Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 350 (2003) 143–151
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Ligand exchange and substitution at platinum(II) complexes: evidence for a dissociative mechanism

Raffaello Romeo [a,*], Luigi Monsù Scolaro [a,b], Maria Rosaria Plutino [a], Fabrizia Fabrizi de Biani [c], Giovanni Bottari [a], Andrea Romeo [a,b]

[a] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, ISMN-CNR, Sezione di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy*
[b] *Istituto Nazionale di Fisica della Materia, INFM, Unità di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy*
[c] *Dipartimento di Chimica, Università di Siena, Via Aldo Moro, 53100 Siena, Italy*

Received 6 June 2002; accepted 25 July 2002

Dedicated in honor of Professor Pierre Braunstein

Abstract

Square-planar complexes of the type *cis*-[Pt(Me)$_2$(Me$_2$SO)(PR$_3$)] (**1**–**6**) where PR$_3$ represents a series of isosteric tertiary phosphanes [P(*4*-MeOC$_6$H$_4$)$_3$, P(*4*-MeC$_6$H$_4$)$_3$, P(C$_6$H$_5$)$_3$, P(*4*-FC$_6$H$_4$)$_3$, P(*4*-ClC$_6$H$_4$)$_3$, P(*4*-CF$_3$C$_6$H$_4$)$_3$] have been synthesised and fully characterised through elemental analysis, ^{1}H and ^{31}P{^{1}H} NMR. The coupling constants $^1J_{PtP}$ with the isotopically abundant ^{195}Pt (33%, $I = 1/2$) of **1**–**6**, as those of the pyridine *cis*-[Pt(Me)$_2$(py)(PR$_3$)] derivatives (**7**–**12**), show linear dependencies on the basicity of the coordinated phosphane. The rates of dimethyl sulfoxide exchange for all the complexes have been measured at relatively low temperatures by ^{1}H NMR isotopic labelling experiments with deuterated chloroform as the solvent. Pyridine for dimethyl sulfoxide substitution has been studied at higher temperatures through conventional spectrophotometric techniques. The rates of both processes show no dependence on ligand concentration, for each complex the value of the rate of ligand substitution is in reasonable agreement with the value of the rate of ligand exchange at the same temperature, and the kinetics are characterised by largely positive entropies of activation. There is a compensation-effect between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, i.e., a greater $\Delta H^{\ddagger}$ is accompanied by a larger positive $\Delta S^{\ddagger}$, indicating that all complexes react via the same mechanism. The basicity of the phosphane does not affect significantly the reaction rates. The general pattern of behaviour indicates that the rate determining step for substitution is the dissociation of the sulfoxide ligand and the formation of a three-coordinated [Pt(Me)$_2$(PR$_3$)] uncharged intermediate.

Keywords: Platinum(II) complexes; Kinetics; Dissociative mechanism; Phosphane effects

1. Introduction

The potential catalytic activity of square planar complexes of d^8 metals is related to the possibility of dissociating a coordinated ligand. The 14-electron species thus formed, in which the metal is coordinatively and electronically unsaturated, is prone to accept and to activate molecular fragments [1–4]. Recently, ligand dissociation has been recognised as the initial step of many fundamental processes involving square-planar organometallic complexes [5]. The most recent studies refer to thermal decomposition of alkyl compounds [6–9], insertion of olefins into the M–H bond [10,11], reductive elimination [12], geometrical isomerisation [13,14], electrophilic attack at the metal–carbon bond [15–18], exchange reactions [19], fluxional motions of coordinated ligands [20–23]. On considering the ease with which a square-planar complex adds a fifth ligand to form five-coordinate species, the possibility of dissociative processes for ligand exchange or substitution reactions has been for a long time rejected by the scientific community [24].

The first convincing evidence for the presence of three-coordinate 14-electron species as key intermediates in nucleophilic substitution reactions comes from

* Corresponding author. Tel./fax: +39-090-39 3756.
E-mail address: raf.romeo@chem.unime.it (R. Romeo).

0020-1693/03/$ - see front matter
doi:10.1016/S0020-1693(02)01505-0

kinetic studies of complexes having a set of donor atoms of the type *cis*-[Pt(C,C)(S,S)] (C a strong σ donor carbon group; S, thioether or sulfoxide) [25]. Factors which concur in promoting dissociation are (i) high electron density at the metal which prevents the approach of the axially incoming nucleophile; (ii) bond weakening at the leaving group due to the *trans* influence of strong σ-donors (in the present cases, the organic carbanions which form strong Pt–C σ-bonds); and (iii) the stabilisation by the remaining set of three in-plane ligands of a three-coordinated 14-electron intermediate without changing the singlet ground state. These favourable factors do not apply in the presence of ligands which exhibit major π-acceptor capabilities. In the complex *cis*-[$PtPh_2(CO)(SEt_2)$], the relief of the excess of electron density at the metal by the carbon monoxide and the presence of a low-lying LUMO, π-delocalised over the Pt–C–O atoms, facilitates a changeover of mechanism from dissociative to associative [26]. Thus, the *cis* ligands play also a crucial role for the electronic properties of the metal centre and, in principle, a fine tuning of the reaction mechanism is possible playing with the σ-donor and π-acceptor capabilities of the ligands. Also, it has become evident that not necessarily the substrate must carry one or more Pt–C bonds to dissociate. In fact, an appropriate set of strong σ-donor groups can favour sufficient accumulation of electron density at the metal and stabilise the 14-e intermediate. This is the case for the complex *cis*-[$Pt(SiMePh_2)_2(PMe_2Ph)_2$], which shows a partial tetrahedral distortion [27].

We report here on ligand exchange and substitution kinetics of the complexes *cis*-[$Pt(Me)_2(Me_2SO)(PR_3)$], where PR_3 represents a series of isosteric tertiary phosphanes. The goal was to check whether the σ-donor capability of the phosphanes, contrary to carbon monoxide, is able to promote a dissociative mechanism. An additional objective was to check at what extent the basicity of the phosphanes controls the reaction rates. We can anticipate that the presence of a phosphane does not induce a changeover of the dissociative mechanism but rather causes an acceleration of the dissociation rate with respect to that of *cis*-[$Pt(Me)_2(Me_2SO)_2$] [28].

