Thermal and Photochemical Oxidative Addition of Alkyl Halides to the Cyclometalated Complex cis-Bis[2-(2'-thienyl)pyridine]platinum(II)

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The homoleptic, cyclometalated complex cis-bis[2-(2'-thienyl)pyridine] platinum(II) (**1**, Pt(2'-thpy)$_2$) undergoes thermal or photochemical oxidative addition (TOA or POA) reactions with a wide range of alkyl halides. These reactions are found to be highly stereoselective, yielding in most cases Pt(IV) complexes with the halide and the σ-bonded C(alkyl) atom in the *cis* position, in a C,C,C-*fac* arrangement. In some cases, *trans* addition of R-X was observed, followed by *trans* → *cis* isomerization, either at room temperature or on heating. Extensive use was made of ^{1}H NMR spectroscopy in assigning the configurations, and the 2-D COSY spectra, measured for a few of the Pt(IV) complexes, were helpful in making the chemical shift assignment. The ^{195}Pt NMR spectra were recorded for five of the Pt(IV) complexes. The resonance of the Pt(IV) nucleus is seen to be very sensitive to the nature of the coordinated halide and alkyl ligands. The X-ray crystal structures were determined for three of the Pt(IV) complexes. Crystals of Pt(2'-thpy)$_2$(benzyl)Br (**8**) are triclinic, space group $P\bar{1}$, a = 9.854(2) Å, b = 15.413(2) Å, c = 17.333(2) Å, α = 63.90(1)°, β = 76.71(1)°, γ = 86.42(1)°, and Z = 4. Final R = 0.030 and R_w = 0.048 for 7758 observed reflections. Crystals of Pt(2'-thpy)$_2$(1-naphthyl)Br (**12**) are also triclinic, space group $P\bar{1}$, a = 7.335(2) Å, b = 10.484(2) Å, c = 16.912(2) Å, α = 84.02(1)°, β = 83.46(1)°, γ = 87.18(2)°, and Z = 2. Final R = 0.044 and R_w = 0.065 for 2966 observed reflections. Both these structures reveal the *cis* addition of R–X and the distorted octahedral coordination sphere of the Pt(IV) atom. Crystals of Pt(2'-thpy)$_2$(CF$_3$CHCl)Br (**20a**) are orthorhombic, space group *Pbca*, a = 17.574(3) Å, b = 9.204(1) Å, c = 26.612(2) Å, and Z = 8. Final R = 0.036 and R_w = 0.068 for 2462 observed reflections. The structure shows the *trans* addition of CF$_3$CHBrCl. The one Pt–N bond is 0.08 Å longer than the other Pt–N bond in **20a**, as well as the Pt–N bonds in **8** and **12**. This is probably due to steric interaction between the "coplanar" 2-thienylpyridine ligands in this isomer.

Introduction

The preparation and characterization of a series of bis-homoleptic and -heteroleptic cyclometalated Pt(II) complexes, of the type Pt(N∧C)$_2$, has previously been reported.[1] The cyclometalating ligand, N∧C, is a C-deprotonated aromatic ligand, with nitrogen as the donor atom, a few examples being phenylpyridine (phpy⁻), 2'-thienylpyridine (2'-thpy⁻), phenylpyrazole (phpz⁻), and diphenylpyridine (H-diphpy⁻). The presence of two carbanions, which lie high in the spectrochemical series, in the inner coordination sphere of these cyclometalated Pt(N∧C)$_2$ complexes has a marked influence on their photophysical properties. The strong Pt–C σ bonds move the d metal orbitals to high energy, and since there is a low-lying π* orbital on the aromatic ligand system, the energy of the MLCT transition is reduced to such an extent that it is observed as the excited state of lowest energy in these complexes. These complexes exhibit some interesting photophysical and photochemical properties. Such species emit light in a rigid nitrile matrix at 77 K, which, for most cases, disappears on warming to room temperature. However, the complexes Pt(2'-thpy)$_2$ (**1**) and Pt(phpz)(2'-thpy) are also found to give a strong luminescence in fluid solution at room temperature.[1f]

Organometallic, square planar Pt(II) complexes are found to be strong nucleophiles[2–4] due to the strong Pt–C σ bonds, which

increase the electron density at the metal center. We have already reported the thermal oxidative (TOA) and photochemical oxidative (POA) addition of a number of substrates to the cyclometalated complexes Pt(2'-thpy)$_2$ (**1**) and Pt(phpy)$_2$.[5] Both these complexes are found to readily undergo a TOA reaction with oxidizing agents such as the dihalogens, I$_2$ and Br$_2$, and alkyl halides such as methyl and ethyl iodide.

From early on in the study of these Pt(N∧C)$_2$ complexes, it became apparent that when solutions of these complexes were irradiated with visible light, especially in halogenated solvents such as dichloromethane and chloroform, this quite often led to the disappearance of the Pt(II) complexes and the formation of new, luminescent cyclometalated Pt(IV) products.[6] Similar photochemical reactions have been reported for only a small number of other Pt(II) complexes.[7–9] A surprising feature of the POA reactions with **1** is their high degree of stereoselectivity. Of the eleven possible isomers,[10] only the C,C,C-*fac* enantiomeric pair (Δ,Λ), shown in Figure 1, is observed.

The oxidative addition of a wide range of alkyl halides to the cyclometalated complex **1** has been systematically investigated,[11] and the results of this study are reported here. Table I lists the alkyl halides that were studied. All the resulting Pt(IV) complexes

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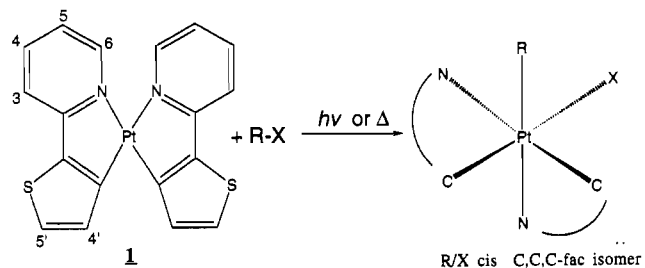(11) Suckling, A. Doctorate Thesis No. 1007, University of Fribourg, 1992.

Figure 1. The TOA and POA of alkyl halides (R–X) to **1** producing, for many R–X molecules, the thermodynamically stable Pt(IV) C,C,C-*fac* isomer with R/X *cis*.

Table I. List of Alkyl Halides Used in the Study of the Oxidative Addition Reaction with Pt(2′-thpy)$_2$ (**1**)

alkyl halide, R–X	TOA^a or POA^b	Pt(2′-thpy)(R)X complex no.
Group I, R = Halogenated Alkane		
ethyl bromide	POA	3
n-propyl bromide	POA	4
n-butyl bromide	POA	5
CH$_2$Br$_2$	POA	6
Group II, R = Aromatic Alkyl Group		
benzyl chloride	TOA	7
benzyl bromide	TOA	8
C$_6$F$_5$CH$_2$Br	TOA	9a, R/X trans
		9b, R/X cis
Ph$_2$CHBr	TOA	10
PhC(CO)Cl	TOA	11
1-BrMe-naphthalene	TOA*	12
2-BrMe-naphthalene	TOA*	13
9-ClMe-anthracene	TOA*	14
Group III, R = Alkyl Group Containing –C=C–		
3-bromopropene	TOA	15
1-bromopropene (cis/trans mixture)	POA	16
Group IV, R = Alkyl Group Containing –C≡CH or –C≡N		
3-bromopropyne	TOA	17
chloroacetonitrile	TOA	18
Group V, R = Alkyl Group Containing Chiral Center		
benzal bromide	TOA*	19
CF$_3$CHBrCl	TOA or POA	10a, R/X trans
		20b, R/X cis

^{a} TOA indicates thermal oxidative addition in aerated solution. TOA* indicates thermal reaction in degassed solution. ^{b} POA indicates photochemical oxidative addition.

were fully characterized by ^{1}H NMR spectroscopy. ^{195}Pt NMR spectra were also recorded for a few of these Pt(IV) complexes. The X-ray crystal structures of three of the cyclometalated Pt(IV) complexes are also reported.

Experimental Section

Nearly all the alkyl halides were purchased from either Aldrich or Fluka and were of purum grade quality where possible. 9-(Chloromethyl)anthracene was prepared according to a literature method.[12] All the liquid alkyl halides were distilled using the Fischer distillation column. Chloroacetonitrile (Fluka) was heated under reflux, over P$_2$O$_5$, for 1 day, and then fractionally distilled before use.[13] Bromodiphenylmethane (Fluka, pract, ~95%) was sublimed under reduced pressure prior to use.

