Ring Closure Kinetics of Bidentate Hemilabile P,N and P,S Ligands on a Platinum(II) Complex

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Complexes of the type *cis*-[$PtPh_2(CO)(\eta^1$-P–N)] and *cis*-[$PtPh_2(CO)(\eta^1$-P–S)], where bidentate phosphorus–nitrogen and phosphorus–sulfur ligands are bound to the metal centre in a monodentate fashion [P–N = $Ph_2PC_5H_4N$ (Ph_2PPy), $Ph_2P(CH_2)_2C_5H_4N$ (ppye), $Ph_2P(o\text{-}C_6H_4)NMe_2$ ($PNMe_2$), $Ph_2P(CH_2)_nNMe_2$ (n = 2, 3, i.e., $peNMe_2$ and $ppNMe_2$) and P–S = $Ph_2P(CH_2)_2SEt$ (P–SEt), $Ph_2P(CH_2)_nSPh$ (n = 1, 2, i.e., P–CH_2SPh and P–SPh)], were prepared in situ by reaction of the hybrid ligands with *cis*-[$PtPh_2(CO)(SEt_2)$]. In each case, the first observed process was the fast substitution of diethyl sulfide by the phosphanyl group leading to the monosubstituted ring-open *cis*-[$PtPh_2(CO)(\eta^1$-P–X)] (X = N or S) complexes, which were characterised in solution by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. These initially formed species undergo a slow ring closure process with extrusion of carbon monoxide and formation of the chelate [$PtPh_2$(P–X)] products, except in the case of the short-bite Ph_2PPy and P–CH_2SPh ligands and of $ppNMe_2$, where ring closure was not observed. The chelate complexes were isolated as solids from the reaction of the ligands with *cis*-[$PtPh_2(Me_2SO)_2$]. A single-crystal X-ray diffractometric study of *cis*-[$PtPh_2$(P–SEt)] (**18**) was performed. The crystal packing showed linear chains originated by weak intermolecular Pt···H–C hydrogen bonding interactions. The chelation kinetics of P–X in the *cis*-[$PtPh_2(CO)(\eta^1$-P–X)] complexes have been monitored in [D]chloroform by ^{1}H and $^{31}P\{^1H\}$ NMR. The rates of ring closure were found to be strongly dependent on the nature (S or N) and steric hindrance of the chelating end of the monocoordinated bidentate P–X ligand, and on the size of the ring formed. In contrast, ring size plays a negligible role, if any, in the dechelation reactions of *cis*-[$PtPh_2$(S–S)] [S–S = 1,2-bis(phenylthio)ethane, dpte and 1,3-bis(phenylthio)propane, dptp] using diphosphanes (dppm and dppp) as reagents. These kinetic data, together with those of previous work, give useful insight into the factors controlling cyclisation reactions and the stability of the rings in square planar platinum(II) complexes.

Introduction

Factors affecting the ease of cyclisation of bifunctional organic chains, such as ring strain and the probability of end-to-end joining, have been well understood and recognised in physical organic chemistry, through detailed kinetic studies. At this stage they are at the basis of synthetic procedures in making rings of all sizes as well as macrocycles.[1,2] By contrast, in coordination or organometallic chemistry, kinetic studies on the formation of chelated rings are relatively scarce because of the difficulty of monitoring the rate of ring closure that, usually, is much faster than the rate of attack of the first end of the bidentate ligand on the metal centre. An old practice of overcoming this difficulty is to render the uncoordinated end of the ligand inactive by steric hindrance or protonation. This latter approach has been used with the formation of certain five- and six-membered chelated rings involving amino acids,[3] amino alcohols,[4] amino sulfides,[5] or diamines,[6−12] in platinum(II) complexes. The rate of ring closure can be modulated through an appropriate control of the acidity of the solution but, in most cases, it is not possible to separate the rate constant for ring closure from the acid dissociation constant of the protonated end of the ligand.

An alternative approach involves the generation in solution of coordinatively unsaturated species by photolysis, in the presence of a bidentate ligand L−L, as for $M(CO)_6$ (M = Cr, Mo, W) complexes.[13−18] The reaction involves photodissociation of one CO ligand to yield an extremely reactive $M(CO)_5$ species which captures L−L, leading to an $M(CO)_5(\eta^1$-L−L) intermediate with a monocoordinate bidentate ligand. Thereby, ring closure follows with loss of

