# A Dissociative Route to C–H Bond Activation: Ligand Cyclometalation in *cis*-Dimethyl[(sulfinyl-κ*S*)bis[methane]][tris(2-methylphenyl)-phosphine]platinum(2+)

by **Raffaello Romeo***[a]), **Maria Rosaria Plutino**[b]), and **Andrea Romeo**[a])

[a]) Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica – Università di Messina, Salita Sperone, 31 – Vill. S. Agata, I-98166 Messina (fax: +39-090-393756; e-mail: raf.romeo@chem.unime.it)
[b]) Istituto Materiali Nanostrutturati, ISMN – CNR, Sezione di Palermo, Unità di Messina, Salita Sperone, 31 – Vill. S. Agata, I-98166 Messina

Dedicated to Prof. *André E. Merbach* in recognition of his prominent contribution to the advancement of inorganic and organometallic reaction mechanisms

The dialkyl compound *cis*-dimethyl[(sulfinyl-κ*S*)bis[methane]][tris(2-methylphenyl)phosphine]platinum(2+) (*cis*-[Pt(Me)$_2$(dmso)(P(*o*-tol)$_3$]; **1**) has been isolated from the reaction of *cis*-dimethylbis[(sulfinyl-κ*S*)bis[methane]]platinum(2+) (*cis*-[Pt(Me)$_2$(dmso)$_2$]) with tris(2-methylphenyl)phosphane (P(*o*-tol)$_3$). Restricted rotation around the P–C$_{ipso}$ bonds of the phosphane ligand generates two different conformers, **1a** and **1b**, in rapid exchange in non-polar solvents at low temperature. Strong through-space contacts between the *ortho*-Me substituent groups on the ligand and the *cis*-Me groups in the coordination plane were determined, which proved useful for identifying the atropisomers formed. At room temperature, $^1$H-NMR spectra of **1** maintain a 'static' pattern upon onset of easy and rapid *ortho*-platination, leading to [[2-[bis(2-methylphenyl)-phosphino-κ*P*]phenyl]methyl-κ*C*]methyl[(sulfinyl-κ*S*)bis[methane]]platinum(2+) (**2**), a new C,P-cyclometalated compound of platinum(II), with liberation of methane. The process has been studied by $^1$H- and $^{31}$P{$^1$H}-NMR in $CDCl_3$, and kinetics experiments were performed by conventional spectrophotometric techniques. The first-order rate constants $k_c$ decrease with the addition of dimethyl sulfoxide until the process is blocked by the presence of a sufficient excess of sulfoxide. This behavior reveals a mechanism initiated by ligand dissociation and formation of a three-coordinate species. The value of the rate constant for dimethyl sulfoxide dissociation $k_1$ has been measured independently over a wide temperature range by both $^1$H-NMR ligand exchange (isotopic labeling experiments) and ligand substitution (stopped-flow pyridine for dimethyl sulfoxide substitution). The rates of the two processes are in reasonable agreement at the same temperature, and a single *Eyring* plot can be constructed with the two sets of kinetics data. However, the value of the derived dissociation constant at 308 K ($k_1 = 6.5 \pm 0.3\ s^{-1}$) is at least two orders of magnitude higher than that of cyclometalation ($k_c = 0.0098 \pm 0.0009\ s^{-1}$ at 308 K). Clearly, the dissociation step is not rate-determining for cyclometalation. A multistep mechanism consistent with mass-law retardation is derived, which involves a pre-equilibrium that controls the concentration of an unsaturated three-coordinate, 14-electron T-shaped *cis*-[PtMe$_2${P(*o*-tol)$_3$}] intermediate. Cyclometalation is initiated in this latter by an agostic interaction with the σ(C–H) orbital of a methyl group. Oxidative addition of the C–H bond follows, yielding a cyclometalated-hydrido 16-electron Pt(IV) five-coordinate intermediate. Finally, reductive elimination and re-entry of dimethyl sulfoxide with liberation of methane should yield the cyclometalated species **2**.

**Introduction.** – Cycloplatinated compounds have been extensively studied [1] and are of interest for several reasons, including their attractive photochemical and photophysical properties [2], their potential use as molecular devices [3], and, more generally, for their potential utility in catalysis and organic synthesis [4]. Several examples can be found in platinum–phosphane chemistry [5]. Recently, we focused

our interest towards understanding whether there is a specific role for cyclometalation and for the in-plane disposition of single aryl ligands in determining the reactivity (through metal-to-ligand $\pi$-back-bonding) and/or the reaction mechanism in substitution reactions at $Pt^{II}$ complexes. A clear demonstration that this is not the case came from the comparison of the structural features and the reactivities of cycloplatinated compounds of the type [Pt(N–N–C)Cl] (N–N–C = anionic ligands derived from deprotonated 6-substituted-2,2′-bipyridines) [6] or [Pt(C–C)$(SR_2)_2$] (C–C = 2,2′-biphenyl dianion; R = Me and Et) [7] with those of corresponding substrates having the same set of donor atoms but less-constrained arrangements of ligands. We found also that complexes of the type *cis*-[Pt$(Me)_2$(dmso)$(PR_3)$] ($PR_3$ = isosteric tertiary phosphanes) [8] behave like complexes having a set of donor atoms *cis*-[Pt(C,C)(S,S)] (C = strong $\sigma$-donor carbanions; S = thioethers or sulfoxides) for which a dissociative mechanism for ligand exchange and substitution of the S-bonded ligand is well established [9][1]). The introduction of a $\sigma$-donor $PR_3$ in the set of ligand donor atoms neither produces a change of mechanism nor greatly affects the ease with which the dissociative activation takes place. During the synthetic work-up, we observed that the phosphane-containing compound *cis*-dimethyl[(sulfinyl-$\kappa S$)bis[methane]][tris(2-methylphenyl)phosphine]platinum(2+) (*cis*-[Pt$(Me)_2$(dmso)$(P(o\text{-tol})_3)$]; **1**) in non-polar solvents undergoes easy and rapid *ortho*-platination, leading to [{2-[bis(2-methylphenyl)phosphino-$\kappa P$]phenyl}methyl-$\kappa C$]methyl[(sulfinyl-$\kappa S$)bis[methane]]platinum(2+) (**2**) with liberation of methane. Therefore, we decided to perform a detailed kinetics study of this process to gain some insight into the role of ligand dissociation in the mechanism of intramolecular C–H bond activation.

**Results.** – *$^1$H-NMR Characterization*. The synthesis of compound **1** from *cis*-[Pt$(Me)_2$$(dmso)_2$], must be carried out with care at low temperature, avoiding local excess of the reagent P(*o*-tol)$_3$. The reaction product was isolated in high yield as a solid and was characterized by elemental analysis and $^1$H- and $^{31}$P{$^1$H}-NMR spectroscopy. The low-temperature $^1$H- and $^{31}$P-NMR spectra in $CDCl_3$ showed that the molecule exists in two differently populated conformations (**1a**/**1b** *ca.* 4:1), each of which display the following features: *i*) a $^{31}$P{$^1$H} *singlet* flanked by platinum satellites ($\delta$ 28.3, $^1J$(Pt,P) = 1824 Hz for **1a** and $\delta$ 27.1, $^1J$(Pt,P) = 1881 for **1b**), *ii*) a set of aromatic proton signals, *iii*) a set of three different *singlets* for the *ortho*-Me substituent groups of the triarylphosphane ligand ($\delta$ 2.84, 1.83, and 1.55 for **1a** and $\delta$ 3.00, 2.05, and 1.53 for **1b**), *iv*) two signals for the Me protons of the DMSO ligand ($\delta$ 2.94, $^3J$(Pt,H) = 13.9 and 2.20, $^3J$(Pt,H) = 13.1 for **1a**; $\delta$ 3.06, $^3J$(Pt,H) = 15.6 and 2.88, $^3J$(Pt,H) = 16.0 for **1b**), each showing that the two Me groups on the S-atom are diastereotopic[2]). These observations are entirely compatible with hindered rotation around the P–$C_{ipso}$ aryl bonds while M–P rotation remains rapid. This has been suggested before for P(*o*-tol)$_3$ and other bulky phosphanes in organometallic compounds [10]. When the temperature was increased, the sulfinyl Me signals underwent only minor broadening, and coupling

---

1) This reference should also be consulted for a discussion of three coordinate intermediates and previous work in the field.