Measurements. Electronic spectra were recorded with a Perkin-Elmer 555 spectrophotometer. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 683 spectrometer, with the samples in compressed KBr disks. ^{1}H and ^{195}Pt NMR spectra were recorded on a Gemini 300 Varian spectrometer, at an operating frequency of 300.075 and 64.355 MHz, respectively. The peak positions for the ^{1}H NMR spectra are relative to TMS. An aqueous solution of K$_2$PtCl$_4$ was used as the external

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reference for the natural abundance ^{195}Pt NMR spectra. The general external reference, K$_2$Pt(CN)$_6$, which is used for Pt(II) complexes is not useful for the Pt(IV) cyclometalated complexes due to its appearance in a spectral window far from the Pt(IV) resonances. The 2-D COSY spectra were obtained from a 0.7-mL CDCl$_3$ solution containing ~15 mg of Pt(IV) complex. The F_1 dimension was equal to the F_2 dimension and ranged from 1735 Hz for **8** to 1255 Hz for **14**. The 2-D spectra arose from 256 increments, each composed of 16 transients stored in 256 data points. A relaxation delay of 4 s was used to ensure an appropriate magnetization equilibrium. Zero filling to 512 × 512 gave the desired matrix. Transformation in both dimensions revealed the 2-D COSY spectra. The spectra were symmetrized by folding about the diagonal to reduce the noise level.

Preparation of the Pt(IV) Complexes. Purification. The Pt(IV) products, which were isolated as pale brown solids from the TOA reactions in aerated solution, were purified by recrystallization from a dichloromethane/hexane solution of the complex. Slow evaporation of CH$_2$Cl$_2$ resulted in crystals after 2–3 days. The Pt(IV) products from the POA and TOA reactions in degassed solutions were purified using preparative thin layer chromatography (PTLC). For the PTLC, 20 × 20 cm^2 glass plates with a 1.5 mm thick layer of silica gel were prepared. A 20–30-mg amount of substance could be applied to one end of the plate and then eluted with CH$_2$Cl$_2$. Due to the small amounts of Pt(IV) products obtained, the elemental analyses were obtained for only a few complexes. The ^{1}H NMR spectra of the purified products gave a good indication of their purity. In all cases only a single Pt(IV) product was observed after purification.

Complexes 3–6 (POA), Pt(2′-thpy)$_2$(R)X, R–X = EtBr (3), *n*-PrBr (4), *n*-BuBr (5), and CH$_2$Br$_2$ (6). A 20 mg amount of **1** was dissolved in a minimum volume of the alkyl bromide and degassed by three freeze–pump–thaw cycles (oil pump, <10^{-3} mbar), with the solution protected from the light during the degassing. The solutions were then irradiated (250-W projector lamp) until the solutions had turned a very pale brown color. The irradiation times with the projector lamp varied: for the reaction with EtBr, t_{irrad} < 1 s (yield = 62%), whereas for *n*-BuBr, t_{irrad} ~ 10 minutes (yield = 50%). The alkyl halide was then removed on the rotavapor, and the complexes were purified using PTLC.

Complexes 7, 11, and 18 (TOA), Pt(2′-thpy)$_2$(R)X, R–X = Benzyl Chloride (7), Benzoyl Chloride (11), and Chloroacetonitrile (18). A 20-mg amount of **1** was dissolved in 20 mL of benzyl chloride, benzoyl chloride, or chloroacetonitrile and heated to 60 °C. The reaction was complete in 10 min. The alkyl chloride was then removed under reduced pressure, and a light brown solid remained, which was recrystallized from a CH$_2$Cl$_2$/hexane mixture (yield = 70–75%).

Complexes 8 and 15 (TOA), Pt(2′-thpy)$_2$(R)X, R–X = Benzyl Bromide (8) and 3-Bromopropene (Allyl Bromide) (15). A 30-mg amount of **1** was dissolved in 20 mL of CH$_2$Cl$_2$, in the dark. A 0.5-mL volume of the alkyl bromide was added, and the solution was left to stir overnight. The solvent was then taken off on the rotavapor. The solid was recrystallized from a mixture of CH$_2$Cl$_2$/hexane (yield = 80%).

Complexes 9a,b (TOA), Pt(2′-thpy)$_2$(C$_6$F$_5$CH$_2$)Br, R/X Trans (9a), R/X Cis (9b). A 30-mg amount of **1** was dissolved in 20 mL of CH$_2$Cl$_2$, in the dark, and 4–5 drops of pentafluorobenzyl bromide were added, the solution was left to stir overnight, and then the solvent was removed on the rotavapor. **9a** was found as the major product (small amount of **9b**) and could be separated using PTLC (yield = 70%). The isomerization of **9a** to **9b** was observed using ^{1}H NMR by heating a sealed NMR tube, containing 10 mg **9a** in 0.7 mL of CDCl$_3$, at 60 °C, and measuring the ^{1}H NMR spectrum periodically until the isomerization was complete (~3 h).

Complex 10 (TOA), Pt(2′-thpy)$_2$(Ph$_2$CH)Br. A 60-mg amount of **1** was dissolved in 30 mL of CH$_2$Cl$_2$, in the dark, and then 120 mg of bromodiphenylmethane was added to this solution, which was left to stir overnight. The solvent was then removed, and the remaining solid was washed with three portions of 10 mL of ethanol to remove the excess alkyl halide. The pale brown solid was recrystallized from an ethanol/CH$_2$Cl$_2$ mixture (yield = 75%).

Complexes 12, 13, and 19 (TOA, Degassed Solution), Pt(2′-thpy)$_2$(R)X, R–X = 1-(Bromomethyl)naphthalene (12), 2-(Bromomethyl)naphthalene (13), and α,α′-Dibromotoluene (Benzal Bromide) (19). Solid **1** and a solution of the alkyl bromide could be simultaneously degassed, prior to mixing, by means of U-tube-shaped glassware, which allowed 20 mg of **1** to be placed in one arm of the U-tube, while 45 mg of the solid alkyl bromide, or ~10 drops of benzal bromide, dissolved in either 20 mL of acetone or acetonitrile, was placed in the other arm. After degassing (three freeze–pump–thaw cycles), the reactants were mixed and stirred

Table II. Crystallographic Data for Pt(2'-thpy)₂(PhCH₂)Br (**8**), Pt(2'-thpy)₂(1-Me-naphthalene)Br (**12**), and Pt(2'-thpy)₂(CF₂CHCl)Br (**20a**)

	8	12	20a
molecular formula	$C_{25}H_{19}BrN_2PtS_2$	$C_{29}H_{21}BrN_2PtS_2$	$C_{20}H_{13}BrClF_3N_3_2PtS_2$
mol wt	686.18	736.24	712.53
space group	$P\bar{1}$	$P\bar{1}$	$Pbca$
$a/\text{Å}$	9.854(2)	7.335(2)	17.574(3)
$b/\text{Å}$	15.413(2)	10.484(2)	9.204(1)
$c/\text{Å}$	17.333(2)	16.912(2)	26.612(2)
α/deg	63.90(1)	84.02(1)	90
β/deg	76.71(1)	83.46(1)	90
γ/deg	86.42(1)	87.18(2)	90
$V/\text{Å}^3$	2298.5(6)	1284.1(5)	4304.5(9)
Z	4	2	8
$\rho_{calcd}/\text{g·cm}^{-3}$	1.984	1.905	2.200
abs coeff ($\mu\alpha$), cm⁻¹	80.8	72.4	87.7
transm	0.594 (max), 0.221 (min)	0.707 (max), 0.358 (min)	0.529 (max), 0.094 (min)
final R value	0.030	0.044	0.036
weighted final R value[a]	0.048	0.065	0.068

[a] $R_w = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|$.

for 1 h. The solvent was then removed, and the complexes were purified using PTLC (yield = 60–70%).

Complex 14 (TOA, Degassed Solution), Pt(2'-thpy)₂(9-Me-anthracene)Cl. The procedure was the same as above. A 50-mg amount of **1** and 130 mg of 9-(chloromethyl)anthracene, dissolved in 30 mL of CH₃CN or (CH₃)₂CO, were mixed after degassing. The solution turns a deep yellow color during 1 h of stirring. The solvent was then taken off on the rotavapor, and a bright yellow solid remained. The Pt(IV) product decomposes on silica gel and aluminium oxide. It was therefore washed three times with hot toluene to remove the excess alkyl chloride. The remaining solid was dissolved in a minimum volume of chloroform. The slow diffusion of ether into this solution resulted in crystals of pure **14** (fine needles) after a day (yield = 63%).

Complex 16 (POA), Pt(2'-thpy)₂(R)X, R–X = 1-Bromopropene (Cis/Trans). Method a. A 20-mg amount of **1** was dissolved in a minimum volume of 1-bromopropene. The solution was degassed and then irradiated. The alkyl halide was removed under reduced pressure.