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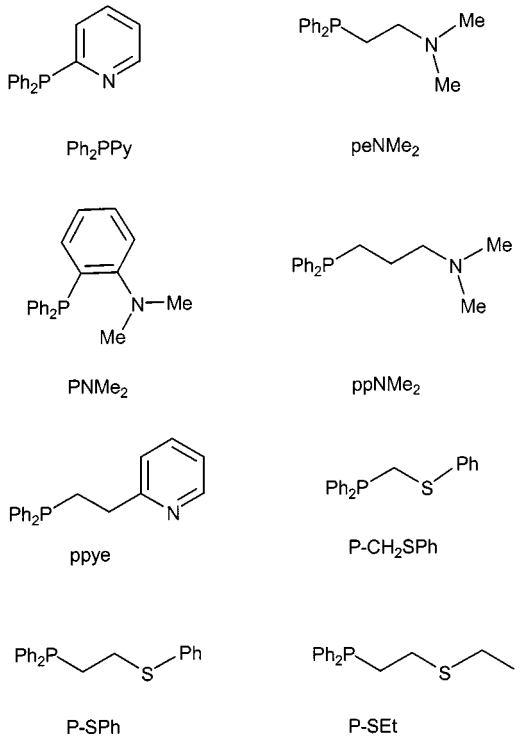
another CO ligand. If this latter process is too rapid, it is necessary to use flash photolysis techniques to initiate the kinetics.[19−24] In some cases the intimate nature of the thermal process was revealed by the determination of the volumes of activation.[20−24]

In the study of the reactivity of the complex *cis*-[$PtPh_2(CO)(SEt_2)$] (**1**) with pyridines[25] and amines[26] we became aware that this substrate contains a labile SEt_2 and a relatively inert CO ligand in the *trans* positions to the firmly bonded phenyl groups. The substrate showed a remarkable selectivity between the two nucleophilic ends of an unsymmetrical bidentate ligand, with a clear preference for the most basic and the less hindered end. Thus, we have exploited this property to prepare stable ring-open species such as *cis*-[$PtPh_2(CO)(\eta^1\text{-}NH_2(CH_2)_4NH_2)$] and *cis*-[$PtPh_2(CO)(\eta^1\text{-}NH_2(CH_2)_2NHPh)$] in solution, to intercept and characterise monocoordinate reaction intermediates of the type *cis*-[$PtPh_2(CO)(\eta^1\text{-}N-N)$] or *cis*-[$PtPh_2(CO)(\eta^1\text{-}P-P)$] in the reactions of this complex with diamines,[27] aminopyridines,[27] or diphosphanes,[28] and to identify the factors controlling the rates of their final conversion into the chelate products with extrusion of CO.

In this paper we have extended the study to so-called "hemilabile" ligands. New classes of unsymmetrical bidentate ligands (P−X) were recently developed and used in organometallic chemistry, which associate the phosphorus atom with donor atoms such as oxygen,[29] nitrogen[30] or sulfur.[31] Indeed it was expected, and it has often been observed, that the non-phosphorus donor X of the ligand is weakly coordinated in solution to the metal centre, generating potential catalytically active systems, by providing, under mild conditions, a vacant site for the coordination and activation of organic substrates. To complete the outline of reactivity of **1** we have chosen a series of hybrid ligands P−X of different chain length, bearing a diphenylphosphanyl group and a substituted sulfur or nitrogen atom of variable electronic and steric properties. The high lability of the SEt_2 group in the starting substrate, combined with the very high nucleophilic power of the phosphorus donor of the bidentate ligands, leads ineluctably to the rapid formation of *cis*-[$PtPh_2(CO)(\eta^1\text{-}P-X)$] and to a subsequent relatively slow ring closure to the final product [$PtPh_2(P-X)$]. The kinetics of ring closure of P−X ligands, together with those of dinitrogen and diphosphane ligands studied previously,[27,28] give a useful insight into the factors controlling these cyclization reactions and the stability of the rings in square-planar complexes.

thioether, a dimethylamino or a pyridyl function, characterised by different steric and electronic properties, and separated from the phosphorus atom by a backbone of variable length. The reaction takes place very rapidly at room temperature and produces the monosubstituted species in quantitative yield. The most interesting feature of this reaction concerns the selectivity of the nucleophilic site of attack of the unsymmetrical ligand that is invariably the phosphanyl group. The phosphorus atom enters the coordination sphere of the metal centre leaving the remaining nitrogen or sulfur atoms free. This is in line with the sequence of reactivity, phosphane[32] >> amine[26] > pyridine[25] of a monodentate ligand replacing SEt_2 from **1**, while the subsequent substitution of the carbonyl group takes place very slowly. Thus, the pattern of behaviour of the P−X ligands reflects the different nucleophilicity of the two donors (P and S or N) of the ligand. This peculiar selectivity of the substrate between the two ends of an unsymmetrical ligand was already shown in the reactions with dinitrogen ligands such as 2-(aminomethyl)pyridine and 2-(2-aminoethyl)-pyridine.[27]



Scheme 1

Results and Discussion

Synthesis and Structural Characterisation of the Complexes

Complexes *cis*-[$Pt(Ph)_2(CO)(\eta^1\text{-}P-X)$] (**4−11**), in which P−X acts as a *P*-bound monodentate ligand, were prepared in situ by treating equimolar amounts of ligand and complex **1**. Sketches of the heteronuclear ligands used are given in Scheme 1. The P−X unsymmetrical species contain on one side a diphenylphosphanyl group and on the other a