2) Because the Me groups in this molecule are diastereotopic, they would not be expected to be equivalent under conditions where rotation about the Pt–S bond is fast.

with $^{195}$Pt was lost, but the signals did not become isochronous. Likewise, the expected collapse of the 2-methylphenyl subspectrum was not observed, and three distinct signals were still seen at room temperature for each rotamer. Thus, the two conformations maintain apparently stereochemically rigid structures in solution because of the high activation barrier for rotation around the P–$C_{ipso}$ bonds. Typically, restricted P–$C_{Ph}$ bond rotation has been observed at low temperature [10][5b], and only one case in which it was still evident at room temperature has been reported [5a]. A proper kinetics study of the fluxional behavior was not possible because **1** was easily converted to the cyclometalated compound **2**. Interestingly, the $^1$H- and $^{31}$P-NMR spectra of analogous *cis*-[$Pt(Me)_2$(dmso)($PR_3$)] complexes in which the phosphanes are unhindered were temperature independent, thus indicating that M–P, M–S, and P–C bond rotations remain rapid on the NMR time scale [8]. The $^1$H-NMR spectrum of **1** is completed by two sets of *multiplets* for the coordinated Me groups with values at $\delta$ 0.47, $^2J$(Pt,H) = 79.2 and 0.43, $^2J$(Pt,H) = 69.8 for **1a** and $\delta$ 0.30, $^2J$(Pt,H) = 69.8 and 0.22, $^2J$(Pt,H) = 78.4 for **1b**. The lowest value of $^2J$(Pt,H) belongs to the Me group *trans* to the strong $\sigma$-donor $PR_3$.

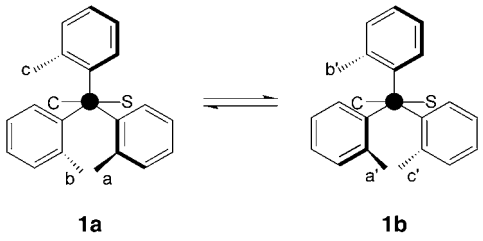
The proton resonances belonging to the species **1a** and **1b** were assigned through NMR spectroscopy from the connectivities in 2D-COSY and NOE cross-peaks in 2D-NOESY experiments. $Exo_2$ conformations[3]) for both rotamers **1a** and **1b** are fully confirmed by NOE cross-peaks between the *ortho*-Me substituents of the triarylphosphane and in the sulfoxide ligands and those coordinated to the metal, *e.g.*, Me–Pt *trans* to the S and P ligands (see *Supplemental Material*, *Table S1* for the relevant observed NOE dipolar contacts[4])). In compound **1a**, strong inter-ligand NOE cross-peaks are evident between $PPh_b$–Me and $PPh_c$–Me with Pt–Me (*trans* to the sulfinyl group), and between the C(6)–H of the $PPh_a$ fragment with $PPh_b$–Me, $PPh_c$–Me and with the sulfinyl Me groups. This experimental evidence is represented with the sketch on the left side of *Scheme 1*, in which the two *ortho*-Me substituents that lie above and below the coordination plane are directed toward the $Pt^{II}$ center (*i.e.*, $PPh_b$–Me and $PPh_c$–Me), while the third *ortho*-Me (*i.e.*, $PPh_a$) is rotated with the C(6)–H closer to the metal. As far as the rotamer **1b** is concerned, an $exo_2$ conformation is confirmed by selective cross-peaks between the Pt–Me *trans* to the phosphane ligand with $PPh_b$–Me, and the Pt–Me *trans* to the sulfoxide group with $PPh_c$–Me , $PPh_b$–Me, and the C(6)–H of $PPh_a$. This conformation is represented in *Scheme 1* (right side), where the positions of all three 2-methylphenyl groups are exchanged relative to the left side. The presence of an intramolecular ring exchange *via* correlated ring rotation for the triarylphosphine conformers **1a** and **1b**, together with mutual intermolecular exchange between the two rotamers **1a** and **1b** is confirmed by the multiplicity of very diagnostic exchange cross-peaks between all six *ortho*-Me substituents (**1a** $\delta$ 2.84, $PPh_c$–Me; 1.83, $PPh_b$–Me; 1.55, $PPh_a$–Me; **1b** $\delta$ 3.00, $PPh_{c'}$–Me; 2.05, $PPh_{b'}$–Me; 1.53, $PPh_{a'}$–Me) and the four Me signals relative to the DMSO group (**1a** $\delta$ 2.94, S–$Me_b$; 2.20, S–$Me_a$; **1b** $\delta$ 3.06, S–$Me_{b'}$; 2.88, S–$Me_{a'}$). As shown in *Fig. 1*, the Me

---

[3]) For a regular trigonal pyramid constructed with the metal center as apex and the three *para* ring C-atoms as the base, a proximal (exo) substituent points away from the base while a distal (endo) substituent points toward the base. The term $exo_2$ defines the number of proximal *ortho* Me groups.

[4]) To view *Supplemental Material*, please contact the corresponding author.

*Scheme 1*




**1a** **1b**

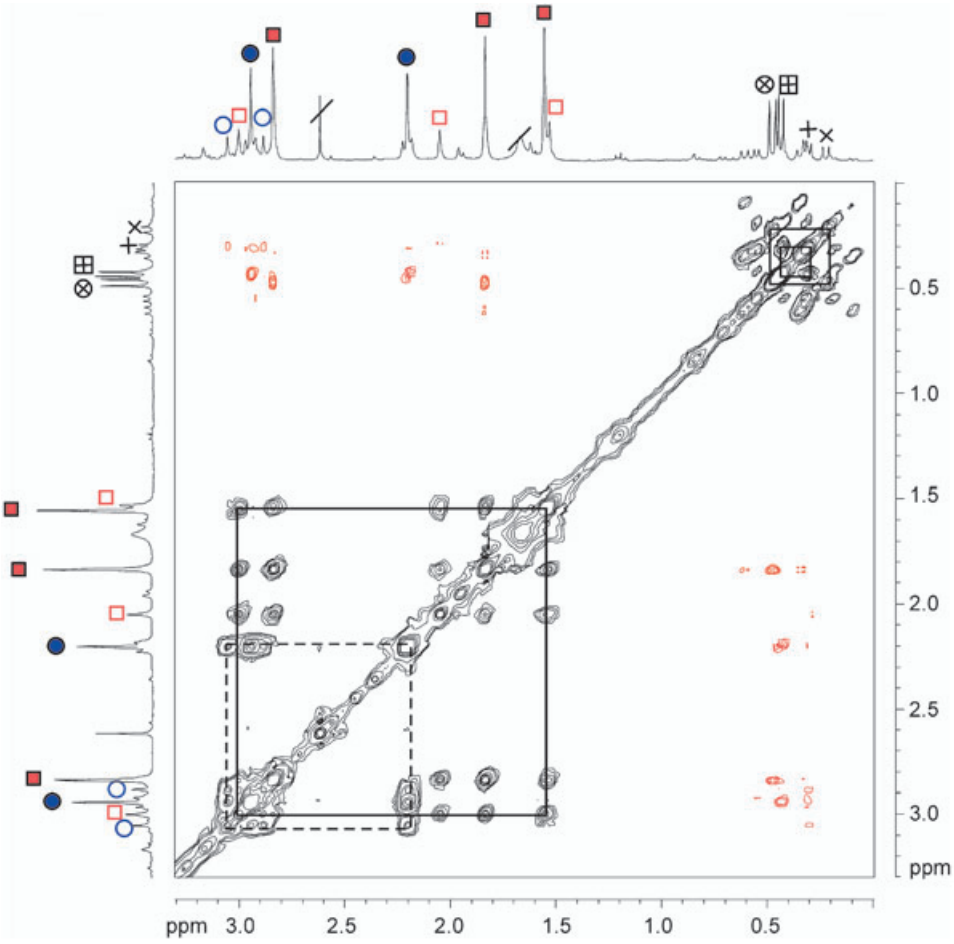



Fig. 1. *Aliphatic section of the phase-sensitive $^1$H-2D-NOESY spectrum of a $CDCl_3$ solution of the two rotamers* **1a** *and* **1b** *at 255.6 K*. The black cross-peaks arise from exchange, whereas the red cross-peaks arise from NOEs.