Method b. A 20-mg amount of **1** was dissolved in 5 mL of alkyl bromide and 15 mL CH₃CN, the solution degassed and irradiated, and the solvent removed. The Pt(IV) complex was purified by PTLC for both methods (yield = 80 and 70% respectively).

Complex 17 (TOA), Pt(2'-thpy)₂(R)X, R–X = 3-Bromopropyne (Propargyl Bromide). Alkyl bromide was bought as a 80 wt % solution in toluene (Aldrich). A 20-mg amount of **1** was added to 10 mL of this solution, and the mixture was stirred for 2 h. The solvent was removed under reduced pressure, and the pale brown solid was recrystallized from CH₂Cl₂/hexane (yield = 76%).

Complexes 20a,b (TOA or POA), Pt(2'-thpy)₂(R)X, R–X = CF₃-CHBrCl (Halothane), R/X Trans (20a) and R/X Cis (20b). TOA Method. A 20-mg amount of **1** was dissolved in a minimum volume of halothane and left in the dark. The thermal reaction was complete after ~1 day. **POA Method.** A 30-mg amount of **1** was dissolved in a solution of 15 mL of CH₃CN/5 mL of R–X, and then the solution was degassed twice (freeze–pump–thaw). The solution started to turn clear while degassing if not completely protected from the light. The major product is **20a** after both TOA and POA (yield = 86 and 74% respectively). **20a** was converted to **20b** by refluxing it in CHCl₃, in the dark, for 3 h.

Kinetic Measurements. In all experiments 1 mg of **1** was dissolved in 20 mL of solvent (9.7 × 10⁻⁵ M) and the initial concentration of alkyl halide varied as 5 × 10⁻³ M, 8 × 10⁻³ M, 1.1 × 10⁻² M, and 1.4 × 10⁻² M. A glass microsyringe was used to add the very small volumes of R–X. [R–X] was kept much greater than [**1**] so as to ensure pseudo-first-order kinetics. The decrease in [**1**] was measured by UV/vis spectrophotometry, by monitoring the decrease in the intensity of the MLCT band of **1** at 420 nm.

X-ray Crystallographic Studies. Suitable crystals for X-ray work were grown by slow evaporation (2–3 days) from dichloromethane/hexane solutions of the complexes. Crystal data and details of the data collection and structure refinement of **8**, **12**, and **20a** are summarized in Table II. The data collection was performed by measuring intensity data on a Stoe-Siemens AED2 four-circle diffractomer (graphite-monochromated Mo Kα radiation) at room temperature. The intensity variations for four standard reflections measured every 1 h were never greater than 3% for each crystal. A numerical absorption correction was applied to the intensity data on the basis of the crystal dimensions using the ABSC

subroutine in the SHELX-76 program.[14] The E statistics clearly indicated the structures to be centrosymmetric, and this was confirmed by the stable refinements. The program NRCVAX[15] was used for all calculations. The Pt atom was located from a Patterson map, and the remaining non-hydrogen atoms were derived from a series of subsequent difference Fourier syntheses. In the final cycles of least-squares refinement the H atoms were included in idealized positions and optimized in an isotropic manner. All the other atoms were treated anisotropically.

Results and Discussion

A. Reactivity of Pt(2'-thpy)₂. Synthesis of the Pt(IV) Complexes. Pt(2'-thpy)₂ (**1**) is found to react, both thermally and photochemically, with a wide range of alkyl halides. The Pt(II) complex is thermally stable in chlorinated alkanes such as CH₂Cl₂ and CHCl₃, even under reflux for extended periods of time. However, exposure of the deaerated or atmosphere-equilibrated solutions to visible light (sunlight or a 250-W halogen lamp) leads to rapid POA of the alkyl chlorides. UV/vis spectra recorded during irradiation show clean isosbestic points indicating a single reaction channel.
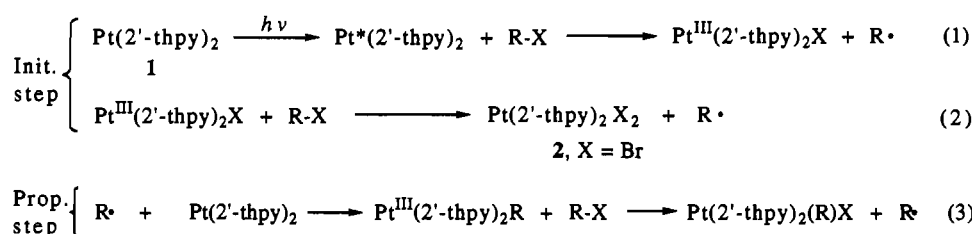
There is a very slow TOA of primary brominated alkanes, R–Br, e.g. R = CH₃–, CH₃CH₂–, at room temperature (1–2 days). Irradiation of these degassed solutions leads to a very fast POA reaction (1–2 s). The photochemical reactions were always found to be cleaner and faster in degassed solution than in aerated solution. When the POA reactions were done on a preparative scale, 20–30 mg of **1** was dissolved in a minimum volume of the neat alkyl bromide and the mixture was degassed and then irradiated. Under these conditions the major product was found to be the Pt(IV) complex, Pt(2'-thpy)₂(R)Br.

As the length of the alkyl chain increased, then the amount of the Pt(2'-thpy)₂(R)Br complex formed on irradiation of the degassed solutions was found to decrease, and the formation of the Pt(IV) dihalide product, Pt(2'-thpy)₂Br₂ (**2**), was observed. For the reaction with n-butyl bromide, **2** is found to be the major product. The mechanism of the photochemically initiated reactions of **1** with CHCl₃ and CH₂Cl₂ has been previously described.[16] For the reaction with CH₂Cl₂, the ·CH₂Cl radical is estimated to carry a chain length of ~40, and so only a very small amount of the Pt(2'-thpy)₂Cl₂ complex is formed in the initiation step of this reaction, eqs 1 and 2 in Scheme I.

For the reaction with n-butyl bromide, the formation of a large amount of **2** is then probably due to a decrease in the efficiency of the chain reaction, eq 3 in Scheme I, for the longer alkyl radical, so that more of **2** is formed in the initiation step.

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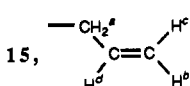(16) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelwesky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720.

Scheme I

$$\text{Init.} \begin{cases} \text{Pt(2'-thpy)}_2 \xrightarrow{h\nu} \text{Pt}^*(2'\text{-thpy})_2 + \text{R-X} \longrightarrow \text{Pt}^{III}(2'\text{-thpy})_2\text{X} + \text{R}\cdot \quad (1) \\ \qquad\quad \mathbf{1} \\ \text{Pt}^{III}(2'\text{-thpy})_2\text{X} + \text{R-X} \longrightarrow \text{Pt}(2'\text{-thpy})_2\text{X}_2 + \text{R}\cdot \quad (2) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{2},\ X = Br \end{cases}$$

$$\text{Prop.} \begin{cases} \text{R}\cdot + \text{Pt(2'-thpy)}_2 \longrightarrow \text{Pt}^{III}(2'\text{-thpy})_2\text{R} + \text{R-X} \longrightarrow \text{Pt}(2'\text{-thpy})_2(\text{R})\text{X} + \text{R}\cdot \quad (3) \end{cases}$$

Table III. ^{1}H NMR Data (ppm) for the 2'-Thienylpyridine Ligands in Complexes 3, 8, 9b, 10, 14, and 15[a]

	chem shift/δ											
complex no.	3a	4a	5a	6a	4'a	5'a	3b	4b	5b	6b	4'b	5'b
3	7.58–7.53	7.9	7.31	9.71 (16.7)	6.1 (20)	7.15 (11.0)	7.48	7.58–7.53	6.79	7.43	7.28	7.58–7.53
8	7.24–7.18	7.62–7.5	6.92	9.23 (15.8)	6.28 (20.2)	7.24–7.18	7.62–7.5	7.62–7.5	6.8–6.65	7.36 (15.6)	7.39 (14.7)	7.65 (10.3)
9b	7.40–7.32	7.88	7.40–7.32	9.69 (15.6)	6.15 (19.9)	7.05 (10.8)	7.51	7.63–7.56	6.79	7.40–7.32	7.63–7.56	7.69 (9.6)
10	7.53–7.35	7.66	6.88–6.8	8.89 (14.2)	6.0 (19.2)	7.17 (12.2)	7.53–7.35	7.53–7.35	6.68	7.13–7.03	6.46 (13.9)	7.28 (10.1)
14	6.35	7.09	6.20	8.70 (15.8)	6.32 (10.2)	6.98 (6.6)	7.57–7.53	7.57–7.53	6.69	7.20	7.77	7.77
15	7.7–7.45	7.87	7.4–7.25	9.70 (16.5)	6.14 (20.3)	7.17 (11.7)	7.7–7.45	7.7–7.45	6.81	7.7–7.45	7.4–7.25	7.7–7.45

[a] Internal standard Me$_4$Si. Solvent CDCl$_3$. Values in parentheses indicate ^3J(Pt,H) coupling constants in Hz.