The complexes [$PtPh_2(SEt_2)]_2$ (**2**) and *cis*-[$PtPh_2(Me_2SO)_2$] (**3**) proved to be very useful synthons for the synthesis of chelate complexes. The addition of an equimolar amount of a P−X ligand to a dichloromethane solution of **3**, according to Equation (1) leads to the rapid substitution of both sulfoxide ligands, yielding chelate compounds in a pure crystalline form and in almost quantitative yield.

$$cis\text{-}[PtPh_2(Me_2SO)_2] + P{-}X \rightarrow cis\text{-}[PtPh_2(P{-}X)] + 2\ Me_2SO \quad (1)$$

In a similar fashion, these compounds were formed starting from the dinuclear complex **2**, in the presence of a moderate excess of SEt_2.The cyclization reaction failed in the case of the short-bite Ph_2PPy and $P{-}CH_2SPh$ ligands and also $ppNMe_2$, but was successful for the formation of the chelate *cis*-$[PtPh_2(S{-}S)]$ complexes, containing the dithioether ligands dpte (**12**) and dptp (**13**). The isolation of the chelate complexes as solid compounds allowed for their complete characterisation through ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes **14**–**18** are characterised by the presence, on the coordination plane, of two phenyl groups in the mutual *cis* position and of a 5- or 6-membered ring, arising from the coordination of the hybrid chelating ligand.

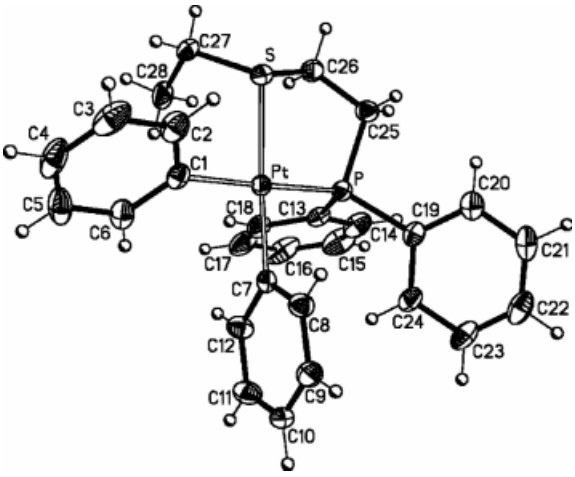


Figure 1. Perspective view and atom numbering scheme of one of the two equal complex units of compound **18**; thermal ellipsoids are drawn at 30% probability, while the H size is arbitrary

X-ray Structure of 18

The crystallographic asymmetric unit contains two independent molecules which are related by a pseudo two-fold screw axis 2_1 parallel to cell edge *a*. However, both are essentially identical structurally (Table 1) and one of them is illustrated in Figure 1. The main differences concern the arrangement of the phenyl groups. The η^1-phenyl rings are almost equally oriented with respect to the Pt coordination plane in the two complexes [53.1(2) vs. 52.8(2)° and 99.0(4) vs. 95.2(4)° for $C1_{Ph}$ and $C7_{Ph}$ planes, respectively] forming a reciprocal dihedral angle of 71.0(4) vs. 63.9(3)°. The same behaviour is exhibited by the phenyl groups of the diphenylphosphane fragment, with the $C13_{Ph}$ ring forming a dihedral angle of 79.2(2) vs. 66.1(3)° with the other $C19_{Ph}$ plane. The square-planar coordination around the two platinum atoms is almost identical and the geometric values are in agreement with those of other arylplatinum[26,33] and 1-(ethylthio)-2-(diphenylphosphanyl)ethane complexes.[31d,34] Both the two Pt–P and Pt–S bonds [mean length 2.280(3) and 2.352(2) Å, respectively] show a significant elongation caused by the strong *trans* influence of the η^1-phenyl acting as a powerful σ-donor, as already reported for the compound *cis*-$[PtPh_2(SMe_2)_2]$.[35] The chelating ligand forms a five-membered puckered ring with a bite angle of 85.97(7) vs. 86.30(8)°. The sulfur atoms display a tetrahedral arrangement acting as a stereogenic akyrotopic centre, but the solid state is a racemic mixture due to centrosymmetric space group.