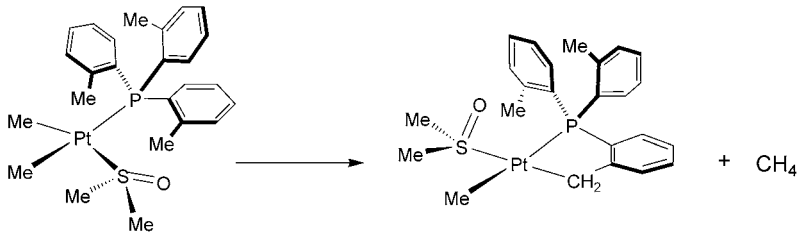
resonances are related to the others by five exchange cross-peaks for the *ortho*-Me substituents of the triarylphosphane ligands, three exchange cross-peaks for the Me groups bound to the sulfur, and a selective exchange cross-peak between the Me groups

directly bound to the $Pt^{II}$ center (**1a**, 0.47 *vs.* **1b**, 0.22 for Pt–Me *trans* to DMSO; **1a**, 0.43 *vs.* **1b**, 0.30 for Pt–Me *trans* to $PR_3$). This experimental evidence accounts for intramolecular ring rotation and for intermolecular exchange between the species **1a** and **1b**. The mechanisms of ring exchange in triarylphosphanes *via* correlated ring rotation have been extensively analyzed by *Mislow et al.* [11]. The most-likely mechanisms involve a three-ring flip in the $exo_2$ conformation, which exchanges the proximal 2-methylphenyl groups but retains the identity of the distal ring, and a two-ring flip mechanism in which ring exchange occurs *via* an $exo_3$ intermediate.

The reaction of **1** with pyridine was carried out *in situ* in an NMR tube. On exchanging pyridine for DMSO, the molecule loses the rigid structure of its precursor, and the $^1$H-NMR spectrum at room temperature shows a single resonance for all Me substituents of the 2-methylphenyl groups at $\delta$ 2.04.

*Cyclometalation Kinetics.* On standing at room temperature in $CHCl_3$, compound **1** yielded the cyclometalated **2** by *ortho* metalation with loss of $CH_4$ as shown in *Scheme 2*. Compound **2** was characterized by elemental analysis and $^1$H- and $^{31}$P-NMR spectra. The $^1$H-NMR spectrum at room temperature showed the expected pattern of signals for the H-atoms of the $CH_2$ group ($\delta$ 3.18, $^2J$(Pt,H) = 87.9), of the Me groups of the coordinated DMSO group ($\delta$ 2.89, $^3J$(Pt,H) = 14.4), and of the Me groups of the (2-methylphenyl)phosphane (at $\delta$ 2.59). These data indicate fast rotation on the NMR time-scale of the P–$C_{ipso}$ bond of the 2-methylphenyl rings. The resonance of the Me group bound to Pt appears as a *doublet* of *pseudotriplets* due to coupling with $^{195}$Pt (69 Hz) and with $^{31}$P (6.6 Hz). The low value of the coupling in the $^{31}$P-NMR spectrum ($^1J$(Pt,P) = 1920) gives unmistakable evidence that the P-atom is *trans* to the strong $\sigma$-donating Me group.

*Scheme 2*




The cyclometalation reaction shown in *Scheme 2* can be followed easily by $^1$H- or $^{31}$P-NMR in $CDCl_3$. There is no evidence for the accumulation of significant amounts of any other intermediate species, and only the starting complex **1**, the cyclometalated complex **2**, and methane are found in solution. The primary kinetics data were collected by monitoring the decrease of the $^1$H-NMR signals of the coordinated Me group and the concomitant increase of the methane signal. The reaction goes to completion in 30 min at 35°. The molar fraction $F$ of free $CH_4$ was obtained by integration of the signals monitored, and the time dependence of $F$ did not follow a simple exponential relationship as expected for a first-order process. Estimates of the initial rates showed $F$ to be also dependent, to some extent, on the concentration of the starting complex; $F$

decreased with increasing concentration of **1**. These deviations could be due to auto-dissociation of both **1** and **2** and were compensated by adding a sufficient excess of DMSO to ensure that its concentration was essentially constant throughout the reaction. Thus, a simple exponential relationship holds (see *Fig. S1*, *Supplemental Material*[4])).

Although the $^{1}$H- and $^{31}$P-NMR spectra provide a clear demonstration of the identities of the reagents and products as well as the absence of any detectable intermediate species, the method suffers from the disadvantage that relatively large concentrations of the complex must be used. The UV/VIS spectrophotometric technique requires far less of the complex, which can be examined at concentrations of less than $0.5 \times 10^{-4}$ M, allowing a sufficient excess of DMSO to ensure pseudo-first-order kinetics. Spectrophotometric kinetics experiments were carried out in $CHCl_3$ solutions in a two-chambered silica cell in the thermostatted cell compartment of the spectrophotometer and were monitored by repetitive scanning of the spectrum at suitable times. The reactions, carried out in the presence of sufficient excess DMSO, went to completion, the final spectra being identical to those of solutions of authentic samples of **2**. All reactions obeyed a first-order rate law until well over 90% conversion. Rate constants $k_{obs}$ ($s^{-1}$) were obtained from non-linear least-squares fits of the experimental data to $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}\, t)$ with $A_0$, $A_\infty$, and $k_{obs}$ as the parameters to be optimized ($A_0$ = absorbance after mixing of reagents, $A_\infty$ = absorbance at completion of reaction) [12]. The pseudo-first-order rate constants $k_{obs}$ for the reaction shown in *Scheme 2* for a range of DMSO concentrations are reported in *Table 1* and illustrated in *Fig.* 2, which also shows the dependence of $k_{obs}$ (and of the reciprocal of $k_{obs}$ (in the inset)) on the DMSO concentration. The variable-temperature rate constants were fit to the *Eyring* equation to give estimates of $\Delta H^{\ddagger} = 82 \pm 4$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -50 \pm 10$ J K$^{-1}$ mol$^{-1}$.

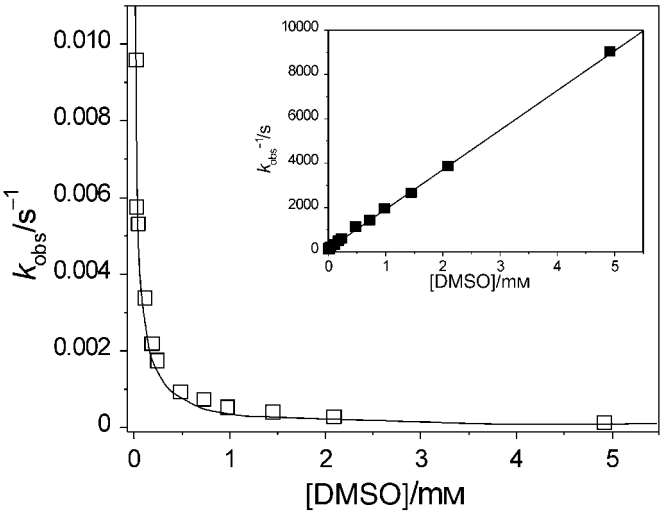



Fig. 2. *Plot showing the dependence of the observed pseudo-first-order rate constants* ($k_{obs}$/s$^{-1}$) *as a function of different amounts of free DMSO for the reaction in* Scheme 2. Reaction conditions: 0.05 mM **1**, $CHCl_3$, 308 K.

Table 1. *Concentration of DMSO and the Temperature Dependence for Rates of Cyclometalation of* **1**[a])

| $T$ [K] | DMSO Concentration [mM] | $10^4\ k_{obs}$ [$s^{-1}$] |
|---|---|---|
| 308 | 0.0246 | $95.7 \pm 0.3$ |
| 308 | 0.0320 | $57.4 \pm 0.2$ |
| 308 | 0.0490 | $52.9 \pm 0.1$ |
| 308 | 0.118 | $33.7 \pm 0.1$ |
| 308 | 0.192 | $21.9 \pm 0.1$ |
| 308 | 0.246 | $17.3 \pm 0.1$ |
| 308 | 0.493 | $9.06 \pm 0.02$ |
| 308 | 0.737 | $7.24 \pm 0.01$ |
| 308 | 0.985 | $5.20 \pm 0.01$ |
| 308 | 1.46 | $3.80 \pm 0.01$ |
| 308 | 2.10 | $2.61 \pm 0.01$ |
| 308 | 4.93 | $1.11 \pm 0.01$ |
| 298 | 1.55 | $1.00 \pm 0.01$ |
| 303 | 1.55 | $1.50 \pm 0.01$ |
| 308 | 1.55 | $2.70 \pm 0.01$ |
| 313 | 1.55 | $5.00 \pm 0.01$ |
| 318 | 1.55 | $7.90 \pm 0.01$ |

[a]) In $CHCl_3$ by spectrophotometry.

*Substitution Reactions.* Nucleophilic substitution reactions of **1** with pyridine in $CHCl_3$ to yield dimethyl(pyridine)[tris(2-methylphenyl)phosphine]platinum(2+) (**3**) were carried out over a range of temperatures and pyridine concentrations and required the use of the stopped-flow technique. Rate constants were evaluated by the *Applied Photophysics* software package [13] and are reported in *Table 2* as average values from five to seven independent experiments.