Table IV. ^{1}H NMR Data (ppm) for the Alkyl Groups in Complexes 3, 8, 9b, 10, 14, and 15

	chem shift/δ	
complex no., R	Pt–CH_n–R (Hz)	–R
3, –CH$_2$CH$_3$	2.83 (J = 7.4, $J_{H,Hgem}$ = 9.7, J(Pt) = 96), 2.27 (J = 7.4, $J_{H,Hgem}$ = 9.7, J(Pt) = 47)	0.37 (J = 7.4, J(Pt) = 49.3)
8, –CH$_2$Ph	4.63 ($J_{H,Hgem}$ = 8.5, J(Pt) = 117.6), 3.60 ($J_{H,Hgem}$ = 8.5, J(Pt) = 56.8)	6.8–6.65
9b, –CH$_2$C$_6$F$_5$	4.13 ($J_{H,Hgem}$ = 10.14, J(F) = 2.4, J(Pt) = 115.6), 3.63 ($J_{H,Hgem}$ = 10.14, J(F) = 2.4, J(Pt) = 78.7)	
10, –CH(Ph)$_2$	6.11 (J(Pt) = 107.8)	7.53–7.35 (2H), 7.13–7.03 (2H), 7.0–6.88 (2H), 6.88–6.80 (4H)
14, –CH$_2$-anthr	5.50 ($J_{H,Hgem}$ = 9.9, J(Pt) = 124.8), 4.89 ($J_{H,Hgem}$ = 9.9, J(Pt) = 64.2)	9.20, 7.54, 7.29, 7.68, 7.64, 7.09, 6.81, 7.37, 7.90
15, —CH$_2^a$ C=C (H^c/H^d/H^b)	3.78 (J(H^d) = 5.8, $J_{H,Hgem}$ = 8.0, J(Pt) = 115.0), 3.01 (J(H^d) = 5.8, $J_{H,Hgem}$ = 8.0, J(Pt) = 60.0)	H^b, 4.38 (J(H^c) = 2.7, J(H^d) = 7.4); H^c, 4.56 (J(H^b) = 2.7, J(H^d) = 17.9); H^d, 5.55 (J(H^b) = 7.4, J(H^c) = 17.9, J(CH$_2^a$) = 5.8)

For the POA with brominated alkanes, in aerated solutions, the reactions were not so clean, and a mixture of products was observed. Although the Pt(2'-thpy)$_2$(R)Br complex could be observed in the ^{1}H NMR spectrum of the crude product after reaction, a number of other Pt(IV) complexes could also be observed, with a large amount of **2** being formed. The scavenging of the alkyl radicals by oxygen accounts for this observation. Puddephatt et al.[17,18] report a similar observation for the free radical reaction of Me$_2$Pt(N∧N)$_2$, where N∧N = phen or bpy, with ^{i}PrI. These authors established a chain length of >1000 for the thermal reaction in the absence of oxygen, and the sole product observed was Me$_2$Pt(N∧N)(^{i}Pr)I. When the reaction was done in aerated solution, a dramatic decrease in the chain length for the free radical reaction was observed, and now both the Pt(IV) products, Me$_2$Pt(N∧N)I$_2$ and Me$_2$Pt(N∧N)(OO-^{i}Pr)I, were also observed in varying amounts, depending on the degree of aeration of the solution. Although we did not isolate a Pt(IV)–peroxy species for the POA reactions of **1** in aerated alkyl halides, such species may account for some of the other Pt(IV) products observed for these reactions.

The purity of the alkyl halides was found to be a very important factor in the study of their oxidative addition to **1**, especially for the reactions that were free radical in nature. For the free radical reactions, any impurity that can scavenge free radicals can have a dramatic effect on the final products. In some instances, such as the reaction with chloroacetonitrile, a slow thermal reaction,

in the dark, produced only a single Pt(IV) complex, whereas when this reaction was photoinduced, although the reaction went much faster, it was not clean, probably due to the presence of minor impurities in this alkyl halide.

There was no thermal reaction with secondary or tertiary alkyl halides. The photochemical reaction with these substrates required long irradiation times and resulted in a mixture of products, the major product being **2**.

There was found to be neither a TOA nor a POA reaction between **1** and aryl halides. Even when **1** was dissolved in the polyhalogenated, electron-deficient benzene derivative bromopentafluorobenzene, no decomposition of **1** was observed after prolonged irradiation of the degassed solution.

There is a fast, clean TOA reaction, producing only a single Pt(IV) product, when **1** is added to neat solutions of benzyl bromide, pentafluorobenzyl bromide, bromodiphenylmethane, 3-bromopropene, and 3-bromopropyne to form the Pt(IV) complexes **8**, **9**, **10**, **15**, and **17**, respectively. A much slower thermal reaction occurs when a 5–10 molar excess of these alkyl halides is added to a CH$_2$Cl$_2$ solution of **1**, in the dark (**1** is photoreactive in CH$_2$Cl$_2$).

A very fast TOA reaction is observed when a 5–10 molar excess of 1-(bromomethyl)naphthalene, 2-(bromomethyl)naphthalene, 9-(chloromethyl)anthracene, or benzal bromide is added to an aerated CH$_2$Cl$_2$ solution of **1**, in the dark. However, these reactions gave a number of Pt(IV) products in aerated solution, and it was very difficult to isolate a pure Pt(IV) product. However, when the TOA reaction was done with these alkyl halides in degassed acetonitrile or acetone, the reaction was found to be much cleaner, and the Pt(IV) products, Pt(2'-thpy)$_2$(R)X, R =

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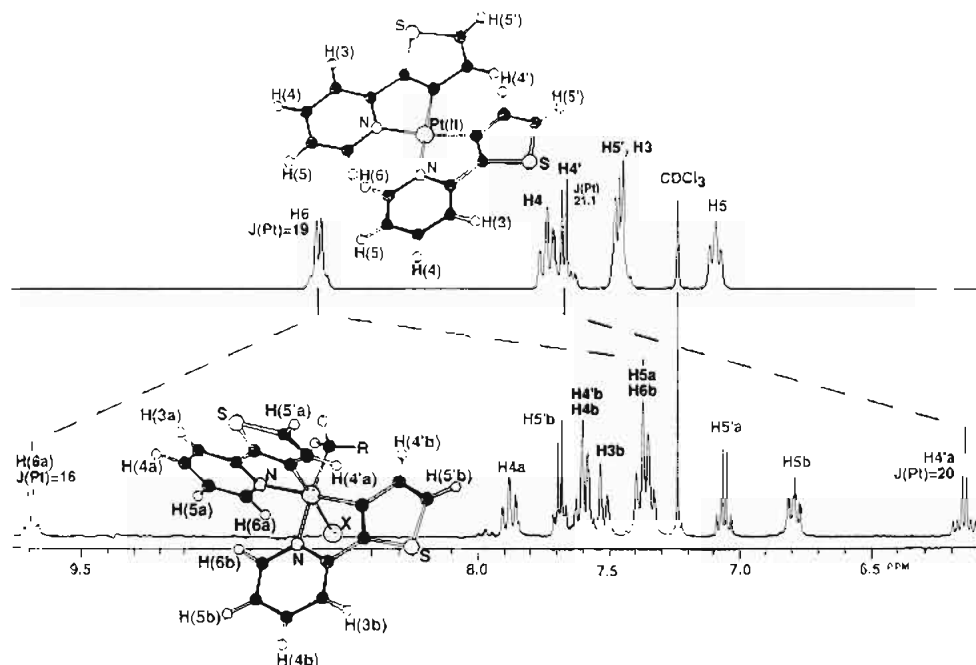
Figure 2. ¹H NMR spectra of **1** (upper spectrum) and Pt(2'-thpy)₂(C₆F₅CH₂–)Br (**9b**) (lower spectrum).

1-Me-naphthalene, X = Br⁻ (**12**), R = 2-Me-naphthalene, X = Br⁻ (**13**), R = 9-Me-anthracene, X = Cl⁻ (**14**), and R = C₆H₅CHBr, X = Br⁻ (**19**), could be isolated and characterized.

Since the bromide atoms in C₆H₅CHBr₂ are prochiral, a chiral center is produced on the alkyl group attached to Pt(IV) in **19** on the TOA of benzal bromide to **1**. The reaction therefore produces two pairs of enantiomers i.e Δ,R/Λ,S and Δ,S/Λ,R, and it is clear from the ¹H NMR spectrum of the product that the one pair of enantiomers is formed in excess, although it is not known which pair.