2. Experimental

2.1. Materials

K_2PtCl_4 (Strem Chemical Co.) was purified from metallic Pt and K_2PtCl_6 by dissolving it in water and filtering. *trans*-[$Pt(CH_3)_2(Me_2SO)_2$] was prepared according to a published method [29], and was crystallised several times from diethyl ether. The phosphorus ligands were purchased from Strem and were crystallised from ethanol by dissolving in the hot solvent, filtering, and cooling the filtrate to 0 °C. Their purity was checked by the measurement of the $^{31}P\{^1H\}$ NMR spectra and the crystals were stored under oxygen-free N_2. All the other reagents were of the highest commercial grade available and were used as received, or were purified by distillation or recrystallisation when necessary. Dimethyl sulfoxide was purified by liquid chromatography on alumina under argon and stored over 4 Å molecular sieves. Other solvents used were purified and dried by standard techniques. Chloroform for use in kinetic runs was degassed by means of a series of 'freezing–pumping' cycles and eventually stored in Schlenk tubes. Deuterated chloroform and dimethyl sulfoxide were used as received from Aldrich Chemical Co. Microanalyses were performed by Redox Analytical Laboratories, Milan.

2.1.1. *cis*-(Dimethyl)(dimethylsulfoxide)(tris(4-methoxyphenyl)phosphane)platinum(II), *cis*-[$PtMe_2(Me_2SO)(P(4\text{-}MeOC_6H_4)_3)$] (**1**)

A solution of $P(4\text{-}MeOC_6H_4)_3$ (105.7 mg, 0.3 mmol) in CH_2Cl_2 (10 ml) was added very slowly dropwise to a solution of *cis*-[$PtMe_2(Me_2SO)_2$] (114.4 mg, 0.3 mmol) in CH_2Cl_2 (30 ml). The reaction mixture was left aside for 1 h, then concentrated under vacuum and the complex (145 mg, 74% yield) separated out as solid upon adding petroleum ether (v/v = 1/1). *Anal*. Calc. for $C_{25}H_{33}O_4PSPt$: C, 45.80; H, 5.07. Found: C, 46.1; H, 4.98%. IR: ν(S=O) 1100 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.53 (m, $^4J_{PH} = 9.9$ Hz, $^3J_{HH} = 8.6$ Hz, 6H, $H_{2,6}$), 6.90 (d, $^3J_{HH} = 8.6$ Hz, 6H, $H_{3,5}$), 3.81 (s, 9H, OCH_3), 2.76 (s, $^3J_{PtH} = 12.8$ Hz, 6H, S–CH_3), 0.57 (m, $^3J_{PH} = 7.5$ Hz, $^2J_{PtH} = 68.2$ Hz, 3H, Pt–CH_3), 0.47 (m, $^3J_{PH} = 9.3$ Hz, $^2J_{PtH} = 79.0$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.9 ($^1J_{PtP} = 1923$ Hz).

All the other phosphane complexes (**2**–**6**) were prepared following a synthetic procedure similar to that described above.

2.1.2. *cis*-(Dimethyl)(dimethylsulfoxide)(tris(4-methylphenyl)phosphane)platinum(II), *cis*-[$PtMe_2(Me_2SO)(P(4\text{-}MeC_6H_4)_3)$] (**2**)

Anal. Calc. for $C_{25}H_{33}OPSPt$: C, 49.42; H, 5.47. Found: C, 49.74; H, 5.54%. IR: ν(S=O) 1093 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (m, $^4J_{PH} = 9.9$ Hz, $^3J_{HH} = 7.4$ Hz, 6H, $H_{2,6}$), 7.18 (d, $^3J_{HH} = 7.4$ Hz, 6H, $H_{3,5}$), 2.76 (s, $^3J_{PtH} = 12.8$ Hz, 6H, S–CH_3), 2.36 (s, 9H, CH_3), 0.57 (m, $^3J_{PH} = 6.7$ Hz, $^2J_{PtH} = 70.4$ Hz, 3H, Pt–CH_3), 0.45 (m, $^3J_{PH} = 9.3$ Hz, $^2J_{PtH} = 80.1$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.5 ($^1J_{PtP} = 1915$ Hz).

2.1.3. *cis*-(Dimethyl)(dimethylsulfoxide)(triphenylphosphane)-platinum(II), *cis*-[$PtMe_2(Me_2SO)(P(C_6H_5)_3)$] (**3**)

Anal. Calc. for $C_{22}H_{27}OPSPt$: C, 46.72; H, 4.81. Found: C, 46.46; H, 4.98%. IR: ν(S=O) 1095 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.66–7.60 (m, 6H, $H_{2,6}$), 7.40–7.37

(m, 9H, $H_4+H_{3,5}$), 2.77 (s, $^3J_{PtH}=13.2$ Hz, 6H, S–CH_3), 0.57 (m, $^3J_{PH}=6.7$ Hz, $^2J_{PtH}=70.7$ Hz, 3H, Pt–CH_3), 0.46 (m, $^3J_{PH}=9.1$ Hz, $^2J_{PtH}=78.7$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.7 ($^1J_{PtP}=1904$ Hz).

*2.1.4. cis-(Dimethyl)(dimethylsulfoxide)(tris(4-fluorophenyl)phosphane)platinum(II), cis-[PtMe$_2$(Me$_2$SO)(P(4-FC$_6$H$_4$)$_3$)] (**4**)*

Anal. Calc. for $C_{22}H_{24}F_3OPSPt$: C, 42.65; H, 3.90. Found: C, 43.89; H, 3.93%. IR: ν(S=O) 1093 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.58 (m, 6H, $H_{2,6}$), 7.11 (m, 6H, $H_{3,5}$), 2.83 (s, $^3J_{PtH}=13.9$ Hz, 6H, S–CH_3), 0.52 (m, $^3J_{PH}=6.6$ Hz, $^2J_{PtH}=69.9$ Hz, 3H, Pt–CH_3), 0.43 (m, $^3J_{PH}=9.8$ Hz, $^2J_{PtH}=78.7$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.3 ($^1J_{PtP}=1898$ Hz).

*2.1.5. cis-(Dimethyl)(dimethylsulfoxide)(tris(4-chlorophenyl)phosphane)platinum(II), cis-[PtMe$_2$(Me$_2$SO)(P(4-ClC$_6$H$_4$)$_3$)] (**5**)*

Anal. Calc. for $C_{22}H_{24}Cl_3OPSPt$: C, 39.50; H, 3.62. Found: C, 39.46; H, 3.73%. IR: ν(S=O) 1083 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (m, $^3J_{PH}=9.8$ Hz, $^3J_{HH}=8.4$ Hz, 6H, $H_{2,6}$), 7.36 (m, $^3J_{HH}=8.4$ Hz, 6H, $H_{3,5}$), 2.84 (s, $^3J_{PtH}=14.2$ Hz, 6H, S–CH_3), 0.52 (m, $^3J_{PH}=6.9$ Hz, $^2J_{PtH}=69.5$ Hz, 3H, Pt–CH_3), 0.43 (m, $^3J_{PH}=9.4$ Hz, $^2J_{PtH}=77.9$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.1 ($^1J_{PtP}=1881$ Hz).