Table 2. *Concentration of Pyridine and Temperature Dependence of the Substitution Rates of* **1**[a])

| $T$ [K] | Pyridine concentration [mM] | $k_{obs}$ [$s^{-1}$] |
|---|---|---|
| 278.0 | 25 | $0.250 \pm 0.008$ |
| 283.0 | 25 | $0.368 \pm 0.006$ |
| 288.0 | 25 | $0.782 \pm 0.005$ |
| 288.2 | 25 | $0.945 \pm 0.004$ |
| 293.1 | 25 | $1.62 \pm 0.05$ |
| 296.6 | 5 | $1.66 \pm 0.05$ |
| 296.6 | 10 | $1.78 \pm 0.08$ |
| 296.6 | 25 | $1.72 \pm 0.07$ |
| 303.0 | 25 | $4.34 \pm 0.05$ |

[a]) In $CHCl_3$ by spectrophotometry.

*Isotope-Exchange Reactions.* The kinetics of ligand exchange between $(D_6)$DMSO and **1** were performed by adding known volumes of $(D_6)$DMSO with a microsyringe to a prethermostatted solution of precisely weighed **1** in $CDCl_3$. The excess of $(D_6)$DMSO over complex used in each experiment was at least fivefold. The isotope exchange was followed by monitoring the increase in intensity of the $^1$H-NMR signal of free

nondeuterated DMSO at $\delta$ 2.63 and the concomitant decrease of the signals of the Me groups on the S-atom coordinated to the metal (at $\delta$ 2.98 and 2.24), as shown in *Fig. 3*.

The spectra were recorded at appropriate time intervals. The mole fraction $F$ ($=[\mathrm{DMSO}]_f/([\mathrm{DMSO}]_f+[\mathrm{DMSO}]_b$) of free DMSO was obtained by integration of the signals and the first-order rate constants $k_{exch}$ ($s^{-1}$) for the exchange of the label were obtained from a non-linear least-squares fit of the experimental data to $F=c_1+c_2$ $\exp(-k_{exch}\,t)$, with $c_1$, $c_2$, and $k_{exch}$ as the parameters to be optimized [12]. A similar analysis can be performed on the mole fraction of bound DMSO. From the *McKay* equation, $R_{exch}=k_{exch}\,ab\,(a+b)^{-1}$ (where $R_{exch}$ is the rate of the exchange process; $a$ is the concentration of complex and $b$ is the concentration of free sulfoxide) the pseudo-first-order rate constants, $k_{obs}=R_{exch}/a$, were calculated and are reported in *Table 3*.

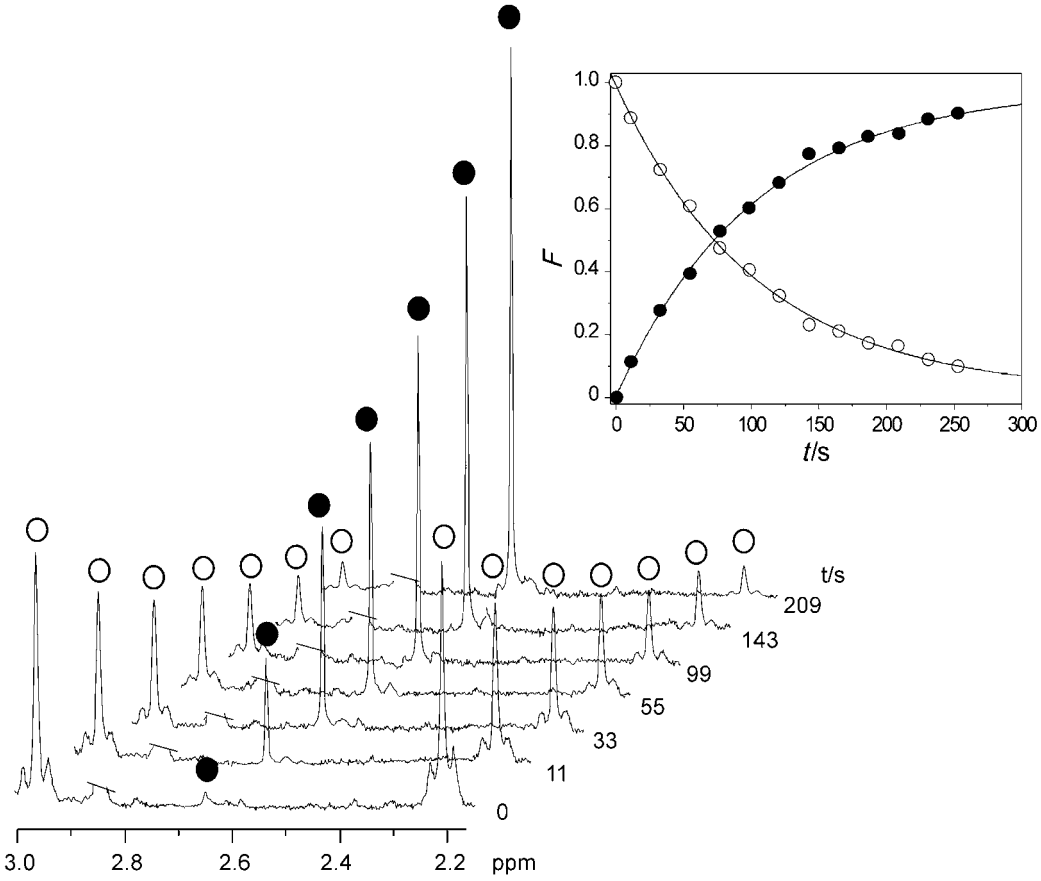



Fig. 3. *$^1$H-NMR Spectra* (300-MHz) *showing DMSO exchange for 2.37 m*m **1** *and 84.3 m*m *($D_6$)DMSO in $CDCl_3$ at 257.8 K as a function of time.* Coordinated DMSO (open circles, $\delta$ 2.94 ppm, $^3J$(Pt,H) = 13.9 Hz and 2.20 ppm, $^3J$(Pt,H) = 13.1); free DMSO (filled circles, $\delta$ 2.63 ppm). Inset: Exponential curves for the molar fractions of coordinated (open circles) and free DMSO (filled circles) as a function of time.

Table 3. *Concentration of ($D_6$)DMSO and the Temperature Dependence for Rates of DMSO Exchange on* **1**[a])

| $T$ [K] | ($D_6$)DMSO Concentration [m*m*] | $10^3$ $k_{obs}$ [$s^{-1}$] |
|---|---|---|
| 230.5 | 84.6 | $0.20 \pm 0.05$ |
| 233.5 | 162.5 | $0.27 \pm 0.01$ |
| 234.5 | 85.2 | $0.38 \pm 0.04$ |
| 241.8 | 85.0 | $0.74 \pm 0.02$ |
| 244.0 | 81.1 | $1.57 \pm 0.09$ |
| 246.9 | 84.6 | $1.5 \pm 0.2$ |
| 248.8 | 81.7 | $2.2 \pm 0.1$ |
| 253.1 | 85.2 | $5.4 \pm 0.4$ |
| 255.6 | 50.3 | $6.6 \pm 0.2$ |
| 255.6 | 81.8 | $6.4 \pm 0.3$ |
| 255.6 | 120 | $6.4 \pm 0.1$ |
| 255.6 | 180 | $6.3 \pm 0.2$ |
| 255.6 | 250 | $6.5 \pm 0.4$ |
| 257.8 | 84.3 | $8.8 \pm 0.6$ |
| 261.7 | 81.7 | $15.5 \pm 0.8$ |
| 263.8 | 84.2 | $22 \pm 1$ |
| 267.2 | 81.2 | $39 \pm 2$ |

[a]) At 2–5 m*m* in $CHCl_3$ by $^1$H-NMR isotope-exchange.

**Discussion.** – *Substitution Mechanism.* The rates of both reactions, *i.e.*, DMSO exchange and pyridine for DMSO substitution, on **1** are not affected by the concentration of the added ligand (pyridine or ($D_6$)DMSO; rate data in *Tables 2* and *3*). The temperature dependency of the substitution reactions (with pyridine) was determined at a higher temperature range than that of the isotopic labeling (($D_6$)DMSO). From the overall set of data, it was possible to construct a single *Eyring* plot, shown in *Fig. 4*, which encompasses the wide temperature range and indicates that DMSO exchange and pyridine substitution have identical values at the same temperature. Values for the activation parameters, $\Delta H^{\ddagger} = 81 \pm 2$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = 32 \pm 6$ J K$^{-1}$ mol$^{-1}$ were calculated by linear-regression analysis of this plot.