The most interesting feature of the solid state is the presence of a weak nonconventional intermolecular hydrogen-bonding interaction between each platinum atom and the terminal methyl group of the diphenylphosphanyl ligand of the adjacent complexes (Figure 2). This interaction corresponds to a 3-centre-4-electron (3c-4e) model, the three centres being the C, H and Pt atoms and the four electrons belonging two each to the C–H bond and to the platinum d_z^2 orbital.[36] The two C–H···Pt interactions are almost equal [C(28)H···Pt = 2.94 vs. 2.88Å, C(28)···Pt = 3.68(1) vs. 3.680(8) Å, C(28)–H···Pt = 135 vs. 141°]. Despite the fairly high electron density available on the metal ion,[37] it seems that the Pt···H interaction is weak owing to the low electropositive character of the interacting hydrogen atom. This hydrogen interaction alternatively connects the two independent complexes of adjacent asymmetric units along the crystallographic axis *a*. The crystal packing is constituted by infinite columns parallel to *a* and interconnected by van der Waals interactions as a monodimensional polymer. The weakness of the hydrogen bond in the solid state precludes its existence in solution, as evidenced by the absence in the ^1H NMR spectrum of **18,** in $CDCl_3$, of upfield or downfield chemical shifts or of scalar ^1H-^{195}Pt couplings.

Table 1. Selected bond lengths [Å], bond and torsional angles [°] for the two independent molecules in the crystal unit

Pt–C(1)	2.069(8)	2.039(8)	P–C(13)	1.807(8)	1.813(9)
Pt–C(7)	2.033(7)	2.016(8)	P–C(19)	1.817(8)	1.800(9)
Pt–P	2.282(2)	2.277(2)	P–C(25)	1.841(7)	1.835(9)
Pt–S	2.353(2)	2.352(2)			
C(7)–Pt–C(1)	88.5(3)	90.6(3)	C(7)–Pt–P	94.2(2)	91.8(2)
P–Pt–S	85.97(7)	86.30(8)	C(1)–Pt–S	91.7(2)	91.9(2)
S–Pt–C(1)–C(2)	−51.6(6)	−50.3(6)	P–Pt–C(7)–C(8)	96.2(6)	95.9(6)
S–Pt–P–C(13)	−101.6(3)	−109.7(3)	S–Pt–P–C(19)	132.4(3)	125.5(3)
P–C(25)–C(26)–S	53.5(7)	37(1)	Pt–S–C(27)–C(28)	−40.8(8)	−43(1)

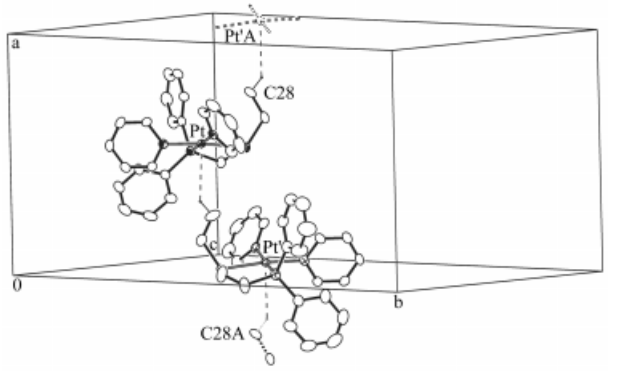


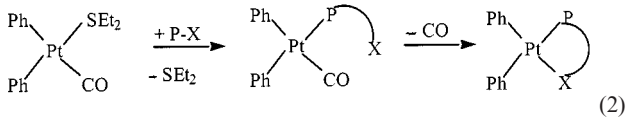
Figure 2. View of crystallographic asymmetric unit showing the intermolecular H bonds between the two independent complexes and the adjacent units translated along the crystallographic *a* axes ($x \pm 1$, y, z); shaded unit is the complex reported in Figure 1; thermal ellipsoids at the 10% probability level while the hydrogen size is arbitrary

NMR Characterisation

Selected ^{1}H and ^{31}P{^{1}H} NMR resonances for ring-open and chelate compounds are given in Table 2. Within the chelate compounds **14−18** the average value of $^1J_{PtP}$ for the ^{31}P{^{1}H} signal is found at 1885 Hz, typical for a phosphorus atom *trans* to a σ-Pt−C bond.[28,32] A remarkable decrease of the $^1J_{PtP}$ coupling constant is found for the ring-open derivatives **4−11** ($^1J_{PtP}$ average value 1603 Hz). For those ligands (peNMe$_2$, PNMe$_2$, P−SPh and P−SEt) which form a 5-membered ring upon chelation, the coordination of the N or S donor is confirmed by the marked downfield shift of the δ^{31}P values. In fact, an increase of ca. 20 ppm is observed for the P−N ligands (in complexes **15** and **16**), while a higher Δδ (ca. 30 ppm) is found for the P−S ligands (in complexes **17** and **18**). These features are in accordance with the criterion proposed by Garrou for assessing chelation in the case of P-containing potentially chelating ligands.[38] Furthermore, the chemical shift values reported here for the P−S species are very close to that found for other Pt^{II} derivatives with the same ligands.[31e] Finally, chelation in compound **14** (where the ligand ppye forms a six-membered ring) is proved on the basis of the existence of a ^{195}Pt-^{1}H scalar coupling between the metal and a proton of the "far-from-P" side of the ligand. In fact, the H^6 nucleus of the pyridine ring at δ = 8.55 exhibits a $^3J_{PtH}$ coupling of 23 Hz, while conversely the same proton in the corresponding ring-open complex **5** exhibits no coupling.