*2.1.6. cis-(Dimethyl)(dimethylsulfoxide)(tris(4-trifluoromethylphenyl)phosphane)platinum(II), cis-[PtMe$_2$(Me$_2$SO)(P(4-CF$_3$C$_6$H$_4$)$_3$] (**6**)*

Anal. Calc. for $C_{25}H_{24}F_9OPSPt$: C, 39.02; H, 3.14. Found: C, 38.43; H, 3.23%. IR: ν(S=O) 1060 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.80–7.60 (m, 12H, $H_{2,6}+H_{3,5}$), 2.88 (s, $^3J_{PtH}=14.3$ Hz, 6H, S–CH_3), 0.56 (m, $^3J_{PH}=6.6$ Hz, $^2J_{PtH}=70.4$ Hz, 3H, Pt–CH_3), 0.45 (m, $^3J_{PH}=9.3$ Hz, $^2J_{PtH}=78.1$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.4 ($^1J_{PtP}=1847$ Hz).

*2.1.7. cis-(Dimethyl)(pyridine)(tris(4-methoxyphenyl)phosphane)platinum(II), cis-[PtMe$_2$(py)(P(4-MeOC$_6$H$_4$)$_3$)] (**7**)*

Prepared 'in situ' by adding a slight excess of pyridine to 0.5 ml of a chloroform-*d* solution of complex **1** in a NMR tube. ^1H NMR ($CDCl_3$): δ 8.33 (d, $^3J_{PtH}=20.9$ Hz, $^3J_{HH}=6.0$ Hz, 2H, $H_{2,6}$–py), 7.43 (m, $^3J_{HH}=7.6$ Hz, 1H, H_4–py), 7.35 (m, $^3J_{HH}=9.1$ Hz, 6H, $H_{2,6}$), 6.90 (m, $^3J_{HH}=6.0$, 7.6 Hz, 2H, $H_{3,5}$–py), 6.74 (m, $^3J_{HH}=9.1$ Hz, 6H, $H_{3,5}$), 3.80 (s, 9H, OCH_3), 0.60 (s, $^3J_{PH}=8.2$ Hz, $^2J_{PtH}=84.1$ Hz, 3H, Pt–CH_3), 0.52 (s, $^3J_{PH}=7.7$ Hz, $^2J_{PtH}=68.2$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.7 ($^1J_{PtP}=1970$ Hz).

All the other pyridine derivatives (**8**–**12**) were prepared following the procedure described above.

*2.1.8. cis-(Dimethyl)(pyridine)(tris(4-methylphenyl)phosphane)platinum(II), cis-[PtMe$_2$(py)(P(4-MeC$_6$H$_4$)$_3$)] (**8**)*

^1H NMR ($CDCl_3$): δ 8.31 (m, $^3J_{PtH}=22.0$ Hz, $^3J_{HH}=6.6$ Hz, 2H, $H_{2,6}$–py), 7.41 (m, $^3J_{HH}=7.8$ Hz, 1H, H_4–py), 7.32 (m, $^3J_{HH}=7.1$ Hz, 6H, $H_{2,6}$), 7.02 (m, $^3J_{HH}=7.1$ Hz, 6H, $H_{3,5}$), 6.88 (m, $^3J_{HH}=6.6$, 7.8 Hz, 2H, $H_{3,5}$–py), 2.31 (s, 9H, CH_3), 0.60 (s, $^3J_{PH}=8.2$ Hz, $^2J_{PtH}=84.1$ Hz, 3H, Pt–CH_3), 0.52 (s, $^3J_{PH}=7.7$ Hz, $^2J_{PtH}=68.2$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.3 ($^1J_{PtP}=1957$ Hz).

*2.1.9. cis-(Dimethyl)(pyridine)(triphenylphosphane)platinum(II), cis-[PtMe$_2$(py)(P(C$_6$H$_5$)$_3$)] (**9**)*

^1H NMR ($CDCl_3$): δ 8.31 (m, $^3J_{PtH}=20.9$ Hz, $^3J_{HH}=5.4$ Hz, 2H, $H_{2,6}$–py), 7.48–7.37 (m, 7H, H_4–py+$H_{2,6}$), 7.20 (m, 9H, $H_{3,5}+H_4$), 6.88 (m, $^3J_{HH}=5.4$, 7.3 Hz, 2H, $H_{3,5}$–py), 0.60 (s, $^3J_{PH}=7.7$ Hz, $^2J_{PtH}=83.8$ Hz, 3H, Pt–CH_3), 0.55 (s, $^3J_{PH}=7.9$ Hz, $^2J_{PtH}=69.4$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.3 ($^1J_{PtP}=1941$ Hz).

*2.1.10. cis-(Dimethyl)(pyridine)(tris(4-fluorophenyl)phosphane)platinum(II), cis-[PtMe$_2$(py)(P(4-FC$_6$H$_5$)$_3$] (**10**)*

^1H NMR ($CDCl_3$): δ 8.31 (m, $^3J_{PtH}=21.7$ Hz, $^3J_{HH}=5.9$ Hz, 2H, $H_{2,6}$–py), 7.48 (m, $^3J_{HH}=7.5$ Hz, 1H, H_4–py), 7.41 (m, 6H, $H_{3,5}$), 6.97 (m, 6H, $H_{2,6}$), 6.88 (m, $^3J_{av}=7$ Hz, 2H, $H_{3,5}$–py), 0.56 (m, $^3J_{PH}=8.0$ Hz, $^2J_{PtH}=84.2$ Hz, 3H, Pt–CH_3), 0.55 (s, $^3J_{PH}=8.0$ Hz, $^2J_{PtH}=69.5$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.2 ($^1J_{PtP}=1940$ Hz).

*2.1.11. cis-(Dimethyl)(pyridine)(tris(4-chlorophenyl)phosphane)platinum(II), cis-[PtMe$_2$(py)(P(4-ClC$_6$H$_4$)$_3$)] (**11**)*

^1H NMR ($CDCl_3$): δ 8.29 (m, $^3J_{PtH}=21.2$ Hz, $^3J_{HH}=6.4$ Hz, 2H, $H_{2,6}$–py), 7.50 (m, $^3J_{HH}=7.8$ Hz, 1H, H_4–py), 7.34 (m, $^3J_{HH}=8.5$ Hz, 6H, $H_{2,6}$), 7.23 (m, $^3J_{HH}=8.5$ Hz, 6H, $H_{3,5}$), 6.97 (m, $^3J_{HH}=6.4$, 7.8 Hz, 5H, $H_{3,5}$–py), 0.57 (m, $^3J_{PH}=7.8$ Hz, $^2J_{PtH}=69.9$ Hz, 3H, Pt–CH_3), 0.55 (m, $^3J_{PH}=7.9$ Hz, $^2J_{PtH}=83.2$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.7 ($^1J_{PtP}=1916$ Hz).