The reaction with the acyl halides, acetyl chloride and benzoyl chloride, was also investigated. CH₃COCl gives a fast TOA reaction in degassed solution, but a number of Pt(IV) products were formed and it was difficult to isolate a single product. **1** gives a slow TOA reaction with PhCOCl, in the dark, from which Pt(2'-thpy)₂(PhCO)Cl (**11**) could be isolated. The presence of a –CO stretching frequency at 1639 cm⁻¹ shows that decarbonylation of **11** to form a Pt(IV)–aryl species has not occurred.⁴⁷

B. Structure and Stereochemistry. ¹H NMR spectroscopy. The proton NMR data for a few of the Pt(IV) complexes are compiled in Tables III and IV. Full tables of NMR data for all the Pt(IV) complexes have been submitted as supplementary material. 2-D COSY spectroscopy was an important tool in making the chemical shift assignment for many of the Pt(IV) complexes. When the terms cis and trans are used, this refers to the mode of R–X addition to **1**.

(a) Cis Addition of R–X. Oxidative addition of R–X to a square-planar metal center with two bidentate C ∧ N-coordinated ligands can give rise to 11 possible isomers, a nonchiral isomer from trans addition of R–X, a chiral isomer from trans addition, and 4 enantiomeric pairs of isomers from cis addition of R–X.¹⁰ In most cases of oxidative addition with the alkyl halides used in this study, a single common pair of enantiomers were observed in the ¹H NMR spectra. A typical spectrum from the oxidative addition of pentafluorobenzyl bromide to **1** is shown in Figure 2, lower spectrum. The upper spectrum is that of **1**. Comparison of these two spectra allows us to draw the following conclusions, from which the stereochemistry of the Pt(IV) isomer can be deduced: (i) It is immediately clear that the number of signals observed in the ¹H NMR spectrum of the Pt(IV) complex shows the inequivalence of the 2'-thienylpyridine ligands, and thus the three isomers from the trans addition of R–X can be ruled out. (ii) Two protons in the β-position with respect to the Pt atom

experience a strong upfield shift on oxidative addition (H–C(4'a) and H–C(6b) in Figure 2). This shielding effect is due to the ring current of a pyridyl or thienyl group in the plane perpendicular to the plane of the ring where these two protons lie. This indicates cis positions for N–Pt–N and C–Pt–C for the chelate ligands.¹⁹⁻²¹ (iii) The values of the ²J(Pt,CH₂) coupling constants are strongly affected by the trans influence and unambiguously differentiate between the two remaining structures with R/X cis. When an alkyl group is attached to the Pt atom via a –CH₂– unit, two signals are observed in the spectrum for these methylene protons. This is due to the chirality of the Pt(IV) coordination sphere, which creates different chemical environments for these prochiral protons. In Pt(2'-thpy)₂(PhCH₂)Br (**8**), the ²J(Pt,CH₂) values are 56.8 and 117.6 Hz. The R group can be either trans to N(aromatic) or trans to C(aromatic). A constant of ~44 Hz is expected for the arrangement trans Me–Pt–Me,²²,²³ and the value for a methyl trans to a pyridine is ~70 Hz. Kuyper²⁴ has reported coupling constants of 88 and 45 Hz for the –CH₂Cl group in the complex cis-Pt(bpy)(Me)₂(CH₂Cl)Cl, where the –CH₂Cl group is trans with respect to the bipyridine. On examination of the ²J(Pt,CH₂) coupling constants for the Pt(2'-thpy)₂(R)X complexes, it is seen that the average of the ²J(Pt,CH₂) values ranges from 72 Hz (**3**) to 107 Hz (**9b**), which is consistent with the ligand trans to CH₂ being moderate-to-weak in trans influence. I.e., the R group is trans to N(aromatic), so that the sole isomer formed on the TOA and POA of R–X to **1** is the enantiomeric C,C,C-fac isomer (Δ,Δ) with R/X cis.

The reaction with 3-bromopropyne, BrCH₂C≡CH, proved to be an exception, since it is the only alkyl halide used in this study that shows the formation of two different isomers on the cis-thermal addition to **1**. The ¹H NMR spectrum of this Pt(IV) product, **17**, shows two nearly identical, overlapping spectra, which suggests that two very similar isomers are formed on addition to **1**. The ²J(Pt,CH₂) values for the one isomer are 106.2 and 73.5 Hz, which agrees with the other Pt(IV) complexes, and so this

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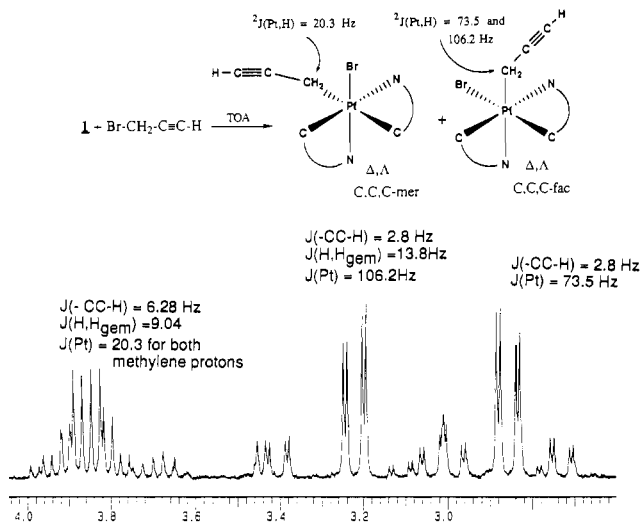**Figure 3.** ^{1}H NMR spectrum of the methylene region of the isomers formed on the TOA of BrCH$_2$C≡CH to **1**.

isomer is assigned as the C,C,C-*fac* isomer. The methylene protons of the other isomer have the same ^2J(Pt,H) value of 20.3 Hz. This big decrease in ^2J(Pt,CH$_2$) agrees with the HC≡CCH$_2$-ligand being *trans* to C(aromatic), and so this second isomer is assigned as the C,C,C-*mer* isomer, with R/Br *cis*, shown in Figure 3. The presence of a triplet in the acetylenic region at 1.67 ppm ($J = 2.8$, J(Pt) = 20 Hz) identifies the –C≡CH proton and excludes the possibility for the formation of Pt(2'-thpy)$_2$-(–CH=C=CH$_2$).

(b) Trans Addition of R–X. *Trans* addition was observed for the oxidative addition of pentafluorobenzyl bromide and halothane (CF$_3$CHBrCl), complexes **9a** and **20a**, respectively. This is clear from their ^{1}H NMR spectra, which show the 2'-thpy⁻ ligands to be equivalent. **9a** is sparingly soluble in CDCl$_3$ but goes into solution on warming as it isomerizes to the *cis* isomer. Although **20a** is fairly soluble in CDCl$_3$, no *trans* ⇒ *cis* isomerization is observed after 1 week at room temperature. On heating of the sample in a sealed NMR tube in CDCl$_3$ at 60 °C, the formation of the thermodynamically more stable *cis* isomer is complete after ∼3 h. A *trans* isomer has also been observed on oxidative addition of methyl iodide to **1**, which isomerizes slowly to the *cis* isomer in a few days.[5,25] A transient isomer corresponding to the *trans* addition of benzyl bromide to **1** has been observed in the ^{1}H NMR spectrum, immediately after addition of the alkyl halide, but this isomerizes readily (∼30 min) at room temperature to the *cis* isomer. The stereochemistry of the product from the oxidative addition of CF$_3$CHBrCl is nice to study using ^{1}H and ^{195}Pt NMR, since in this case we have a chiral alkyl group attached to the platinum center. The crystal structure determination of the *trans* product, **20a**, shows that the two chelate rings are not coplanar (dihedral angle ∼9°, see Figure 6) due to an antitwist distortion, and so the complex has helical chirality (Δ,Λ). Since the alkyl group sitting above the plane of the ligands has a chiral center (R,S), there are four isomers, i.e two diastereomers, each with its enantiomer: Δ,R/Λ,S and Δ,S/Λ,R. The difference in the chemical environment of the diastereotopic protons is just discernible in the ^{1}H NMR spectrum of the *trans* complex, Figure 4, upper spectrum. Whereas the signal for H–C(6) is a broad doublet in the complexes of *trans* addition when the alkyl ligand is achiral, e.g. R = benzyl, in the ^{1}H NMR spectrum of **20a**, the overlapping signals for H–C(6) appear as a broad triplet. The diastereotopic protons of H–(5) and H–C(4) are also observed. It is seen that both diastereomers are present in equal amounts. On heating **20a**, the –CF$_3$CHCl and Br⁻ ligands rearrange to the C,C,C-*fac* isomer, where they are *cis* with respect to each other,

and now the differences in the chemical environment of the diastereotopic protons are much greater, so that well resolved signals for H–C(6a) are observed, as well as for most of the other 2'-thienylpyridyl protons. It is also interesting that, as for the reaction with benzal bromide, the one diastereomer is in a large excess over the other (∼2:1), Figure 4, lower spectrum. This *trans* ⇒ *cis* isomerization is also observed in the ^{195}Pt NMR spectra of these isomers, Figure 4. In the *trans* isomer a single peak is observed, which splits into two peaks after heating, due to the different chemical environments of the Pt atoms in these two diastereomers. The integration of the two peaks in the ^{195}Pt spectrum agrees with that of the ^{1}H spectrum and shows that the one diastereomer is in excess.