Ring Closure Reactions

As described above, the formation of the chelate complexes occurs in two steps, according to Equation (2): (i) a fast formation of the ring-open species, on mixing equivalent amounts of complex and ligand, (ii) a subsequent slow ring closure. The course of the reaction can be effectively monitored in [D]chloroform by ^{1}H or ^{31}P{^{1}H} NMR spectroscopy, through the changes in intensity of appropriate signals.



(2)

Typical time-resolved NMR spectra for a kinetic run with ppye are shown in Figure 3. The mol fraction F = [**A**]/([**A**] + [**B**]) of the unchanged complex **A** was obtained by integration of the signals and the first-order rate constant k_c [s^{-1}] for ring closure was obtained from a nonlinear least-squares fit of the experimental data to $F = c_1 + c_2 \exp(-k_c t)$, with c_1, c_2, and k_c as the parameters to be optimised. A similar analysis can be performed using the mol fraction of the chelate product **B**. In order to account for the possible re-entry of carbon monoxide into the coordina-

Table 2. Selected ^{1}H and ^{31}P NMR spectroscopic data for ring-open *cis*-[Pt(Ph)$_2$(CO){η^1-(P−X)}] (numbers in square brackets) and chelate [PtPh$_2$(P−X)] complexes[a]

No.	P−X	^{1}H	^{31}P
[4]	PPh$_2$Py	8.83 (*H*^{6}-py)	20.1 (1636)
[5]	ppye	2.74 (C*H*$_2$−P), 2.55 (C*H*$_2$−N), **8.39** (*H*^{6}-py)	12.9 (1592)
14	ppye	3.59 (C*H*$_2$−P), 2.36 (C*H*$_2$−N), **8.55** (23) (*H*^{6}-py)	16.4 (1886)
[6]	peNMe$_2$	2.01 (C*H*$_3$−N)	**9.8** (1585)
15	peNMe$_2$	2.72, 2.57 (18) (C*H*$_3$−N), 2.34	**31.0** (1915)
[7]	ppNMe$_2$	2.02 (C*H*$_3$−N), 1.94, 1.83, 1.43	13.8 (1598)
[8]	P−NMe$_2$	**2.71** (C*H*$_3$−N)	11.1 (1679)
16	P−NMe$_2$	**3.10** (17) (C*H*$_3$−N)	31.1 (1990)
[9]	P−CH$_2$SPh	3.37 (13.0) (C*H*$_2$−P)	12.9 (1593)
[10]	P−SPh	2.66, **2.26**	11.4 (1570)
17	P−SPh	2.99 (C*H*$_2$−P), **2.38** (C*H*$_2$−S)	41.6 (1803)
[11]	P−SEt	2.32, 2.24 (C*H*$_2$, CH$_3$−C*H*$_2$−S), **1.07** (C*H*$_3$−CH$_2$−S)	11.5 (1576)
18	P−SEt	2.80 (C*H*$_2$−P), 2.66 (CH$_3$−C*H*$_2$−S), 2.49 (C*H*$_2$−S), **1.20** (C*H*$_3$−CH$_2$−S)	40.2 (1832)

[a] In CDCl$_3$ at 298.2 K. Chemical shifts (δ) are reported in ppm downfield from TMS. Coupling constants with ^{195}Pt ($^3J_{PtH}$ and $^1J_{PtP}$) in Hz are given in parentheses. Peaks reported in bold were used for monitoring kinetics.

tion sphere of the metal ion, all the rate data were recalculated by using SCIENTIST[39] and the equation $-d[\mathbf{A}]/dt = k_c[\mathbf{A}] - k_2[\mathbf{B}][CO]$, where [**A**], [**B**] and [CO] are the concentrations of the ring-open complex, the chelate complex and carbon monoxide, respectively; k_c and k_2 are the rate constants for ring closure [s^{-1}] and ring opening [$M^{-1}\ s^{-1}$]. For the short-bite ligands Ph_2PPy (**4**), $P-CH_2SPh$ (**9**) as well as for $ppNMe_2$ (**7**) the only reaction observed was the fast formation of the ring-open species stable in solution for a long time before decomposition occurs. A summary of the relevant kinetic data for ring closure reactions are given in Table 3 together with data relative to diphosphanes and dinitrogen symmetrical and unsymmetrical ligands obtained in previous work.[27,28]