*2.1.12. cis-(Dimethyl)(pyridine)(tris(4-trifluoromethylphenyl)phosphane)platinum(II), cis-[PtMe$_2$(py)(P(4-CF$_3$C$_6$H$_4$)$_3$] (**6**)*

^1H NMR ($CDCl_3$): δ 8.30 (m, $^3J_{PtH}=20.3$ Hz, $^3J_{HH}=6.0$ Hz, 2H, $H_{2,6}$–py), 7.7–7.4 (m, 13H, $H_{3,5}+H_4$–py+$H_{2,6}$), 7.29 (m, $^3J_{HH}=6.0$, 7.7 Hz, 2H, $H_{3,5}$–py), 0.64 (s, $^3J_{PH}=8.3$ Hz, $^2J_{PtH}=70.4$ Hz, 3H, Pt–CH_3), 0.59 (s, $^3J_{PH}=8.3$ Hz, $^2J_{PtH}=83.6$ Hz, 3H, Pt–CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.5 ($^1J_{PtP}=1884$ Hz).

2.2. Instruments

^1H and $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ solution on a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13 and 121.49 MHz, respectively. ^1H chemical shifts were measured relative to the residual solvent peak and are reported in δ units downfield from Me_4Si. $^{31}P\{^1H\}$ chemical shifts, in parts per million, are given relative to external phosphoric acid. The temperature within the probe was checked using the methanol or ethylene glycol method [30]. Slow spectrophotometric kinetics were carried out with a rapid-scanning Hewlett–Packard Model 8452 A spectrophotometer or, at a selected wavelength, with a Perkin–Elmer Lambda 3 spectrophotometer, interfaced with a microcomputer for data collection and equipped with a cell compartment thermostated by a Perkin–Elmer Peltier temperature programmer (PTP). The temperature accuracy was ± 0.05 °C. Stopped-flow kinetic runs were recorded on the HP8452A spectrophotometer equipped with a Hi-Tech SFA-20 Rapid Kinetic Accessory. Rate constants were evaluated using the SCIENTIST software package [31].

3. Results

3.1. ^1H NMR characterisation

The synthesis of the phosphane compounds **1**–**6**, according to reaction (1)

$$cis[Pt(Me)_2(Me_2SO)_2] + PR_3 \rightarrow cis[Pt(Me)_2(Me_2SO)(PR_3)] + Me_2SO \quad (1)$$

must be carried out with extreme care to avoid local excess of reagent and the easy formation of disubstituted *cis*-$[Pt(Me)_2(PR_3)_2]$ products.

The reaction products were isolated as pure solid compounds and fully characterised by elemental analysis and spectrometric techniques. Selected ^1H and $^{31}P\{^1H\}$ NMR data are collected in Table 1. The ^1H NMR spectra contain at low fields the expected resonances of the phosphane phenyls, an average resonance at $\delta = 2.81 \pm 0.05$ due to Me_2SO with a coupling constant $^3J_{PtH} = 13.5 \pm 0.5$ Hz with the isotopically abundant ^{195}Pt (33%, $I = 1/2$), and two multiplets for the coordinated methyl groups with average values at $\delta = 0.55 \pm 0.02$ ($^2J_{PtH} = 70 \pm 1$ Hz) and at $\delta = 0.45 \pm 0.02$ ($^2J_{PtH} = 78.8 \pm 0.8$ Hz), respectively. The two methyl groups can be unambiguously identified on the basis of the different *trans* influence of PR_3 and Me_2SO, and the magnitude of values observed for the methyl $^2J_{PtH}$ coupling constants. The lowest value of $^2J_{PtH} = 70$ Hz (at $\delta = 0.55$) belongs to the methyl group *trans* to the strong σ-donor PR_3, while, for the methyl group *trans* to Me_2SO, the coupling constant increases to $^2J_{PtH} = 78.8$ Hz (at $\delta = 0.45$). Additional methyl signals of the *para*-substituents groups are observed for compounds **1** and **2**. The ^{31}P resonance has an average value at $\delta = 28 \pm 2$ but the coupling constants show a significant dependence on the nature of the coordinated phosphanes.

The reactions of **1**–**6** with pyridine to yield the compounds **7**–**12** were carried out 'in situ' in an NMR tube. On changing pyridine for Me_2SO the average value of the chemical shift of the *trans* methyl increases to $\delta = 0.59 \pm 0.02$ ($^2J_{PtH} = 83.8 \pm 0.4$ Hz) while that of

Table 1
Selected ^1H and $^{31}P\{^1H\}$ NMR data for complexes of the type *cis*-$[PtMe_2(Me_2SO)(PR_3)]$ (**1**–**6**), and for the relative pyridine *cis*-$[PtMe_2(py)(PR_3)]$ derivatives (**7**–**12**) [a]

R	*n*	$\delta(^1H)$			$\delta(^{31}P)$
		CH_3–Pt [b]	CH_3–Pt [c]	Others	
4-$MeOC_6H_4$	1	0.47(79)	0.57(68)	2.76(13, CH_3–S)	24.9(1923)
4-MeC_6H_4	2	0.45(80)	0.57(70)	2.76(13, CH_3–S)	26.5(1915)
C_6H_5	3	0.46(79)	0.57(71)	2.77(13, CH_3–S)	28.7(1904)
4-FC_6H_4	4	0.43(79)	0.52(70)	2.83(14, CH_3–S)	27.3(1898)
4-ClC_6H_4	5	0.43(78)	0.52(70)	2.84(14, CH_3–S)	28.1(1881)
4-$CF_3C_6H_4$	6	0.45(78)	0.56(70)	2.88(14, CH_3–S)	30.4(1847)
4-$MeOC_6H_4$	7	0.60(84)	0.52(68)	8.33(21, $H_{2,6}$–py)	25.7(1970)
4-MeC_6H_4	8	0.60(84)	0.52(68)	8.31(22, $H_{2,6}$–py)	27.3(1957)
C_6H_5	9	0.60(84)	0.55(69)	8.31(21, $H_{2,6}$–py)	29.3(1941)
4-FC_6H_4	10	0.56(84)	0.55(70)	8.31(22, $H_{2,6}$–py)	27.2(1940)
4-ClC_6H_4	11	0.55(83)	0.57(70)	8.29(21, $H_{2,6}$–py)	27.7(1916)
4-$CF_3C_6H_4$	12	0.59(84)	0.64(70)	8.30(20, $H_{2,6}$–py)	29.5(1884)

[a] Recorded in $CDCl_3$ as solvent at 298.2 K. Chemical shifts (δ) in ppm relative to TMS; ^{195}Pt coupling constants, given in parentheses together with the assignment, are in Hz.
[b] CH_3 *trans* to Me_2SO or pyridine.
[c] CH_3 *trans* to phosphane ligand.

the methyl *trans* to PR_3 remains substantially unchanged ($\delta = 0.56 \pm 0.04$, $^2J_{PtH} = 69.0 \pm 0.9$ Hz).