^{195}Pt NMR Spectroscopy. The values of the ^{195}Pt chemical shifts for five of the Pt(IV) cyclometalated complexes are given in Table V. The δ value for **1** and for some other related homoleptic, cyclometalated Pt(II) complexes[1b] are also given here. The platinum chemical shifts are sensitive to geometry, and the chemical shifts for *cis* and *trans* isomers differ by several hundred ppm. The differences in ppm values for the Pt(N ∧ C)$_2$ complexes are insignificant, since they cover only a small part of the chemical shift range of platinum compounds, which spread over 13 000 ppm.[26] Therefore, the negligible differences of the measured resonances exclude a different geometry for the Pt(II) complexes. The *cis* configuration was deduced from their ^{1}H NMR spectra, and the crystal structure of Pt(phpy)$_2$[1a] confirmed this assignment.

On oxidative addition of R–X to **1** (δ = 715.4 ppm) there is a shift of ∼1600 ppm to low field. It is common for the platinum nucleus to be deshielded on oxidation, and so the observed shift on oxidative addition of R–X to **1** is in keeping with the usual trend.

Both the Pt(II) and Pt(IV) cyclometalated complexes have broad signals with Δ$\nu_{1/2}$ varying from 77 to ∼250 Hz. It is not unusual for Pt complexes containing ligating atoms with electric quadrupole moments, such as ^{14}N, to have Δ$\nu_{1/2}$ values of several hundred hertz.[26] The Δ$\nu_{1/2}$ values for the Pt(IV) complexes are more than twice that of **1**. This is probably due to the presence of the halide atom, which also has a quadrupolar moment, in the octahedral coordination sphere of the Pt(IV) complexes. The signal for Pt(2'-thpy)$_2$(PhCH$_2$)Br (**8**), lies ∼105 ppm upfield from the signal for Pt(2'-thpy)$_2$(PhCH$_2$)Cl (**7**). This is an example of the "heavy-atom effect", where it is usually found that as one moves down a group, there is often (but not always) a shielding of the platinum nucleus. Another example of this is observed for the complexes *trans*-[PtClX(SMe^2)$_2$], X = Cl, Br, and I, where the δ(^{195}Pt) values are 1178, 936, and –1371, respectively.[27] There is a small downfield shift of ∼20 ppm on exchanging the benzyl group by anthracyl, on going from **7** to **14**. This may be due more to the greater size of the anthracyl group as compared to the benzyl, rather than due to a change in the aromaticity of the alkyl ligand. It has been noticed that in a number of series of Pt(II) complexes, as the ligand becomes larger, there is a downfield shift of the platinum signal;[26] e.g., the shift for *trans*-PtCl^2-(NHMe$_2$)(C$_2$H$_4$) = 1428 ppm and that for *trans*-PtCl$_2$-(NHMe^{i}Pr)(C$_2$H$_4$) = 1472 ppm. For the series of complexes [Pt(p-XC$_6$H$_4$)$_2$(COD)], there does not seem to be a pronounced aromatic resonance effect on δ(^{195}Pt). The change in metal chemical shift as a function of the para substituent, X, is <20 ppm for the above series.[28]

The ^{195}Pt signals for the *trans* and *cis* addition products of CF$_3$CHBrCl to **1** reflect, first, the sensitivity of the δ(^{195}Pt) values to isomerization and, second, to diastereomerism. On *trans* ⇒ *cis* isomerization there is an upfield shift of ∼125 ppm. In the *cis*-isomer two well-resolved signals are observed, with a difference

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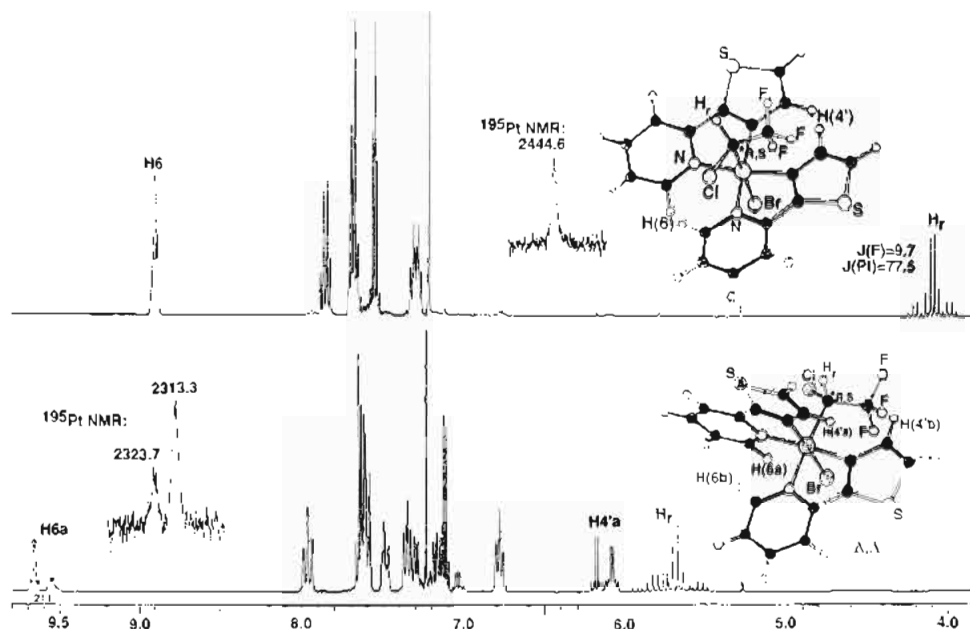
Figure 4. ¹H and ¹⁹⁵Pt NMR spectra of the product from the *trans* addition of CF₃CHBrCl to **1** (upper spectrum, **20a**) and the isomer with R/Br *cis* (lower spectrum, **20b**) after heating **20a** at 60 °C in CDCl₃ for 3 h.

Table V. ¹⁹⁵Pt NMR Chemical Shifts for the Pt(IV) Complexes **7**, **8**, **14**, **20a**, **20b**, and Related Pt(II) Complexes[a]

complex	δ(¹⁹⁵Pt) (ppm)[b]	line width at half-height, $\Delta\nu_{1/2}$ (Hz)
Pt(II)		
Pt(2'-thpy)₂ (**1**)	715.4	115[1b]
Pt(Phpy)₂[c]	721	77[1b]
Pt(Phpz)₂[c]	729.3	
Pt(IV)		
Pt(2'-thpy)₂(PhCH₂)Cl (**7**)	2309.6	243
Pt(2'-thpy)₂(PhCH₂)Br (**8**)	2205.0	248
Pt(2'-thpy)₂(9-Me-anthr)Cl (**14**)	2330.9	256
Pt(2'-thpy)₂(CF₃CHCl)Br (**20a**), trans addition	2444.6	188
Pt(2'-thpy)₂(CF₃CHCl)Br (**20b**), cis isomer	2323.7, 2313.3	194, 255

[a] Solvent is CHCl₃. Ξ(¹⁹⁵Pt) = 21.4 MHz. [b] All shift values are given relative to PtCl₆²⁻ (4522 ppm). For the measurements K₂PtCl₄(aq) (2888 ppm) and K₂Pt(CN)₆(aq) (667 ppm) were used as external references for the Pt(IV) and Pt(II) complexes, respectively. [b] Phpy– = phenylpyridine; Phpz– = phenylpyrazole.

of 10 ppm between them, corresponding to the two pairs of enantiomers present in solution on isomerization, i.e. Δ,*R*/Λ,*S* and Δ,*S*/Λ,*R* (see Figure 4). Kostic et al.[29] report resolved signals of 6–35 ppm for a series of diastereomeric Pt(II) thioether complexes.