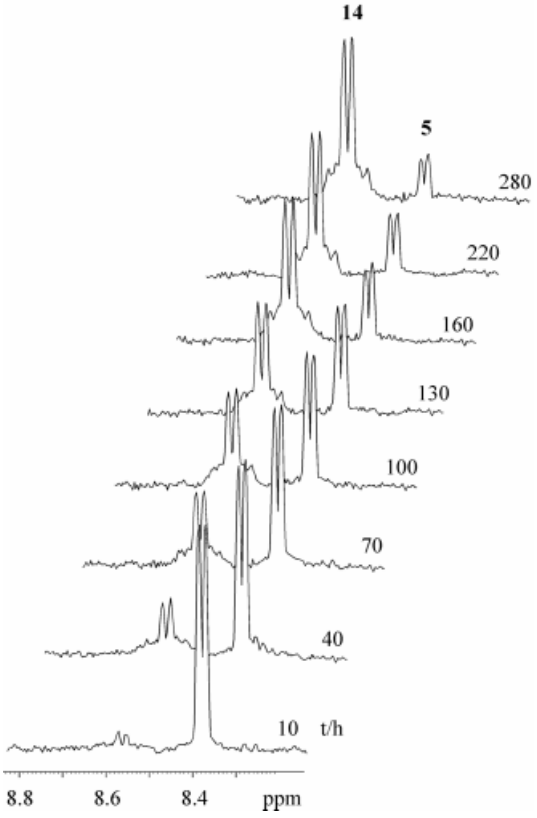
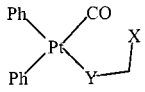
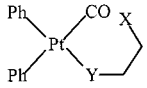
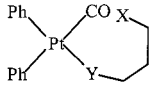
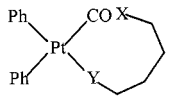


Figure 3. ^1H NMR spectral changes associated with ring closure on *cis*-[$PtPh_2$(CO)(η^1-ppye)] (**5**) in $CDCl_3$ at 298 K; the signals monitored are those of the H^6-py proton at $\delta = 8.39$ for the ring-open and at $\delta = 8.55$ for the chelate [$PtPh_2$(ppye)] (**14**) complex, respectively

Table 3. Summary of kinetic data for ring closure of dinitrogen, diphosphane and hybrid P−X (X = N, S) ligands[a]

	Ligand	Y	X	$10^5 k_c/s^{-1}$
4-membered rings	dppm	PPh_2	PPh_2	1980 ± 100[b]
	Ph_2PPy	PPh_2	py	0[c]
	$P-CH_2SPh$	PPh_2	SPh	0[c]
5-membered rings	dppe	PPh_2	PPh_2	very fast[b]
	P–SEt	PPh_2	SEt	340 ± 10[c]
	P–SPh	PPh_2	SPh	0.65 ± 0.03[c]
	$peNMe_2$	PPh_2	NMe_2	18 ± 2[c]
	$PNMe_2$	PPh_2	NMe_2	6.9 ± 0.4[c]
	en	NH_2	NH_2	136 ± 3.2[d]
	2-ampy	NH_2	py	31.0 ± 0.55[d]
	N-(Ph)en	NH_2	NHPh	0[d]
6-membered rings	dppp	PPh_2	PPh_2	very fast[b]
	ppye	PPh_2	py	0.43 ± 0.02[c]
	$ppNMe_2$	PPh_2	NMe_2	0[c]
	dap	NH_2	NH_2	14.0 ± 0.34[d]
	2-aepy	NH_2	py	2.72 ± 0.34[d]
	dpy	py	py	4.16 ± 0.10[d]
	dps	py	py	18.8 ± 0.3[d]
7-membered rings	dppb	PPh_2	PPh_2	273[b]
	dab	NH_2	NH_2	0[d]

[a] In $CDCl_3$ at 298 K, unless otherwise mentioned. [b] From ref.[28] [c] This work. [d] From ref.[27], in CD_2Cl_2 as solvent. Abbreviations for ligands not encountered in the text: dppe = 1,2-bis(diphenylphosphanyl)ethane; en = 1,2-ethylenediamine; 2-ampy = 2-(aminomethyl)pyridine; *N*-(Ph)en = *N*-phenylethylendiamine; dap = 1,3-diaminopropane; 2-aepy = 2-(2-aminoethyl)pyridine; dpy = dipyrid-2-ylamine; dps = dipyrid-2-yl sulfide; dppb = 1,4-bis(diphenylphosphanyl)butane; dab = 1,4-diaminobutane

Dechelation Reactions

Complexes of the type [$PtPh_2$(S−S)] [S−S = dpte (**12**), dptp (**13**)] were easily prepared in high yield by reaction of **2** with the appropriate dithioether ligand S−S in dichloromethane at room temperature. Any attempt to prepare platinum(II) derivatives with shorter or longer S−S ligands [i.e. bis(phenylthio)methane and 1,4-bis(phenylthio)butane] failed, due to the instability of four- and seven-membered chelate rings. The analysis of the ^1H NMR spectral changes during the course of the reaction with diphosphane ligands (P−P = dppm, dppe, dppp) showed a single-stage conversion from the starting complex to the final chelate compound, according to Equation (3).