3.2. Kinetics

3.2.1. Isotopic exchange

The rates of sulfoxide exchange on *cis*-[$PtMe_2(Me_2SO)(PR_3)$] (**1**–**6**) were obtained by isotopic labelling, at a low temperature range (253–283 K). A known volume of dimethyl sulfoxide-d_6 was added with a microsyringe into a 5 mm NMR tube containing a prethermostated solution of complex in chloroform-*d*. At least a sevenfold excess of $(CD_3)_2SO$ over complex was ensured in any run. The rate of exchange (Fig. 1, upper plot) was monitored through the increase in intensity of the signal at δ 2.63 ppm relative to the free Me_2SO and the matching decrease of the signal at 2.76 ppm for the bound Me_2SO. The molar fraction of free Me_2SO, $F_f = [Me_2SO]_f/([Me_2SO]_f + [Me_2SO]_b)$, was obtained by integration of both signals. The exchange of the label follows a first-order rate law (Fig. 1, lower plot) and the first-order rate constant, k_{exch} (s^{-1}), was obtained from the nonlinear regression analysis of the equation

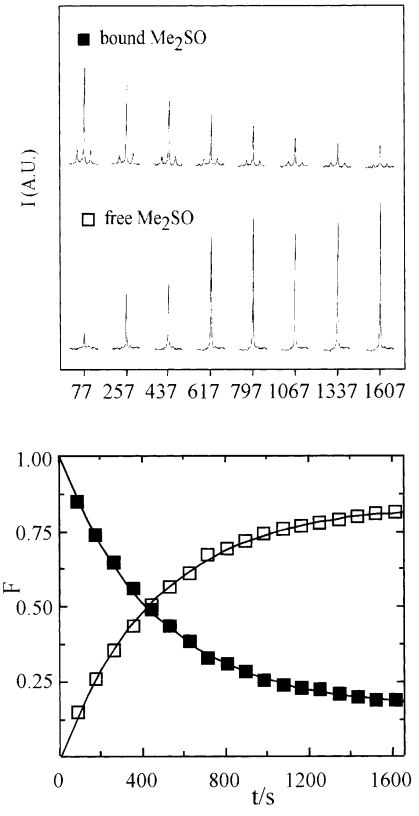


Fig. 1. 300-MHz ^1H NMR spectra of a 3.67 m*m* *cis*-[$PtMe_2(Me_2SO)P(4\text{-}MeC_6H_4)_3$] and 250 m*m* $(CD_3)_2SO$ solution in deuterated chloroform at 273 K as a function of time. Upper plot: coordinated Me_2SO ($\delta = 2.76$ ppm, $^3J_{PtH} = 12.8$ Hz); free Me_2SO ($\delta = 2.63$ ppm). Lower plot: Exponential curves for the change with time of the molar fraction of coordinated and free dimethylsulfoxide.

$F_f = c_1 + c_2 \exp(-k_{exch}t)$, with c_1, c_2 and k_{exch} as the parameters to be optimised. A similar analysis was performed on the molar fraction of the nondeuterated bound dimethyl sulfoxide. From the McKay equation, $R_{exch} = k_{exch}ab(a+b)^{-1}$ (where R_{exch} is the rate of the exchange process, a the concentration of complex, and b the concentration of free sulfoxide) the pseudo-first-order rate constants, $k_{obs} = R_{exch}/a$, were calculated and their values are collected in Table S1 in Section 6. The exchange rate constants were independent of the added dimethyl sulfoxide concentration.

3.2.2. Spectrophotometric kinetics

The substitution reactions of Me_2SO from *cis*-[$PtMe_2(Me_2SO)(PR_3)$] (**1**–**6**) by pyridine (py), according to Eq. (2):

$$cis[PtMe_2(Me_2SO)(PR_3)] + py \rightarrow cis[PtMe_2(py)(PR_3)] + Me_2SO \quad (2)$$

were carried out in the temperature range of 308–280 K. Slow kinetics were carried out in a double-set silica cell located in the thermostated cell compartment of the spectrophotometer and monitored by repetitive scanning of the spectrum at suitable times, using chloroform as the solvent. The reactions, carried out in the presence of at least a tenfold excess of pyridine. There was no indication of the presence of side reactions or of significant amounts of any intermediate species and the conversion of the substrate into the product is seen as a single step. All reactions obeyed a first-order rate law until well over 90% conversion. Fastest reactions required the use of stopped-flow spectrophotometry under pseudo-first-order conditions. 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_∞, and k_{obs} as the parameters to be optimised (A_0, absorbance after mixing of reagents; A_∞, absorbance at completion of reaction). The pseudo-first-order rate constants k_{obs} for reaction (2) are reported in Table S1 inSection 6 for a range of temperature and py concentrations. The exchange rate constants were independent of the added pyridine concentration. The variable-temperature rate constants, taken together with those for isotopic labelling (Section 3.2.1) were fitted to the Eyring equation and the derived activation parameters are reported in Table 2.

4. Discussion

Organometallic complexes of the type *cis*-[$PtMe_2(Me_2SO)(PR_3)$] (**1**–**6**) can be prepared from the reaction of *cis*-[$Pt(Me)_2(Me_2SO)_2$] and phosphanes in an

Table 2
Ligand properties of phosphorus(III) compounds, spectroscopic properties, rate constants and activation parameters for ligand exchange and substitution reactions of the complexes (**1**–**6**)

n	χ [a]	$^1J_{PtP}$ [b]	$^1J_{PtP}$ [c]	k_1 [d]	$\Delta H^{\ddagger}$ [e]	$\Delta S^{\ddagger}$ [f]	$\Delta G^{\ddagger}$ [g]
1	10.5	1923	1970	0.0519	91.0±0.3	36±3	80.3
2	11.5	1915	1957	0.0588	89.5±0.7	32±2	80.0
3	13.25	1904	1941	0.0616	87.0±0.8	24±3	79.8
4	15.7	1898	1940	0.0415	85.0±0.7	14±2	80.8
5	16.8	1881	1916	0.0327	84.4±0.9	10±3	81.4
6	20.5	1847	1884	0.0275	89.0±0.3	24±1	81.8

[a] Values in cm^{-1} taken from ref. [32].
[b] $^1J_{PtP}$ coupling constants in Hz relative to compounds **1**–**6**.
[c] $^1J_{PtP}$ coupling constants in Hz relative to compounds **7**–**12**.
[d] Dissociation rate constants (s^{-1}) for dimethylsulfoxide exchange and substitution at 298 K.
[e] Enthalpies of activation (kJ mol^{-1}) from variable-temperature kinetics.
[f] Entropies of activation (J K^{-1} mol^{-1}).
[g] Gibbs free energies of activation (kJ mol^{-1}) at 298 K.