The experimental kinetics evidence points unequivocally to a dissociative mode of activation. The assessment of a dissociative mechanism can be made essentially on the basis of: *i*) the dissociation rate being independent of the nature and concentration of the entering group, *ii*) the rate of dissociation being identical to the rate of ligand exchange, and *iii*) the positive sign and magnitude of $\Delta S^{\ddagger}$. The solvent used was not sufficiently coordinating to actively contribute to associative processes. The pattern of behavior is strictly similar to that found in our previous study on *cis*-[$PtMe_2(PR_3)$-(dmso)] complexes [8] or on *cis*-[$PtMe_2$(dmso)$_2$] [14][15] and other dialkyl and diaryl systems [9][1]) [16], where the easy dissociation of thioethers or sulfoxides was shown to be the rate-determining step of the substitution. The same dissociative mechanism (*Scheme 3*) applies, involving *i*) dissociative loss of DMSO from the substrate ($k_1$ path) to yield a three-coordinate 14-electron T-shaped intermediate, *ii*) competition for the intermediate between re-entry of DMSO (*via* $k_{-1}$) and attack of another ligand (either ($D_6$)DMSO or pyridine *via* $k_2$) to yield the observed products. Application of the steady-state approximation to the three-coordinate intermediate gives the rate law in *Eqn. 1:*

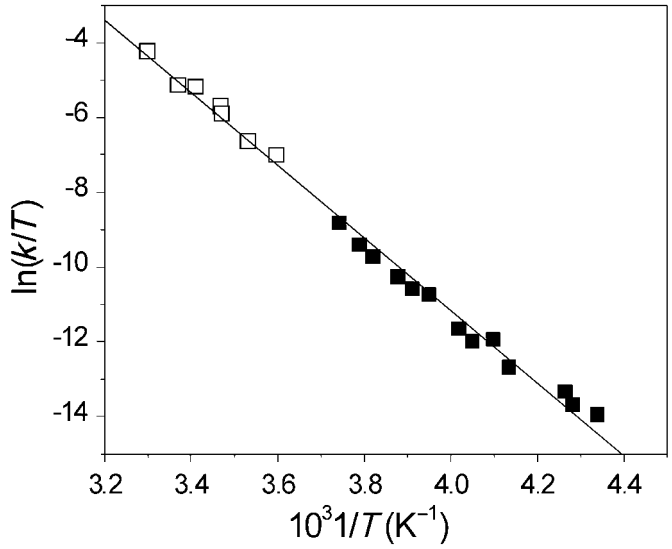
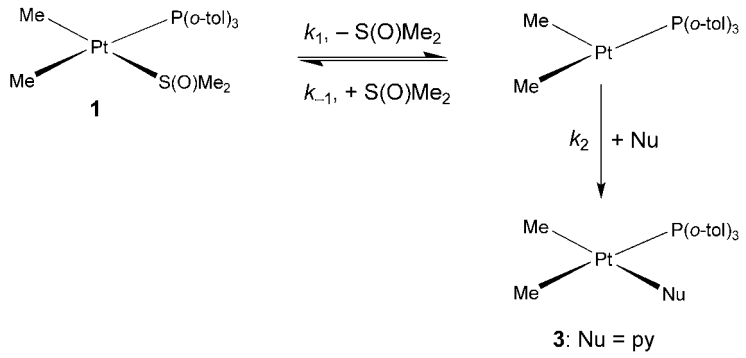



Fig. 4. Eyring *plot constructed with rate data from isotope-labeling experiments* (filled squares) *and pyridine/DMSO substitution reactions* (open squares) *on* **1**

*Scheme 3*




$$k_{obs} = k_1\, k_2[\mathrm{Nu}]/\{(k_{-1}[\mathrm{DMSO}] + k_2[\mathrm{Nu}]\} \quad (1)$$

The steady-state treatment requires that the two processes in competition for the intermediate, $k_{-1}$[DMSO] and $k_2$[Nu], have comparable values. For the limiting situation $k_2[\mathrm{Nu}] \gg k_{-1}[\mathrm{DMSO}]$, *Eqn. 1* reduces to $k_{obs} = k_1$. For **1** at 308 K, $k_1 = 6.5 \pm 0.3\ s^{-1}$; $\Delta H^{\ddagger} = 81 \pm 2$ kJ mol$^{-1}$, and $\Delta S^{\ddagger} = 32 \pm 6$ J K$^{-1}$ mol$^{-1}$, compared to $k_1 = 0.062\ s^{-1}$, $\Delta H^{\ddagger} = 90 \pm 2$ kJ mol$^{-1}$, and $\Delta S^{\ddagger} = 32 \pm 6$ J K$^{-1}$ mol$^{-1}$ for *cis*-[PtMe$_2$(dmso)(P(*p*-tol)$_3$)] [8]. As expected, steric congestion (the *Tolman*'s cone angle for P(*o*-tol)$_3$ is 178°) makes dissociation and removal of DMSO from **1** faster and easier than in a comparatively unhindered parent compound (the cone angle for P(*p*-tol)$_3$ is 145°). Strong $\sigma$-donation from the carbanions and from the coordinated phosphane confers

sufficient thermodynamic stability to the T-shaped intermediate formed from dissociation of **1**.

*Cyclometalation Mechanism*. The conversion of **1** to **2** shows a remarkable rate effect: the process is slowed by the addition of DMSO and halted in the presence of high concentrations of added ligand. The rate law ($CHCl_3$, 308 K) is of the type $k_{obs} = a/(b[DMSO]+1)$ and values of $a = 0.0098 \pm 0.0009\ s^{-1}$ and $b = (1.76 \pm 0.01) \times 10^4\ M^{-1}$ were derived from a non-linear least-squares analysis of the curve in *Fig. 2* or from a linear fit of the plot in the inset[5]). The value of *a* calculated (rate of cyclometalation at 308 K, in the absence of added DMSO) differs markedly and is very much smaller than that of $k_1 = 6.51 \pm 0.3\ s^{-1}$ at 308 K. As matter of fact, it must be concluded that dissociation of DMSO from **1** and formation of the three-coordinate 14-electron intermediate is a preliminary step but not the rate-determining step for cyclometalation, because the subsequent cyclometalation takes much longer to occur. In formulating a mechanism, it must be assumed that, even in the absence of added DMSO, the rates for the dissociation and reassociation steps in *Scheme 3* are much greater than the rate of C–H bond activation in the three-coordinate intermediate ($k_2 \ll k_1$ or $k_{-1}$). In other words, this means that a pre-equilibrium (defined by $k_1/k_{-1} = K_e$) is established, and the cyclometalation is controlled by two factors, namely *i*) the extension of the dissociation pre-equilibrium, which determines the concentration of the three coordinate intermediate and, *ii*) the subsequent C–H bond activation on this latter, $k_2$ assumed as the rate-determining step. A pre-equilibrium treatment to a reaction scheme similar to that in *Scheme 3*, where dissociation enables cyclometalation instead of nucleophilic attack leads to the rate law in *Eqn. 2:*

$$k_{obs} = k_2/(K_e^{-1}\,[DMSO]+1) \qquad (2)$$

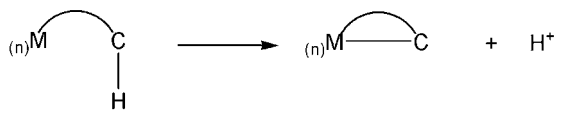
From this rate expression, it is possible to estimate a value for $k_2$, the rate constant for cyclometalation of the three-coordinate intermediate, which corresponds to $a = 0.0098 \pm 0.0009\ s^{-1}$ and for $K_e$, the equilibrium constant for dissociation, which corresponds to $b^{-1} = K_e = (5.7 \pm 0.1) \times 10^{-5}$ M. A much smaller value of $K_e = (4.3 \pm 0.8) \times 10^{-7}$ M was reported by *Espinet* and co-workers [17] for the equilibrium in $CDCl_3$ between the 16-electron species *cis*-[Pd(2-$C_6BrF_4$)$_2$(tht)$_2$] (tht = tetrahydrothiophene) and the 14-electron species obtained from ligand (tht) dissociation, a key intermediate for the subsequent overall atropisomerization process. On the basis of the value of $K_e$ derived by us is reliable, at the low concentrations of complex (*ca.* 0.05 mM) used for the spectrophotometric kinetics experiments, we would have expected extensive dissociation of the complex in solution, which does not seem to be the case.