$$[PtPh_2(S\text{-}S)] \xrightarrow[+\ (P\text{-}P)]{k_{obs}} cis\text{-}[PtPh_2(\eta^1\text{-}S\text{-}S)(\eta^1\text{-}P\text{-}P)] \xrightarrow[-\ (S\text{-}S)]{fast} [PtPh_2(P\text{-}P)] \quad (3)$$

For example, the ^1H NMR spectrum of [$PtPh_2$(dpte)] in $CDCl_3$ at 298 K showed a broad singlet for the methylene protons (at $\delta = 3.03$; $^3J_{PtH} = 16.6$ Hz) and a doublet ($\delta = 7.38$; $^3J_{PtH} = 76$ Hz) in the aromatic region, relative to the *ortho*-protons of the coordinated phenyl rings. By addition of dppm, in an 1:1 ratio, these peaks begin to decrease in intensity and new signals appear which belong to [$PtPh_2$(dppm)] (methylene proton signals at $\delta = 4.36$), together with a sharp singlet at $\delta = 3.10$ of free dpte. The $^{31}P\{^1H\}$ NMR spectrum of the reaction product shows a singlet at $\delta = -37.6$ with platinum satellites of 1392 Hz, typical of the four-membered diphosphane chelate ring. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the compound agree

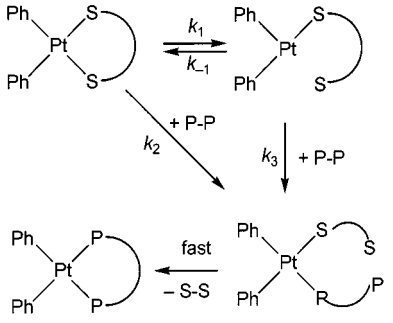
with its formulation as a diaryl(phosphanyl)platinum chelate complex.[28] No intermediate species were detected in solution during the reaction and addition of excess dppm does not significantly affect the reaction. The same behaviour was observed using dppe or dppp as reagents, with formation of the phosphane-chelated derivatives [$PtPh_2$(dppe)] and [$PtPh_2$(dppp)], respectively.

Reaction according to Equation (3) (P−P = dppm, dppp) was carried out under pseudo-first-order conditions in dichloromethane at 298.2 K, using spectrophotometric techniques. The kinetics were monitored by repetitive scanning of the spectrum at suitable times in the wavelength range 315−350 nm, where the absorbance of the free diphosphane ligand is negligible. The reactions went to completion, the final spectra being identical to those of authentic samples of [$PtPh_2$(P−P)] complexes.[28] Abstract factor analysis[40] of the spectral changes confirmed the presence of only two absorbing species in solution, i.e. the starting complex [$PtPh_2$(S−S)] and the final diphosphane product [$PtPh_2$(P−P)]. The pseudo-first-order rate constants k_{obs} calculated from the kinetic traces, are listed in the Supporting Information (Table SI1, see footnote on the first page of this article). On plotting k_{obs} as a function of the entering diphosphane concentration straight lines were obtained with a y axis intercept different from zero. Linear regression analysis applied to the rate data and fitted with the simple two-term Equation (4) gave the following values of the rate constants for the two systems: (i) for [$PtPh_2$(dpte)], $k_1 = (0.004 \pm 0.0008)\ s^{-1}$, $k_2 = (1.04 \pm 0.03)\ M^{-1}s^{-1}$ in the reaction with dppm, and $k_1 = (0.007 \pm 0.0001)\ s^{-1}$, $k_2 = (1.86 \pm 0.05)\ M^{-1}s^{-1}$ with dppp; (ii) for [$PtPh_2$(dptp)] $k_1 = (0.004 \pm 0.0008)\ s^{-1}$, $k_2 = (1.00 \pm 0.03)\ M^{-1}s^{-1}$ in the reaction with dppm.