1:1 ratio. If the synthetic procedure is carried out with the necessary precautions to avoid the fast and easy removal of both molecules of sulfoxide to yield bis-substituted phosphane products [13], the reactions go to completion and the desired products are obtained in high yield and purity.

4.1. Stereoelectronic analysis of $^1J_{PtP}$ coupling constants

The values of $^1J_{PtP}$ coupling constants of the *cis*-[$PtMe_2(Me_2SO)(PR_3)$] (**1**–**6**) and *cis*-[$PtMe_2(py)(PR_3)$] (**7**–**12**) complexes in Table 2 are in the range typical of a phosphorus atom *trans* to carbon in platinum(II) compounds [13]. They encompass a range of 76–86 Hz and appear to be dependent on the nature of the coordinated phosphane. Usually the equations and the protocol to perform quantitative (QALE) analysis of a physicochemical property, as suggested by Giering et al. [32], imply the knowledge of electronic parameters such as χ (an infrared parameter) [33] which measures the σ donicity of the ligand (the electron-donor ability decreases as χ increases), or E_{ar} (the aryl-effect parameter) [34] which depends on the number of pendent aryl groups on the phosphane and of θ Tolman's cone angle [35], that measures the steric requirements of the ligand. Since the response of the analysed property to χ is assumed to be linear over the entire range of ligands, while the response to the steric parameter θ is not linear, the possibility of the onset of a steric threshold (θ_{st}) must be taken into consideration. In previous studies we have performed a complete QALE analysis on the $^1J_{PtP}$ values of the complexes *trans*-$[Pt(PR_3)_2(Me)(MeOH)]^+$ [13], *cis*-$[PtPh_2(CO)(PR_3)]$ [36], $[Pt(N{-}N{-}C)(PR_3)]^+$-(N–N–CH=6-(1-methylbenzyl)-2,2′-bipyridine) [37], and *cis*-$[PtMe_2(PR_3)_2]$ [13]. The values of the coupling constants ($^1J_{PtP}$) were resolved quantitatively into steric, electronic and aryl contributions of the phosphane ligands, by use of multiparameter equations. In the present case, since the phosphanes are isosteric and contain the same number of aryl rings, the values of θ and E_{ar} are constant for all the phosphanes, and therefore, the only variable of interest is χ, the σ donicity of the ligand. The electronic profiles seen in Fig. 2 were constructed by linear regression analysis of the simple equation:

$$^1J_{PtP} = \omega + \alpha(\chi) \quad (3)$$

and show that the value of the Pt–P coupling constant for **1**–**6** and **7**–**12** is enhanced as the phosphanes become better electron donors (smaller χ). The values of α (-7.2 ± 0.8 Hz cm for **1**–**6**, and -8.1 ± 0.9 Hz cm for **7**–**12**), which represent the sensitivity of $^1J_{PtP}$ to the inductive effects brought about by substituents on phosphorous, are comparable to those of other complexes having a C–Pt–P bond axis ($\alpha = -6.89\pm0.2$ Hz cm for *cis*-$[PtMe_2(PR_3)_2]$ and $\alpha = -8.2\pm0.9$ Hz cm for *cis*-$[PtPh_2(CO)(PR_3)]$). Coupling constants $^1J_{PtP}$ of closely related planar platinum(II) complexes can be regarded as a good diagnostic probe of the extent of the covalence of the Pt–P bond [38]. Smaller values of $^1J_{PtP}$ correspond to longer Pt–P bond distances and to higher *trans* influences of groups in *trans* position to the bond [39]. Steric effects play also a significant role [40]. Steric repulsion prevents maximum overlap of phosphorus and platinum bonding orbitals and changes the s character present in the metal–phosphorus bond. In the QALE analysis this is characterised by the onset of a steric threshold in the plot of $^1J_{PtP}$ versus the cone angle and by a sharp change in the direction of steric effects. For the complexes *cis*-$[PtMe_2(PR_3)_2]$ [13], the steric threshold observed in the steric profile of the $^1J_{PtP}$ coupling constants, corresponds to a value of Tolman's cone

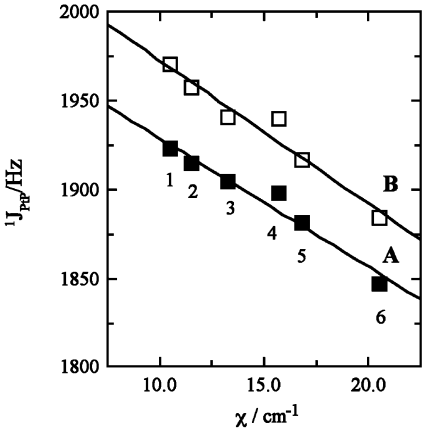


Fig. 2. Electronic profiles, showing the dependence of the coupling constants $^1J_{PtP}$ upon the electronic parameter χ for *cis*-$[PtMe_2(Me_2SO)(PR_3)]$ (plot A) and for *cis*-$[PtMe_2(py)(PR_3)]$ (plot B). Numbers refer to the phosphane ligands as listed in Table 2.

angle (149°) above which the P_A–Pt–P_B angle and the Pt–P bond separation of the two phosphane ligands suddenly increase, as a result of a strong steric congestion at the square coordination plane. Accordingly, the relative stability of the dimethyl-bisphosphane platinum(II) complexes was found by Nolan et al. [41] to be strongly influenced by the size of the phosphane, with larger cone angles resulting in less thermodinamically stable complexes.

4.2. Analysis of the kinetic data

The rates of both reactions on *cis*-[$PtMe_2(Me_2SO)(PR_3)$] (**1**–**6**) (sulfoxide exchange and pyridine for sulfoxide substitution (eq.2)) are not affected by the concentration of the added ligand. The temperature dependency of the substitution reactions ($CHCl_3$ as the solvent) was determined at a higher range than that of the isotopic labelling ($CDCl_3$ as the solvent). From the overall data set it is possible to construct a unique Eyring plot, as that shown in Fig. 3, which encompasses a rather wide range of temperatures. From similar plots values of the activation enthalpies $\Delta H^{\ddagger}$ and of the activation entropies $\Delta S^{\ddagger}$ were derived. Interestingly, dissociation rate constants (s^{-1}) for dimethylsulfoxide exchange and substitution have identical values at the same temperature. The values of the rate constants k_1 at various temperatures and ligand concentrations are collected in Table S1 in Section 6. Values of the unique rate constants k_1 at 298 K and of the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ are reported in Table 2.

