, with $^1J_{\text{PtP}}$ = 1214 Hz). We therefore suggest that the intermediate **6**, as was pointed out above regarding the structure of complex **3**, is also obtained as a statistical 1:1:2 mixture of three stereoisomers and although, because of the possibility of rotation around one or two of the Pt−P bonds, it is impossible to actually propose any particular configuration for any of the conformers because of the limited data, the suggested relative disposition of the different ligands on each Pt center, as indicated in Scheme 2, seems to be reasonable. After 100 min (temperature 278 K) all the signals, except a small amount of the complex **2**, disappeared. It is to be noted that when the temperature was raised up to room temperature, signals due to the remaining small amount of complex **2** completely disappeared after 1 h, and the final Pt(IV)−Pt(IV) product **3** was purely obtained.

(iii) Kinetic Studies Using UV−vis Spectroscopy. The binuclear complex **1** contains a MLCT band in the visible region that could be used to monitor its reaction with MeI and study the kinetics of the reaction by using UV−vis spectroscopy. Thus, an excess of MeI was used at 25 °C and the disappearance of the metal-to-ligand charge-transfer (MLCT) band at λ = 360 nm in a CHCl$_3$ solution was used to monitor the reaction. The change in the spectrum during a typical run is shown in Figure 6.

The time-dependence curves of the spectra of the reaction in CHCl$_3$ at this condition are shown in Figure 7. Thus, the pseudo-first-order rate constants k_{obs} were evaluated by nonlinear least-squares fitting of the absorbance-time profiles to the monophasic first-order equation (eq 1). Plots of the first-order rate constants, k_{obs}, versus [MeI] was linear with no intercepts (Figure 8), showing a first-order dependence of the rate on the concentration of MeI. The slope in each case gave the second-order rate constant, and the results are collected in Table 3. Therefore, the reaction obeys a simple second-order rate law, first order in both the corresponding dimer and MeI. The reproducibility of the data was remarkable (4%). The same method was used at other temperatures, and activation parameters were obtained from the Eyring

Table 3. Rate Constants (L mol^{-1} s^{-1}) for the Reaction of the Complexes with MeI in CHCl$_3$

	$T = 10$ °C	$T = 15$ °C	$T = 20$ °C	$T = 25$ °C	$T = 30$ °C
complex **1**, 10^2k_2 [a]	1.11 ± 0.02	1.57 ± 0.02	2.17 ± 0.03	3.00 ± 0.05	3.79 ± 0.06
complex **A**, 10^2k_2				0.85 ± 0.02	1.10 ± 0.04

[a] Activation parameters for the reaction of complex **1** with MeI were calculated as $\Delta H^\ddagger = 41.8 \pm 1.2$ (kJ mol^{-1}) and $\Delta S^\ddagger = -134 \pm 4$ (J K^{-1} mol^{-1}).
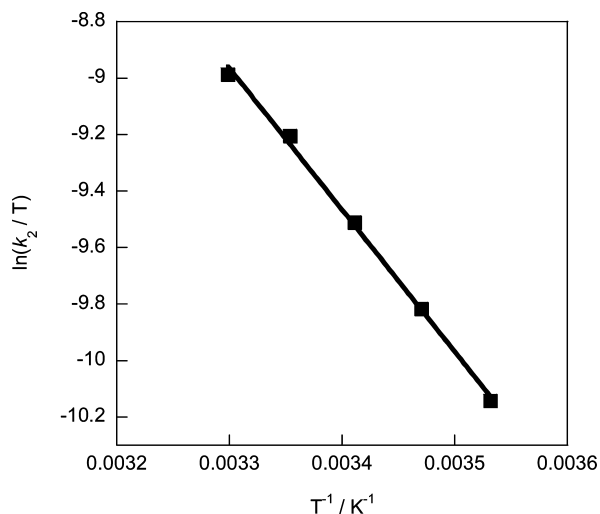
Figure 9. Eyring plot for the reaction of complex **1** with MeI in CHCl$_3$.

equation (see eq 3 and Figure 9). The data are collected in Table 3.

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \qquad (3)$$

In a comparative study, we studied the kinetics of reaction [PtMe(ppy)(PPh$_3$)], **A**, with MeI as a "calibration reaction" to evaluate the effect of dppf ligand on the rate of the reaction of MeI with complex **1**. The monomeric Pt(II) complex **A** also contains a MLCT band in the visible region and was used similarly to study the kinetics of its reaction by using UV−vis spectroscopy in CHCl$_3$ at $\lambda = 358$ nm. The data are collected in Table 3.