Once we have provided convincing evidence that the 16-electron metal complex **1** is kinetically inert and prepare for subsequent intramolecular C–H activation by vacating a coordination site, we must address the problem of understanding the intimate mechanism of C–H bond cleavage by the central atom. An *Eyring* treatment of the kinetics data at various temperatures (obtained in the presence of an excess of added DMSO) affords the following activation parameters: $\Delta H^{\ddagger} = 81.5 \pm 4$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -48 \pm 10$ J K$^{-1}$ mol$^{-1}$. The interpretation of these values is not straightfor-

[5]) The reciprocal plot is preferred because dispersion of the $a^{-1}$ values is more regular than that of *a*.

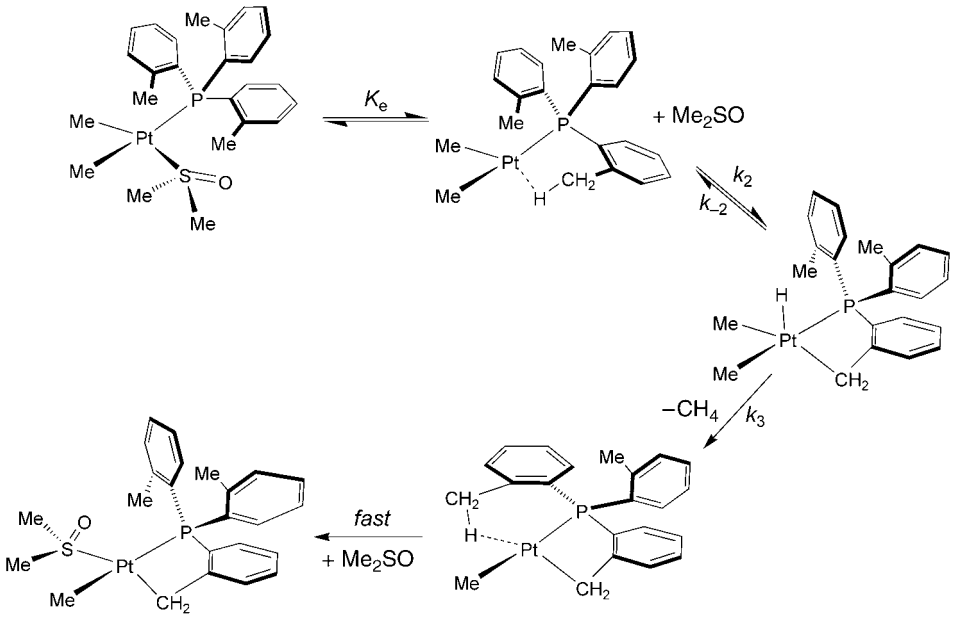
ward as for the kinetics of ligand dissociation, because they cannot be assigned to a single step, and cannot discriminate between the two most-conceivable reaction mechanisms, electrophilic attack and oxidative addition. The electrophilic-attack mechanism is a very common pathway for cyclopalladation and has been proposed occasionally also for $Pt^{II}$ chemistry [18]. It does not require formation of a metal hydride, the central atom does not change oxidation number, and the H-atom dissociates as a free or a bound proton (*Scheme 4*). However, there is a continuously growing wealth of evidence for the operation of an oxidative-addition mechanism not only in intramolecular but also in intermolecular processes of C–H bond activation by $Pt^{II}$ compounds. Hydridoplatinum(IV) intermediates have been proposed, although not detected directly, in the synthesis of cyclometalated complexes containing bidentate (C,N) or terdentate (C,N,N′) ligands [19]. Similar intramolecular C–H bond activation was proposed in the thermolysis of different platinum dialkyl complexes that lack $\beta$-H-atoms, leading to the formation of metallacycles along with the corresponding hydrocarbons [20]. Intermolecular C–H activation of alkanes and arenes is accomplished under mild conditions by complexes of the form $[Pt(N{-}N)(Me)(solv)]^+$, where N–N is a bidentate N-centered ligand and 'solv' is a weakly coordinating solvent, and involve coordinatively unsaturated $Pt^{II}$ species as intermediates and a stepwise process of oxidative addition/reductive elimination [21]. A useful synthetic route to $Pt^{IV}$ complexes $[PtX(H)R_2(N{-}N)]$ (X = halide, R = alkyl or aryl) is the addition of acid to $[PtR_2(N{-}N)]$ and the decomposition of these $Pt^{IV}$ species by reductive elimination of RH to yield [PtXR(N–N)] [22]. Hydrido(methyl)platinum(4+) complexes with triethylphosphane ligands have also been identified by low-temperature NMR techniques [21a][23].

*Scheme 4*




On the basis of the above, we are inclined to think that the most likely mechanism for the cyclometalation of **1** involves preliminary Pt–S bond dissociation, as depicted in *Scheme 5*. The coordinative and electronic unsaturation at the metal atom in the three-coordinate, 14-electron T-shaped **1** might be stabilized by an agostic interaction involving the empty $\sigma$ orbital on Pt and the electron pair of the C–H bond at one of the *ortho* sites. This hypothesis is strongly supported by the observation that bulky ligands favor the formation of agostic interactions between the metal and C–H bonds [24] and that cyclometalation is initiated by an agostic interaction with the $\sigma$(C–H) orbital followed by back-donation to the $\sigma^*$(CH) orbital [25]. Oxidative addition of the C–H bond follows this preliminary Pt–CH interaction, yielding a cyclometalated-hydrido 16-electron $Pt^{IV}$ five-coordinate intermediate. Several theoretical studies have indicated that these reaction intermediates should have square-pyramidal geometry [26], but, only recently, two papers appeared describing the isolation and structural characterization of such compounds [27]. Finally, reductive elimination and re-entry of DMSO should yield the cyclometalated species **2** with liberation of methane.

*Scheme 5*




Cyclometalation on **1** develops along the same key steps recognized for the dinuclear $Pt^{II}$ compound of formula $[Pt_2(\mu\text{-}SEt_2)_2(Hbph)_4]$ ($Hbph^- =$ biphenyl-4-yl monoanion) in forming $[Pt_2(\mu\text{-}SEt_2)_2(bph)_2]$, containing the planar biphenyl-2,2′-diyl ligand ($bph^{2-}$) [9][1]).

Considering the equilibrium dissociation constant $K_e = k_1/k_{-1}$, and applying the steady-state approximation to the cyclometalated-hydrido $Pt^{IV}$ five-coordinate intermediate, we obtain *Eqn. 3:*

$$k_{obs} = k_2\, k_3\, K_e/((k_{-2} + k_3)[DMSO] + (k_{-2} + k_3)\, K_e) \tag{3}$$

that is formally similar to *Eqn. 2* with $a = k_2k_3/(k_{-2} + k_3)$ and still $b = K_e^{-1}$ and also explains the retarding effect of the addition of DMSO. The two expressions become identical when one assumes that $k_3 \gg k_{-2}$. An appropriate measure of the extent to which dissociation proceeds deserves further investigations.

Summing up, although the cycloplatination process discussed follows indeed a dissociative pathway, the dissociation step is not rate determining. It influences the rate because a pre-equilibrium is established that controls the concentration of the unsaturated three-coordinate T-shaped intermediate. A multistep mechanism of oxidative addition/reductive elimination follows, and, at this stage, it is difficult to assess with confidence which of these two steps is rate limiting.

## Experimental Part

*General*. All syntheses were performed under a dry, $O_2$-free $N_2$ atmosphere by standard *Schlenk*-tube techniques, or in a glove box; however, the products could be worked up and handled in air. All solvents were analytical reagent grade (*Lab-Scan Ltd.*) and were used in the synthetic procedures after distillation under a $N_2$ atmosphere from appropriate drying agents: $Et_2O$ from sodium benzophenone ketyl; $CH_2Cl_2$ from BaO; DMSO from $CaH_2$, at low pressure after preliminary filtration through alumina. All solvents were stored in $N_2$-filled flasks over activated 4-Å molecular sieves. $CHCl_3$ for use in kinetics experiments by spectrophotometry was degassed by means of a series of 'freezing-pumping' cycles and eventually stored in *Schlenk* tubes. $CDCl_3$ (99.96 + %, *C. I. L. Inc.*) was dried by allowing it to stand many days over $CaH_2$, distilled under $N_2$ over activated $MgSO_4$ and $Na_2CO_3$, and then stored over activated 4-Å molecular sieves. $K_2PtCl_4$ (*Strem*) was purified by dissolving in $H_2O$ and filtering. *cis*-$[Pt(Me)_2(dmso)_2]$ was prepared according to a published method and was crystallized several times from $Et_2O$ [28]. All phosphane ligands used in these studies were purchased from *Strem* or *Aldrich*, and crystallized from EtOH. All the other reagents were of the highest commercial grade available and were used as received or were purified by distillation or recrystallization when necessary. UV/VIS: *Rapid-Scanning Hewlett-Packard 8452 A* diode-array spectrophotometer or *Applied Photophysics Bio Sequential SX-MX Stopped-Flow ASVD* spectrofluorometer. (temp. accuracy ± 0.05°). Rate constants were evaluated with the SCIENTIST software package. IR Spectra: *Perkin-Elmer 883* spectrophotometer; $\nu$ in $cm^{-1}$ (nujol mulls). $^1H$- and $^{31}P\{^1H\}$-NMR Spectra: *Bruker AMX-R-300;* $\delta$ in ppm referenced to TMS for $^1H$ and to $H_3PO_4$ for $^{31}P$; *J* in Hz. The probe temp. was checked by means of the MeOH or ethylene glycol method [29]. 2D-$^1H$-NMR Spectra: *Bruker AMX-R-300;* 2D-COSY experiments were performed with gradient selection in QF mode; phase-sensitive 2D-$^1H$-NOESY experiments were performed with a standard pulse sequence and a mixing time of 0.4 s (**1a**,**b**). Elemental analyses were performed at the Analytical Services Unit, Department of Chemistry, University College Dublin, Ireland.