The experimental kinetic evidence points unequivocally to a dissociative mode of activation for the compounds examined (**1**–**6**). The assessment of a dissociative mechanism can be made essentially on the basis of: (i) the independence of the dissociation rate on the nature and concentration of the entering group; (ii) the identity of the rate of dissociation with the rate of ligand exchange; and (iii) the sign and the magnitude of the entropy of activation always positive. The solvents used were insufficiently coordinating to give an associatively activated contribution. The pattern of behaviour is strictly similar to that found in our previous studies on *cis*-[$PtMe_2(Me_2SO)_2$] [28] and other dialkyl and diaryl systems [25], where the easy dissociation of thioethers or sulfoxides was shown to be the rate determining step of the substitution. The same dissociative mechanism (Scheme 1) applies which involves, (i) dissociative loss of Me_2SO from the substrate (k_1 path) to yield a three-coordinated 14-electron intermediate; (ii) competition for it between the reentry of Me_2SO (via k_{-1}), and the attack of a ligand (either *Me_2SO or py, via k_2) to yield the observed products. The rate law is given by the equation:

$$k_{obs} = k_1[Nu]/\{(k_{-1}/k_2)[Me_2SO] + [Nu]\} \quad (4)$$

that for $k_2 \gg k_{-1}$ reduces to $k_{obs} = k_1$.

The circumstance that complexes **1**–**6** react with a dissociative mechanism, like to the analogous di-alkyl [28] or di-aryl [25] bis-sulfoxideplatinum(II) complexes, suggests that PR_3 for Me_2SO substitution does not imply a changeover of mechanism as found on changing CO for Me_2SO. This contrasting behaviour stems from the enormous difference of σ-donor and π-acceptor abilities of PR_3 and CO ligands. The complexes *cis*-[$PtMe_2(Me_2SO)_2$] [28] [$k_1 = (1.18 \pm 0.1) \times 10^{-2}$ s^{-1}, $\Delta H^{\ddagger} = 86 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -3 \pm 2$ J K^{-1} mol^{-1}, $\Delta G^{\ddagger} = 84$ kJ mol^{-1} in benzene at 303 K] and *cis*-[$PtPh_2(Me_2SO)_2$] [42] [$k_1 = (1.40 \pm 0.2) \times 10^{-2}$ s^{-1}, $\Delta H^{\ddagger} = 64 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -66 \pm 8$ J K^{-1} mol^{-1}, $\Delta G^{\ddagger} = 84$ kJ mol^{-1} in benzene at 303 K] show comparable reactivity and free energy of activation, while *cis*-[$PtMe_2(Me_2SO)(PPh_3)$] [$k_1 = (6.16) \times 10^{-2}$ s^{-1}, $\Delta H^{\ddagger} = 87.0 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = 24 \pm 3$ J K^{-1} mol^{-1}, $\Delta G^{\ddagger} = 79.8$ kJ mol^{-1} in $CHCl_3$ at 298 K] appears to be somewhat more inclined to dissociation. It must be concluded that it is sufficient to transmit a reasonable excess of electronic density into the metal by 'non innocent' ligands to induce dissociation. Overflow of electron density at the metal has the effect of (i) destabilising the ground state; (ii) decreasing the electrophilic ability of the substrate; (iii) preventing the

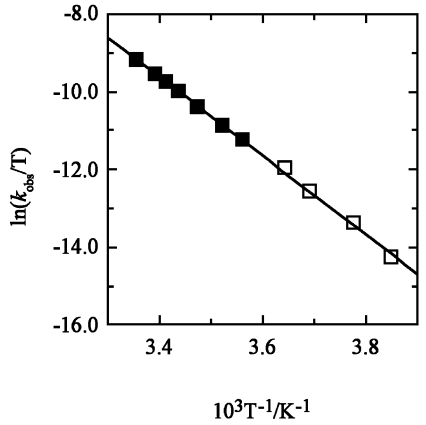
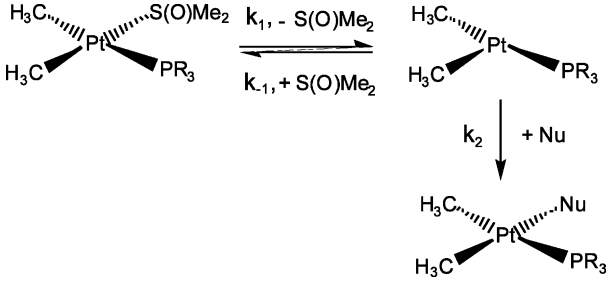


Fig. 3. Eyring plot constructed by use of the rate data of both isotopic labelling experiments (empty squares) and pyridine for Me_2SO substitution reactions (filled squares) on the complex *cis*-[$PtMe_2(Me_2SO)P(4\text{-}ClC_6H_4)_3$].



Scheme 1.

approach of the lone pair of a nucleophile to the metal; (iv) favouring the complete loss of the leaving group with its lone pair and the formation of a three-coordinate intermediate in which the total concentration of charge density around the metal is largely decreased. Strong σ-donation from the η^1-carbanions and from the coordinated phosphane confer sufficient thermodynamic stability to the T-shaped intermediates formed from dissociation of **1**–**6**.

The stereoelectronic analysis of the coupling constants $^1J_{PtP}$ for **1**–**6** has shown that there is an efficient flow of charge density along the P–Pt–C bond axis on changing the basicity (χ values) of the coordinated phosphane. This electronic flow hardly affects the individual rates of the various complexes (the average value of the free activation energy being $\Delta G^{\ddagger}_{av} = 80.7 \pm 0.8$ kJ mol^{-1}), even if linear correlations with χ are observed for the activation enthalpy [$\Delta H^{\ddagger} = (102 \pm 1) - (1.0 \pm 0.1)\chi$] and for the activation entropy [$\Delta S^{\ddagger} = (80 \pm 1) - (4.17 \pm 0.07)\chi$], considering rogue point the data for complex **6**. Thus, on increasing the phosphane basicity both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase and $\Delta G^{\ddagger}$ remains substantially constant. This result for a *cis*-effect is not surprising once we have seen that the change of the nature of the coordinated *cis*-group (from Me_2SO to PR_3) has had so little effect on the reactivity. The correlations observed for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with χ imply a linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ [isokinetic plot, $\Delta H^{\ddagger} = (81.7 \pm 0.8) + (0.25 \pm 0.03)\Delta S^{\ddagger}$]. The application of the Linert method [43] to check whether we are really dealing with an isokinetic plot and with an isokinetic temperature, or simply with a 'compensation effect' has revealed that this latter is the case. The compensation suggests, as expected, that all complexes react with the same mechanism.