(iv) Mechanistic Interpretation of the Data. A mechanism, as shown in Scheme 2, therefore has been suggested for the reaction of complex **1** with MeI. As described above, the suggested mechanism has been supported by low temperature ^{31}P NMR study, ^{1}H NMR spectroscopy and also by kinetic studies using UV−vis spectrophotometry. Thus, MeI is first *trans* oxidatively added to one of the platinum(II) centers of complex **1** by a classical S$_N$2 reaction with a rate constant k_2, yielding intermediate **5**. The latter has undergone a relatively fast conversion of the *trans* arrangement of the Me and I ligands on the platinum(IV) center to the *cis* arrangement to form complex **4**. Then, the latter would either react with MeI to form intermediate **6** by a classical S$_N$2 reaction or disintegrate to form a pair of species **M** and **N**, with the suggested structures shown in Scheme 2. Formation of the Pt(II) species **M** by such a dissociative process could probably be the best explanation for the formation of complex **2** during the reaction, and the unusual penta-coordinated Pt(IV) species that should subsequently be released is best suggested to dimerize to form **N**. We believe that **2** and **N** could then slowly reassociate back to **4** which would then lead to **3** by reaction with MeI through the intermediate **6**. The disappearance of **2**, as monitored by ^{1}H NMR spectroscopy, was slow, and the rate constant $k_1 = 1.04(\pm0.04) \times 10^{-3}$ s^{-1} (at 27 °C) was some 30 times slower than the initial S$_N$2 attack of complex **1** to MeI (see Table 3). The intermediate **6** would then quickly perform a facile *trans* to *cis* isomerization of the Pt(IV) center having Me and I in *trans* disposition to form the final product **3**.

4. Conclusions

The Pt(II)−Pt(II) dimer [Pt$_2$Me$_2$(ppy)$_2$(μ-dppf)], **1**, is an interesting case of the less common diplatinum complexes containing an "open bridge" dppf. On the basis of the NMR spectra, the two PtMe(ppy) species are shown to be identical and the four α protons (or the four β protons) of the Cp rings of the dppf spacer ligand are also equivalent. This shows that the conformation of dppf[5a] has most probably an ideal "antiperiplanar staggered" conformation with a Cp(centroid)···Fe···Cp(centroid) twist angle $\tau = 180°$. This is preferred to an "anticlinal eclipsed" conformation with $\tau = 108°$, as the latter would require an extra conformational flipping of "open bridge" dppf to make the above mentioned equivalency of the α and β protons of the Cp rings.

The [PtMe(dppf)(ppy-κ^1C)] complex, **2**, is a common example of complexes with the preferred chelating conformation of dppf. This complex is formed when the starting complex [PtMe(SMe$_2$)(ppy)], containing a chelating cyclometalated ligand, is reacted with 1 equiv of dppf. It thus appears that the chelating ability of dppf is actually dominated and has caused the rather strong cyclometalated chelate to open up from the N donor atom. The NMR spectra indicated that the staggered conformation of the dppf ring, as determined by X-ray crystallography, is rigid in solution. The Pt−P distance for P atom *trans* to Me is rather longer than that of the P atom *trans* to the C atom of ppy ligand. The difference, although modest, indicates that the Me ligand probably exerts a higher *trans* influence than the ppy-κ^1C ligand. This is in contrast to the reports that Ph or p-MeC$_6$H$_4$ ligands exert a higher *trans* influence than the Me ligand,[22] and this has been attributed to the higher s character of Pt−C(sp^2) for aryl ligands as compared to Pt−C(sp^3) for Me.

When the dimer **1**, with two square-planar Pt(II) centers, was reacted with excess MeI, based on the observations, the normal Me and I *trans* oxidative addition occurred. However, the structure of the final product Pt(IV)−Pt(IV) dimer complex **3**, as determined by multinuclear NMR studies, indicated that further *trans* to *cis* isomerization would have happened to place the added ligands, Me and I, in a *cis* position to each other. We believe that a steric effect has probably been responsible for the isomerization to occur. An "antiperiplanar staggered" conformation has been suggested

for the dppf spacer ligand. Although the relative disposition of the different ligands on each Pt center as indicated in Scheme 2 was well established, it was impossible to propose any "frozen" conformer for complex **3** resulting from rotation around one or two of the Pt–P bonds. As twice the "expected" number of signals was observed in the NMR spectra of complex **3**, the formation of a statistical 1:1:2 mixture of three stereoisomers (the first two being enantiomers that are not distinguishable by NMR spectroscopy) may be a reasonable explanation. To the best of our knowledge, no Pt(IV)–Pt(IV) dimer with a dppf spacer ligand has already been reported.

The kinetic studies in the present work indicated that MeI was initially reacted with one of the Pt(II) centers of [Pt$_2$Me$_2$(ppy)$_2$(μ-dppf)], **1**, with a rate significantly higher by a factor of 3.5 than that of the corresponding reaction involving the mononuclear complex [PtMe(ppy)(PPh$_3$)], **A**, which was studied as a "calibration reaction". This has been attributed to more electron donating ability of the P ligands in complex **1** as compared to the P ligands of PPh$_3$ in complex **A** because of the presence of ferrocenyl moieties

in the dppf containing complex **1**. After the addition of MeI to the first Pt(II) center of complex **1**, measurement of the rate of the addition of MeI to the second Pt(II) center was not possible. This was indicated to be due to the occurrence of a slow side reaction in between the two steps involving stepwise addition of MeI to the two Pt(II) centers.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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