*Preparation of Complexes.* cis-*Dimethyl[(sulfinyl-κS)bis[methane]][tris(2-methylphenyl)phosphine]platinum(2+)* (cis-*[$PtMe_2$(dmso){P(o-tol)$_3$}]*; **1a**,**b**). A cold soln. of tris(2-methylphenyl)phosphane ($P(o\text{-tol})_3$; 91.3 mg, 0.3 mmol) in $CH_2Cl_2$ (10 ml) was added very slowly dropwise and under continuous stirring to a $CH_2Cl_2$ soln. (30 ml) of *cis*-dimethylbis[(sulfinyl-κ*S*)bis[methane]]platinum(2+) (*cis*-$[PtMe_2(dmso)_2]$; 114.4 mg, 0.3 mmol) immersed in a ice bath. The mixture was kept for 1 h at 0° and then concentrated under vacuum with the temp. maintained at *ca.* 5° until the first white crystals of the product began to form. Addition of 1 vol. petroleum ether with cooling at −35° promoted complete precipitation of the solid. IR: 1108 $cm^{-1}$ (S=O). Anal. calc. for $C_{25}H_{33}OPPtS$: C 49.20, H 5.90, S 5.25; found: C 49.28, H 5.73, S 5.13.

*Data of* **1a**: $^1H$-NMR ($CDCl_3$, 255.6 K): 8.85 (*m*, $^3J$(P,H) = 17.2, $^3J$(H,H) = 6.7, $^4J$(H,H) = 2.5, C(6)−H of $Ph_a$); 7.34 (*m*, C(3)−H of $Ph_c$); 7.32 (*m*, C(5)−H of $Ph_a$); 7.24 (*m*, C(6)−H of $Ph_c$); 7.18 (*m*, C(6)−H of $Ph_b$); 7.14 (*m*, C(4)−H of $Ph_a$); 7.10 (*m*, C(5)−H of $Ph_b$); 7.09 (*m*, C(5)−H of $Ph_c$); 7.07 (*m*, C(3)−H, C(4)−H of $Ph_b$); 7.04 (*m*, C(3)−H, C(4)−H of $Ph_a$); 2.94 (*s*, $^3J$(Pt,H) = 13.9, $SMe_b$); 2.84 (*s*, $Ph_cMe$); 2.20 (*s*, $^3J$(Pt,H) = 13.1, $SMe_a$); 1.83 (*s*, $Ph_bMe$); 1.55 (*s*, $Ph_aMe$); 0.47 (*m*, $^3J$(P,H) = 8.8, $^2J$(Pt,H) = 79.2, PtMe *trans* to dmso); 0.43 (*m*, $^3J$(P,H) = 6.7, $^2J$(Pt,H) = 69.8, 3 H, PtMe *trans* to $PR_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 255.6 K): 28.3 ($^1J$(Pt,P) = 1824).

*Data of* **1b**: $^1H$-NMR ($CDCl_3$, 255.6 K): 8.70 (*m*, $^3J$(P,H) = 16.0, $^3J$(H,H) = 7.6, $^4J$(H,H) = 2.5, C(6)−H of $Ph_a$); 7.39–7.03 (*m*, 11 arom. H); 3.06 (*s*, $^3J$(Pt,H) = 15.6, $SMe_{b'}$); 3.00 (*s*, $Ph_cMe$); 2.88 (*s*, $^3J$(Pt,H) = 16.0, $SMe_{a'}$); 2.05 (*s*, $Ph_{b'}Me$); 1.53 (*s*, $Ph_{a'}Me$); 0.30 (*m*, $^3J$(P,H) = 6.7, $^2J$(Pt,H) = 69.8, PtMe *trans* to $PR_3$); 0.22 (*m*, $^3J$(P,H) = 8.4, $^2J$(Pt,H) = 78.4, PtMe *trans* to dmso). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 255.6 K): 27.1 ($^1J$(Pt,P) = 1881).

*[[2-[Bis(2-methylphenyl)phosphino-κP]phenyl]methyl-κC]methyl[(sulfinyl-κS)bis[methane]]platinum(2+)* (**2**). The procedure described above for the synthesis of the precursor **1** was repeated at r.t. Afterwards, the soln. was refluxed for 2 h until most of the solvent evaporated, and precipitation of a white solid was incipient, petroleum ether (1 vol.) was added to the soln., and the mixture was placed in the freezer (−30°) overnight. IR: 1102 (S=O). $^1H$-NMR ($CDCl_3$, 298.3 K): 7.4–6.8 (*m*, 12 H); 3.18 (*m*, $^2J$(Pt,H) = 87.9, $^3J$(P,H) = 3.8, $PtCH_2$); 2.89 (*s*, $^3J$(Pt,H) = 14.4, 2 SMe); 2.59 (*s*, 2 Ph*Me*); 0.45 (*m*, $^2J$(Pt,H) = 69.3, $^3J$(P,H) = 6.6, PtMe). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298.3 K): 36.3 ($^1J$(Pt,P) = 1920). Anal. calc. for $C_{24}H_{29}OPPtS$: C 48.72, H 4.94; found: C 48.63, H 4.92.

cis-*Dimethyl(pyridine)[tris(2-methylphenyl)phosphine]platinum(2+)* (cis-*[$PtMe_2$(py){P(o-tol)$_3$}]*; **3**). A slight excess of pyridine was added *in situ* to 0.5 ml of a $CDCl_3$ soln. of **1a** in a NMR tube. $^1H$-NMR ($CDCl_3$, 298.3 K): 8.20 (*m*, H−C(2), H−C(6) of py); 7.46 (*m*, H−C(4) of py); 7.40–6.90 (*m*, 12 arom. H); 6.86 (*m*, H−C(3), H−C(5) of py); 2.04 (*m*, 3 Ph*Me*); 0.47 (*m*, $^3J$(P,H) = 7.4, $^2J$(Pt,H) = 70.6, PtMe *trans* to $PR_3$); 0.27 (m, $^3J$(P,H) = 8.8, $^2J$(Pt,H) = 84.6, PtMe *trans* to py).

## REFERENCES


[1] A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403; A. J. Canty, in 'Comprehensive Organometallic Chemistry II: A Review of the Literature 1982–1994', Eds. E. F. Abel, F. G. A. Stone, G. Wilkinson, Pergamon, Oxford, New York, 1995, Vol. 9, p. 225; G. R. Newkome, W. E. Puckett, V. K. Gupta, G. Kiefer, *Chem. Rev.* **1986**, *86*, 451; C. Anderson, M. Crespo, *J. Organomet. Chem.* **2004**, *689*, 1496.

[2] V. W. W. Yam, K. M. C. Wong, N. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 6506; S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* **1999**, *38*, 913; A. Caubet, C. Lopez, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* **2003**, *669*, 164; G. Y. Zheng, D. P. Rillema, *Inorg. Chem.* **1998**, *37*, 1392; J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055.

[3] M. Hissler, J. E. Mc Garrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115, and refs. cit. therein.

[4] B. S. Williams, P. Dani, M. Lutz, A. L. Speck, G. van Koten, *Helv. Chim. Acta* **2001**, *84*, 3519; A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov, J. A. K. Howard, L. G. Kuz'mina, M. S. Datt, C. Sacht *Organometallics* **1998**, *17*, 3615; J. Campora, P. Palma, E. Carmona, *Coord. Chem. Rev.* **1999**, *193–195*, 207; I. Omae, *Chem. Rev.* **1979**, *79*, 287; I. Omae, *Coord. Chem. Rev.* **1988**, *83*, 137.