5. Conclusion

A complex having a set of donor atoms of the type *cis*-[Pt(C,C)(S)(P)] (C = strong σ-donor η^1-carbanions; S, sulfoxide; P, tertiary phosphane) behaves like *cis*-[Pt(C,C)(S,S)] for which a dissociative mechanism for ligand exchange and substitution is well established. Contrary to the pattern shown by a strong π-electron acceptor (carbon monoxide) the change from Me_2SO to the σ-donors PR_3, as that from CH_3 to C_6H_5, does not produce a changeover of mechanism or greatly affects the ease with which the dissociative activation takes place. The possible stabilisation of the T-shaped three-coordinate intermediate by electron donation of the phosphane ligands or by interaction between the metal and the *ortho* hydrogens in the phenyl rings play little, if any, part in promoting the dissociative nature of the process.

6. Supplementary material

Table S1 giving primary kinetic data (pseudo-first-order rate constants, k_{obsd} (s^{-1}), for isotopic labelling experiments and for nucleophilic substitution on compounds **1**–**6**) as a function of temperature and ligand concentration. This material is available from the authors on request.

Acknowledgements

The authors wish to thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000–2002, the Università degli Studi di Messina and CNR for funding this work.

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.C. Finke, Principle and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
[2] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley-Interscience, New York, 1994.
[3] G.W. Parshall, Homogeneous Catalysis, Wiley-Interscience, New York, 1980.
[4] A. Yamamoto, Organotransition Metal Chemistry, Wiley, New York, 1986.
[5] R. Romeo, Comm. Inorg. Chem. 11 (1990) 21.
[6] G. Alibrandi, M. Cusumano, D. Minniti, L. Monsù Scolaro, R. Romeo, Inorg. Chem. 28 (1989) 342 (and references therein).
[7] For general reviews of β-elimination reactions, see R.J. Cross, in: F.R. Hartley, S. Patai, (Eds.), The Chemistry of the Metal–Carbon Bond, vol. 2, Wiley, New York, 1985, Chapter 8, and Refs. [8,9].
[8] G.M. Whitesides, Pure Appl. Chem. 53 (1981) 287.
[9] A. Yamamoto, T. Yamamoto, S. Komiya, F. Ozawa, Pure Appl. Chem. 56 (1984) 1621.
[10] R. Romeo, G. Alibrandi, L. Monsù Scolaro, Inorg. Chem. 32 (1993) 4688.
[11] B.B. Coussens, F. Buda, H. Oevering, R.J. Meier, Organometallics 17 (1998) 795 (and references therein).
[12] R.S. Paonessa, W.C. Trogler, J. Am. Chem. Soc. 104 (1982) 3529.
[13] G. Alibrandi, R. Romeo, Inorg. Chem. 36 (1997) 4822 (and references therein).
[14] A.L. Casado, J.A. Casares, P. Espinet, Inorg. Chem. 37 (1998) 4154.
[15] R. Romeo, M.R. Plutino, L.I. Elding, Inorg. Chem. 36 (1997) 5909 (and references therein).
[16] M.W. Holtcamp, J.A. Labinger, J.E. Bercaw, Inorg. Chim. Acta 265 (1997) 117.
[17] S.S. Stahl, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 5961.
[18] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[19] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643 (and references therein).
[20] J.A. Casares, S. Coco, P. Espinet, Y.S. Lin, Organometallics 14 (1995) 3058.
[21] A. Gelling, K.G. Orrell, A.G. Osborne, V. Sik, J. Chem. Soc., Dalton Trans. (1998) 937.

[22] R. Romeo, L. Fenech, L. Monsù Scolaro, A. Albinati, A. Macchioni, C. Zuccaccia, Inorg. Chem. 40 (2001) 3293.
[23] R. Romeo, L. Fenech, S. Carnabuci, M.R. Plutino, A. Romeo, Inorg. Chem. 41 (2002) 2839.
[24] F. Basolo, Coord. Chem. Rev. 154 (1996) 151.
[25] M.R. Plutino, L. Monsù Scolaro, R. Romeo, A. Grassi, Inorg. Chem. 39 (2000) 2712 (and references therein).
[26] R. Romeo, A. Grassi, L. Monsù Scolaro, Inorg. Chem. 31 (1992) 4383.
[27] O.F. Wendt, R.J. Deeth, L.I. Elding, Inorg. Chem. 39 (2000) 5271.
[28] D. Minniti, G. Alibrandi, M.L. Tobe, R. Romeo, Inorg. Chem. 26 (1987) 3596.
[29] C. Eaborn, K. Kundu, A.J. Pidcock, J. Chem. Soc., Dalton Trans. (1981) 933.
[30] (a) A.L. Van Geet, Anal. Chem. 40 (1968) 2227;
(b) A.L. Van Geet, Anal. Chem. 42 (1970) 679.
[31] SCIENTIST, Micro Math Scientific Software, Salt Lake City, UT.
[32] A.L. Fernandez, A. Prock, W.P. Giering, The QALE Web Site, rhttp://www.bu.edu/qale/.
[33] T. Bartik, T. Himmler, H.G. Schulte, K. Seevogel, J. Organomet. Chem. 272 (1984) 29.
[34] M.R. Wilson, D.C. Woska, A. Prock, W.P. Giering, Organometallics 12 (1993) 1742.
[35] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[36] R. Romeo, G. Arena, L. Monsù Scolaro, Inorg. Chem. 31 (1992) 4879.
[37] R. Romeo, M.R. Plutino, L. Monsù Scolaro, S. Stoccoro, Inorg. Chim. Acta 265 (1997) 225.
[38] F.H. Allen, A. Pidcock J. Chem. Soc. (A) (1968) 2700.
[39] T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.
[40] R. Romeo, Comm. Inorg. Chem. 23 (2002) 79.
[41] C.M. Haar, P.S. Nolan, W.J. Marshall, K.G. Moloy, A. Prock, W.P. Giering, Organometallics 18 (1999) 474.
[42] G. Alibrandi, G. Bruno, S. Lanza, D. Minniti, R. Romeo, M.L. Tobe, Inorg. Chem. 26 (1987) 185.
[43] (a) W. Linert, R.F. Jameson, Chem. Soc. Rev. 477 (1989) 18;
(b) W. Linert, Inorg. Chim. Acta 233 (1988) 141.