X-ray Crystal Structures. Table VI contains some selected bond lengths and bond angles for the structures **8**, **12**, and **20a**. The structures of **8** and **12** reveal a distorted octahedral coordination sphere for the Pt(IV) center. The C,C,C-*fac* isomer, with R/X lying *cis* to each other, is indeed found to be the case, as was deduced from their ¹H NMR spectra. Two independent molecules were found in the unit cell of structure **8**. A perspective view of these molecules is shown in Figure 5. Inspection of these two molecules shows that there are no major differences between them. The bond lengths and bond angles are very similar, but there is a difference in the position of the phenyl group. In molecule A the phenyl group lies over the pyridine moiety of the 2'-thpy– ligand, while in molecule B there has been a rotation around the Pt–CH₂ bond, so that the phenyl group is now lying

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Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for **8**, **12**, and **20a**

	structure		
	8 (molecules A and B)	**12**	**20a**
Bond Lengths			
Pt–N(1a)	2.152(4), 2.153(4)	2.150(10)	2.162(10)
Pt–N(1b)	2.160(4), 2.173(4)	2.159(16)	2.240(9)
Pt–C(5'a)	2.003(5), 1.999(5)	2.053(12)	2.030(11)
Pt–C(5'b)	1.992(5), 2.009(5)	1.994(13)	2.005(10)
Pt–CH₂–	2.114(5), 2.114(5)	2.128(13)	2.085(11)
Pt–Br	2.5619(7), 2.5637(7)	2.5300(16)	2.5274(12)
C(2a)–C(2'a)	1.443(8), 1.438(8)	1.444(20)	1.398(18)
C(2b)–C(2'b)	1.446(8), 1.452(8)	1.417(19)	1.433(16)
Bond Angles			
C(2'a)–Pt–N(1a)	80.16(19), 79.86(19)	79.3(5)	78.9(4)
C(3'b)–Pt–N(1b)	79.59(20), 80.14(20)	79.7(5)	79.0(4)

between the pyridine and thienyl groups i.e over the C(2'a)–C(2a) bond. It appears that packing considerations may play a more important role. As can be seen from Figure 5, there is a favorable packing arrangement, with the thienyl moiety of a 2'-thpy– ligand on molecule B "sandwiched" between the phenyl group of the same molecule and a pyridine moiety on molecule A. Although these stacked π rings are not parallel, the S(1'a) to phenyl distance is 3.49 Å and the S(1'a) to pyridine (molecule A) distance is 3.51 Å. The phenyl group in **8** has been replaced by a naphthyl group in **12**, and although both structures crystallize in the same space group, i.e. P1̄, there is only one independent molecule per unit cell in **12**. The naphthyl group is centered over the pyridine ligand, and there is no disorder of this naphthyl ligand. Structure **20a** shows the *trans* addition of CF₃CHBrCl to **1**; see Figure 6. As can be seen from this figure, mutual steric interaction between the pairs of hydrogen atoms H–C(6a)/H–C(6b) and H–C(4')/H–C(4'b) causes an antitwist distortion of the thienylpyridine ligands from a planar arrangement. The dihedral angle between the 2'-thpy– ligands in **20a** is 8.7(3)°.

The Pt–N and Pt–C bond lengths in these Pt(IV) cyclometalated complexes agree very closely, within experimental error, with those in related Pt(II)cyclometalated complexes. For instance, the Pt–N and Pt–C bond lengths in Pt(phpy)₂[1a] are 2.129, 2.127 Å and 1.989, 1.988 Å, respectively. This agrees with the very similar radii of Platinum(II) (square-planar) and
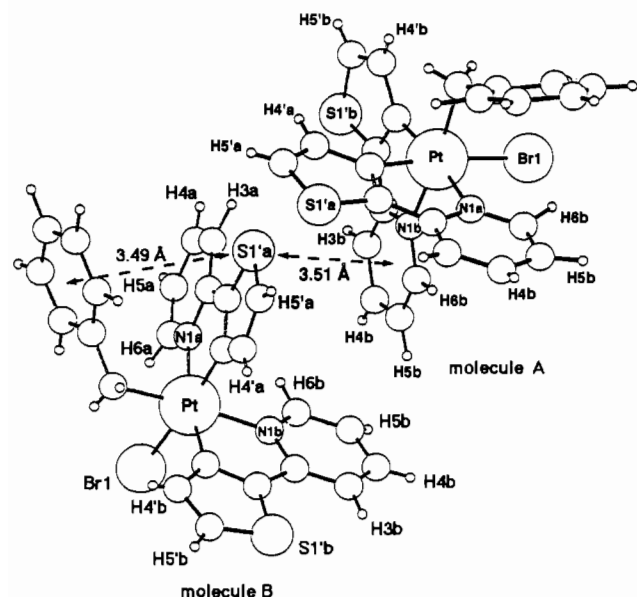
Figure 5. Perspective view of the two independent molecules in the crystal structure of **8**.
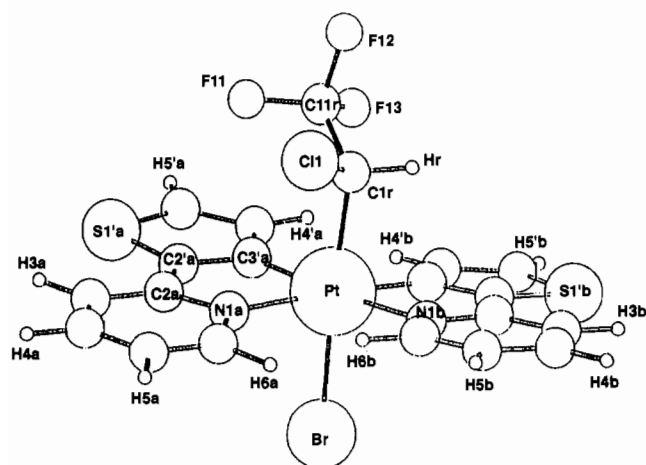

Figure 6. Perspective view of the structure of **20a**, from the *trans* addition of CF₃CHBrCl to **1**.

platinum(IV) (octahedral).[30,31] Structure **20a** has an unusually long Pt–N bond length of 2.240 Å, i.e. ~0.08 Å longer than the other Pt–N bond in the same molecule, as well as the Pt–N bonds in **8** and **12**. The complex from *trans* addition of CF₃CHClBr is shown not to be the most thermodynamically stable one, since this complex rearranges to the isomer with R/Br *cis* on heating. We believe that the driving force for this *trans* ⟹ *cis* isomerization is due to the steric interaction between the "coplanar" 2-thpy⁻ ligands in the *trans* isomer, which gives rise to the longer than usual Pt–N distance in **20a**. Further evidence for the breaking of a bond to Pt during the isomerization comes from the observation that for the reaction between **1** and CH₃CHBrCl, the *trans* isomer is not observed, and only the isomer with R/Br *cis* is found after reaction. A similar situation is found for the reactions with C₆F₅CH₂Br and C₆H₅CH₂Br, where the isomer with R/Br *trans* is seen to isomerize very slowly for the fluorinated alkyl halide, but is fast (~30 min) for the latter. It may be that since the alkyl group attached to Pt(IV) is a stronger electron withdrawer when it is fluorinated, as opposed to when the fluorines have been replaced by hydrogens, the Pt(IV) metal center is more electron deficient, which would result in stronger σ bonds to Pt(IV). If the isomerization involves the breaking of a bond to

platinum, then a slower isomerization is expected for the *trans* isomers with fluorinated alkyl groups attached, which agrees with our observations.

The Pt–C bond lengths in both these Pt(II) and Pt(IV) cyclometalated complexes are relatively short, if compared to other Pt–carbon compounds, which tend to have Pt–C bond distances in the order of 2.05[32,33]–2.18 Å.[34] Short Pt–C distances have, however, been observed in a complex with a platinum–chloride bond *trans* to the carbon ligand: Pt–C = 1.94 Å.[35] For the structure of the Pt(II) complex Pt(2′-thpy)(H-2′-thpy)I, which has one chelating N∧C 2′-thpy⁻ ligand and a monodentate, N-coordinating ligand, the Pt–C bond, which is *trans* to iodide, is reported to be 1.97(2) Å.[36]

The ligand C–C bond distances (1.40–1.45 Å) connecting the pyridine to the thienyl ring, i.e. C(2′)–C(2a) and C(2′)–C(2b), lie between a C–C single bond (1.54 Å) and an aromatic bond (1.39 Å), indicating a significant amount of conjugation between the two aromatic rings of the ligand. The same is observed in coordinated bpy.[37,38]

The bite angle of the N∧C ligands (N(1a)–Pt–C(3′a) and N(1b)–Pt–C(3′b)) varies from 78.9(4)° in **20a** to 80.16(19)° in **8**. This agrees well with the angle of 80.4(5)° reported for Pt(2′-thpy)(H-2′-thpy)I and also with the bond angles for bipyridyl complexes, which have been reported to vary from 72 to 80°.[39]