[5] a) J. Fornies, A. Martin, R. Navarro, V. Sicilia, P. Villarroya, *Organometallics* **1996**, *15*, 1826; b) S. D. Chappell, D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* **1983**, 1051; c) A. J. Cheney, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1972**, 754; d) E. C. Alyea, G. Ferguson, J. Malito, B. L. Ruhl, *Organometallics* **1989**, *8*, 1188; e) E. C. Alyea, J. Malito, B. L. Ruhl, *J. Organomet. Chem.* **1988**, *340*, 119; f) C. Scheffknecht, A. Rhomberg, E. P. Müller, P. Peringer, *J. Organomet. Chem.* **1993**, *463*, 245; g) H. C. Clark, A. B. Goel, R. G. Goel, S. Goel, *Inorg. Chem.* **1980**, *19*, 3220.

[6] R. Romeo, M. R. Plutino, L. Monsù Scolaro, S. Stoccoro, G. Minghetti, *Inorg. Chem.* **2000**, *39*, 2712.

[7] M. R. Plutino, L. Monsù Scolaro, R. Romeo, A. Grassi, *Inorg. Chem.* **2000**, *39*, 4749.

[8] R. Romeo, L. Monsù Scolaro, M. R. Plutino, F. Fabrizi de Biani, G. Bottari, A. Romeo, *Inorg. Chim. Acta* **2003**, *350*, 143.

[9] M. R. Plutino, L. Monsù Scolaro, A. Albinati, R. Romeo, *J. Am. Chem. Soc.* **2004**, *126*, 6470.

[10] J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb, D. Hezroni-Langerman, *Inorg. Chem.* **1991**, *30*, 4685; J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb, D. Hezroni-Langerman, *Organometallics* **1993**, *12*, 1694.

[11] K. Mislow, *Chemtracts: Org. Chem.* **1989**, *2*, 151; K. Mislow, *Acc. Chem. Res.* **1976**, 9, 26; K. Mislow, *Pure Appl. Chem.* **1971**, *225*, 549; K. Mislow, D. Gust, P. Finocchiaro, R. J. Boettcher, *Topics Curr. Chem.* **1974**, *47*, 1.

[12] SCIENTIST, Micro Math Scientific Software, Salt Lake City, UT.

[13] Applied Photophysics Bio Sequential SX-17 MV, sequential stopped flow ASVD spectrofluorimeter, Software manual: Applied Photophysics Ltd., 203/205 Kingstone Road, Leatherhead KT22 7PB, U.K.

[14] D. Minniti, G. Alibrandi, M. L. Tobe, R. Romeo, *Inorg. Chem.* **1987**, *26*, 3596.

[15] U. Frey, L. Helm, A. E. Merbach, R. Romeo, *J. Am. Chem. Soc.* **1989**, *111*, 8161.

[16] R. Romeo, *Comments Inorg. Chem.* **1990**, *11*, 21.

[17] A. C. Albeniz, A. L. Casado, P. Espinet, *Inorg. Chem.* **1999**, *38*, 2510.

[18] D. L. Thorn, *Organometallics* **1998**, *17*, 348.

[19] C. M. Anderson, M. Crespo, M. C. Jennings, A. J. Lough, G. Fergurson, R. J. Puddephatt, *Organometallics* **1991**, *10*, 2672; C. M. Anderson, M. Crespo, M. Font-Bardia, A. Klein, X. Solans, *J. Organomet. Chem.* **2000**, *601*, 22; M. E. van der Boom, J. Ott, D. Milstein, *Organometallics* **1999**, *18*, 3873; M. Crespo, X. Solans, M. Font-Bardia, *Organometallics* **1995**, *14*, 355.

[20] P. Foley, G. M. Whitesides, *J. Am. Chem. Soc.* **1979**, *101*, 2732; P. Foley, R. Di Cosimo, G. M. Whitesides, *J. Am. Chem. Soc.* **1980**, *102*, 6713; S. S. Moore, R. Di Cosimo, A. F. Sowinski, G. M. Whitesides, *J. Am. Chem. Soc* **1981**, *103*, 948; R. Di Cosimo, S. S. Moore, A. F. Sowinski, G. M. Whitesides, *J. Am. Chem. Soc.* **1982**, *104*, 124; S. D. Chappell, D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.* **1980**, 38; D. C. Griffiths, G. B. Young, *Polyhedron* **1983**, *2*, 1095; M. Hackett, J. A. Ibers, G. M. Whitesides, *J. Am. Chem. Soc* **1988**, *110*, 1436; D. C. Griffiths, G. B. Young, *Organometallics* **1989**, *8*, 875.

[21] a) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 5961; b) G. Gerdes, P. Chen, *Organometallics* **2003**, *22*, 2217; c) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; d) H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378; e) L. Johansson, M. Tilset, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2000**, *122*, 10846; f) J. Procelewska, A. Zahl, R. van Eldik, H. A. Zhong, J. A.

Labinger, J. E. Bercaw, *Inorg. Chem*. **2002,** *41*, 2808; g) L. Johansson, O. B. Ryan, M. Tilset, *J. Am. Chem. Soc.* **1999**, *121*, 1974; h) L. Johansson, O. B. Ryan, C. Römming, M. Tilset *J. Am. Chem. Soc.* **2001**, *123*, 6579; i) L. Johansson, M. Tilset, *J. Am. Chem. Soc.* **2001**, *123*, 739; l) M. W. Holtcamp, L. M. Henling, M. W. Day, J. A. Labinger, J. E. Bercaw, *Inorg. Chim. Acta* **1998**, *270*, 467; m) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560; n) D. D.Wick, K. I. Goldberg, *J. Am. Chem. Soc.* **1997**, *119*, 10235.

[22] V. de Felice, A. de Renzi, A. Panunzi, D. Tesauro, *J. Organomet. Chem*. **1995**, *488*, C13; G. S. Hill, L. M. Rendina, R. J. Puddephatt, *Organometallics* **1995**, *14*, 4966; J. G. Hinman, C. R. Baar, M. C. Jennings, R. J. Puddephatt, *Organometallics* **2001**, *19*, 563; C. M. Ong, M. C. Jennings, R. J. Puddephatt, *Can. J. Chem.* **2003**, *81*, 1; R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *157*, 219; R. J. Puddephatt, *Angew. Chem., Int. Ed.* **2002**, *41*, 261.

[23] S. S. Stahl, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1995**, *117*, 9371; M. W. Holtcamp, J. A. Labinger, J. E. Bercaw, *Inorg. Chim. Acta* **1997**, *265*, 117.

[24] M. Brookhart, M. L. H. Green, *J. Organomet. Chem.* **1983**, *250*, 395; F. A. Cotton, T. LaCour, A. G. Stanislowski, *J. Am. Chem. Soc.* **1974**, *96*, 754.

[25] R. H. Crabtree, E. M. Holt, M. Lavin, S. M. Morehouse, *Inorg. Chem.* **1985**, *24*, 1986; M. Lavin, R. H. Crabtree, *Organometallics* **1989**, *8*, 99.

[26] G. S. Hill, R. J. Puddephatt, *Organometallics* **1998**, *17*, 1478; P. E. M. Siegbahn, R. H. Crabtree, *J. Am. Chem. Soc*. **1996**, *118*, 4442; K. L. Bartlett, K. I. Goldberg, W. T. Borden, *J. Am. Chem. Soc.* **2000**, *122*, 1456; K. L. Bartlett, K. I. Goldberg, W. T. Borden, *Organometallics* **2001**, *20*, 2669; H. Heiberg, L. Johansson, O. Gropen, O. B. Ryan, O. Swang, M. Tilset, *J. Am. Chem. Soc.* **2000**, *122*, 10831; T. M. Gilbert, I. Hristov, T. Ziegler, *Organometallics* **2001**, *20*, 1183.

[27] U. Fekl, W. Kaminsky, K. I. Goldberg, *J. Am. Chem. Soc.* **2001**, *123*, 6423; S. Reinartz, P. S. White, M. Brookhart, J. L. Templeton, *J. Am. Chem. Soc.* **2001**, *123*, 6425.

[28] C. Eaborn, K. Kundu, A. J. Pidcock, *J. Chem. Soc., Dalton Trans.* **1981**, 933.

[29] A. L. Van Geet, *Anal. Chem.* **1968**, *40*, 2227; A. L. Van Geet, *Anal. Chem.* **1970**, *42*, 679.

*Received October 29, 2004*