C. Mechanism of Oxidative Addition. TOA reaction. From the preparative scale thermal reactions of **1** with the alkyl halides listed in Table I, a number of observations can be made: (i) A single Pt(IV) product is formed for the reaction in aerated solution with some alkyl halides (TOA in Table I). (ii) The thermal reaction with some other alkyl halides produced a mixture of products in aerated solution but gave a single Pt(IV) product in degassed solution (TOA* in Table I). This suggests that the mechanism of these oxidative addition reactions is dependent on the alkyl halide. Three mechanisms have been identified for the oxidative addition of alkyl halides to metal complexes:[40–43] (i) an S_N2-type reaction, with the metal center acting as a nucleophile; (ii) a free radical cage recombination; (iii) a free radical chain reaction. The mechanistic details for the reaction of **1** with a few of the alkyl halides in Table I were investigated. The thermal reaction of **1** with benzyl bromide was studied in some detail. The second order rate constants were determined for the reaction of **1** with this alkyl bromide in three solvents of different polarity, i.e. in acetonitrile, acetone, and ethyl acetate. Since the Pt(IV) product has no MLCT band in the visible region of the UV/vis spectrum, the kinetics of the reaction could be followed conveniently by monitoring the decay of the MLCT band due to **1** by UV/vis spectrophotometry. The changes in the spectrum during a typical run showed clean isosbestic points, indicating that a single Pt(IV) product is formed (confirmed by TLC and ¹H NMR), via a single reaction pathway. The concentration of alkyl halide was kept in excess to ensure pseudo-first order kinetics.

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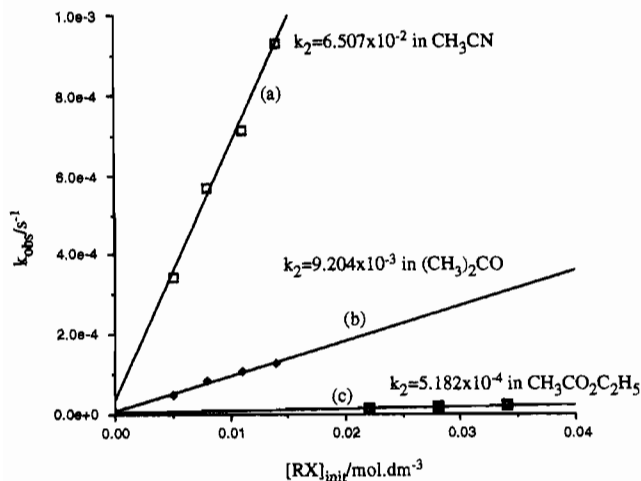
Figure 7. Graph of [R–X]$_{init}$ vs k_{obs} for the reaction of benzyl bromide with **1** in acetonitrile (a), acetone (b), and ethyl acetate (c).

Graphs of $\ln(A_t - A_\infty)$ vs time gave good straight lines indicating a first order dependence of the rate on the concentration of **1**, and the pseudo-first order rate constants obtained were proportional to the initial concentration of alkyl bromide for a given solvent, as shown in Figure 7. Thus the reactions are first order in both platinum complex and alkyl bromide. The resulting second-order rate constants for the reaction in the three solvents, at 298 K, are given in Figure 7. It is seen from these results that as the solvent polarity increases, the rate of reaction with benzyl bromide increases by a factor of $\sim$18 on going from ethyl acetate to acetone and by a factor of $\sim$7 on going from acetone to acetonitrile. The increasing value of k_2 with increasing solvent polarity suggests a polar transition state for the reaction, i.e. an S_N2-type mechanism, is being followed. The reaction with benzyl bromide was also monitored in an acetonitrile solution containing 5% (with respect to [Pt^{II}]) duroquinone. If free radicals are involved in the reaction, then duroquinone acts as an effective scavenger of these free radicals[40] and so should have an appreciable influence on the rate of the reaction. However, the presence of duroquinone was found to have little influence on the value of k_{obs}. This is further evidence that free radicals are not implicated in the reaction mechanism for this alkyl halide. Puddephatt and Jawad[3] have studied the rates of oxidative addition of methyl iodide to the complexes [PtR₂(bpy)], where R = Me, Ph, and 4-XC₆H₄ (X = F, Cl, Me, OMe). For the complexes where R is an electron-releasing group, there is destabilization of the d orbitals on platinum, and so the MLCT band moves to lower energy. They found a correlation between the energy of the MLCT transition in the UV/vis spectra of these complexes and their reactivity toward the oxidative addition of methyl iodide. Therefore as the electron density on the metal increases, so does its reactivity, which suggests that the oxidative addition in these complexes is primarily dependent on the energy of the filled d orbitals on platinum in the Pt(II) complexes. It is therefore not surprising that **1** shows a high reactivity toward the oxidative addition of electrophiles, since the two coordinated 2'-thpy⁻ ligands are good σ-donors and thus make the Pt(II) a strong nucleophile. **1** is also easily oxidized electrochemically (E_p = 0.33V vs SCE), which is also evidence for filled d-orbitals lying high in energy.

The study of other organometallic Pt(II) complexes, such as the cyclometalated complex [PtBr(NCN)], where NCN is the terdentate, monoanionic ligand (2,6-{Me₂NCH₂}₂C₆H₃),[44] shows that it is the d$_{xz}$ and d$_{z^2}$ orbitals that lie highest in energy.[45] One can then envisage the electron pair in the d$_{z^2}$ orbital on Pt(II),

in **1**, attacking the sp³ carbon atom of benzyl bromide, with the formation of a Pt–C bond and the concomitant breaking of the C–bromide bond, via a polar transition state, which eventually leads to the five-coordinate cationic intermediate, [Pt(2'-thpy)₂R]⁺Br⁻. Rapid formation of the Pt–Br bond, *trans* to the Pt-alkyl bond, results in the formation of the observed Pt(IV) product. This is the same mechanism as that proposed by Puddephatt and Crespo[46] for the reaction between [PtMe₂(bpy)] and MeI or benzyl bromide. Using low-temperature ¹H NMR, at –40 °C in CD₃CN they were able to identify the intermediate [Pt^{IV}Me₂(CD₃CN)(bpy)R]⁺X⁻, where R = C₆H₅CH₂– or CH₃– and X = Br⁻ or I⁻, respectively. Therefore, the reaction between **1** and benzyl bromide was studied at –40 °C in CD₃CN, using ¹H NMR, to see if the [Pt^{IV}(2'-thpy)₂(CD₃CN)(Ph-CH₂)]⁺Br⁻ intermediate could be detected. However, the system does not react at this temperature, but a slow reaction does occur on warming to –20 °C. Only the product from *trans* addition of R–Br is observed at this temperature. Of course, this does not exclude the possibility for the formation of the cationic intermediate, and the fact that it was not observed is probably due to a very rapid substitution of CD₃CN by Br⁻, at this temperature, to form the observed product.

It is likely that the other alkyl halides in Table I, which reacted thermally with **1** to give a clean, single Pt(IV) product in aerated solution, also follow a reaction pathway which is S_N2 in nature. The rate of these reactions appeared to be similar, under the same conditions, as for the reaction with benzyl bromide (k_2 = 5.926 × 10⁻² at 298 K in CH₃CN for the reaction with bromodiphenylmethane), and there was never any evidence for the incorporation of oxygen into the Pt(IV) products.

On the other hand, when the thermal reaction was performed with 1-(bromomethyl)naphthalene, under the same conditions used for the mechanistic study with benzyl bromide, i.e. in aerated CH₃CN and the same concentration of R–Br and **1**, the rate of reaction was too fast for it to be measured using conventional UV/vis spectrophotometry. When the thermal reactions with 1- and 2-(bromomethyl)naphthalene, 9-(chloromethyl)anthracene, and benzal bromide were done on a preparative scale in aerated solution, in the dark, ¹H NMR showed a mixture of products, sometimes containing only small amounts of the desired Pt(IV) product. However, in degassed acetonitrile solutions these thermal reactions were much cleaner, and pure Pt(2'-thpy)₂(R)X products could be isolated. These results suggest that a different mechanism is operating for the reactions with the above four alkyl halides and that it is most likely free radical in nature. Some preliminary spin-trapping experiments, using ‘BuNO as spin-trap, support the view that free radicals are involved in these reactions. However, nothing can be said at the moment whether the thermal reactions with these four substrates follows a free radical chain or cage mechanism.

POA Reaction. The excited-state mechanism of the POA reaction between **1** and CH₂Cl₂ or CHCl₃ has already been studied in detail by Balzani et al.[16]

Supplementary Material Available: Full tables of ¹H NMR data for all the Pt(IV) complexes and tables of crystallographic data, atomic coordinates (Tables VII–IX), isotropic thermal parameters, and anisotropic thermal parameters for complexes **8, 12,** and **20a** (8 pages). Ordering information is given on any current masthead page.

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