$$k_{obs} = k_1 + k_2\,[\text{P-P}] \quad (4)$$

We know from previous studies[37] that complexes containing ligands with an array of donor atoms of the type *cis*-[Pt(C,C)(S,S)] (C = alkyl or aryl; S = thioether or sulfoxide) show a great propensity to undergo substitution of one sulfur ligand through a dissociative mechanism. The reasons for the observed behaviour are a combination of (i) ground-state destabilisation (lengthening of the Pt−S bond), (ii) increase of electron density at the metal centre preventing the approach of weak nucleophiles, and (iii) stabilisation of the coordinatively unsaturated three-coordinated intermediate. The most likely mechanism that can be envisaged for substitution reactions of the chelated [$PtPh_2$(S−S)] complexes, on the basis of the behaviour of strictly similar substrates containing monodentate thioethers,[41] is depicted in Scheme 2, and involves: (i) dissociative opening of the chelate S−S ring (k_1 path) to yield a ring-open three-coordinated 14-electron intermediate, (ii) competition for it between ring closure (k_{-1} path) and the attack of one end of the diphosphane ligand (via k_3) to form a doubly ring-open species and, (iii) final fast ring closure of P−P to yield the observed products. The pathway via k_2 represents the usual direct bimolecular attack of the nucleophile on the substrate. The rate law derived for this mechanism obeys Equation (5) which reduces to $k_{obs} = k_1 + k_2\,[\text{P−P}]$, when $k_{-1} << k_3\,[\text{P−P}]$.

$$k_{obs} = k_1 k_3\,[\text{P−P}]/(k_{-1} + k_3\,[\text{P−P}]) + k_2\,[\text{P-P}] \quad (5)$$



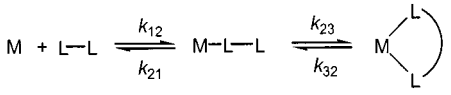
Scheme 2

Thus, the values derived for k_1 and k_2 represent the rate constants for ring opening upon dissociation of the Pt−S bond (k_1 [s^{-1}]) and upon bimolecular attack of the nucleophile (k_2 [$M^{-1}s^{-1}$]). The values of k_1 and k_2 derived for the two complexes do not show appreciable differences, indicating that both the pathways for dechelation (dissociative and associative) are hardly affected by the length of the ring (five- or six-membered).

The Chelate Effect

The formation constant of a metal−chelate complex is related to the rate constants of the separate bond-making and bond-breaking steps in Scheme 3 by the expression $K_f = k_1k_3/k_2k_4$. For octahedral systems, such as Co^{III} and Ni^{II} chelates, there is increasing evidence indicating that the processes of metal−ligand bond formation (k_1 and k_3) and loss of a monodentate ligand (k_2) hardly affect the stability of the chelate. An unexpected slowness of the ring-opening reaction (k_4) accounts for the high formation constant of the chelates,[42] while the effect has traditionally been associated with a high chelate ring-closing rate constant (k_3). Two different explanations have been given to account for the slowness of this dissociatively activated pathway (k_4). For ethylendiamine complexes of relatively small ions, Funahashi et al.[43] have proposed that the elongation of the M−N separation, along the coordinate reaction, forces the metal−nitrogen−carbon (M−N−C) angle to decrease, thus increasing the energy involved in the formation of the transition state. In the case of a monodentate amine such angular distortion around the leaving nitrogen donor is absent. Very recently, Blackman, Clark et al.[44] have given an alternative explanation for the much slower rate of chelate ring-opening in $[Co(cyclen)(diamine)]^{3+}$ compared to the loss of NH_3 from $[Co(cyclen)(NH_3)_2]^{3+}$, based on the reduced ability of the former system to allow the bond angle expansion required to produce the S_N1CB trigonal-bipyramidal intermediate. Formation of the latter from the conjugated base $[Co(cyclen\text{-}H)(diamine)]^{2+}$ requires expansion

of the bond angles in the equatorial plane from ca. 90° to 120°, and the in-plane bidentate ligand will hinder this expansion, while the loss of NH_3 from $[Co(cyclen-H)(NH_3)_2]^{2+}$ is not restricted in this way. Clearly, the energy barrier for the rate-determining Co−N bond cleavage and the formation of the dissociative five-coordinate intermediate is increased by the structural restriction imposed by the retention of the diamine chelate character.



Scheme 3

The mechanistic picture for ring opening and closure in a square-planar complex appears to be much simpler than that of an octhaedral complex, since both processes (k_3 and k_4) are characterised by an associative mode of activation. We have shown above that the rates of dechelation of 5- and 6-membered rings in the complexes $[PtPh_2(S-S)]$ (S−S = dpte, dptp) have very similar values. This is in line with the results of previous studies showing that the rate constants for ring opening of complexes of the type $[Pt(Me_2SO)(N-N)Cl]^+$ (N−N = en, tn, bn) do not differ significantly from one complex to another.[10] The same complexes, in their ring-open $[Pt(Me_2SO)(N-NH)Cl_2]^+$ protonated forms, showed a marked dependence of the rate of ring closure on the ring size. The same strong dependence on ring size characterises the ring-closing kinetics of *trans*-$[PtCl_2(NH_3)(N-NH)]^+$.[12] Therefore, as for the relationships between the formation constant of square-planar complexes and the size of the chelate ring, it is possible to conclude that the rates of ring closure (k_3) have a dominant effect while ring opening (k_4) makes a relatively small contribution. The formation of 4-membered rings is hindered by ring strain and the formation of large rings (7- or 8-membered rings) must compete with other reaction pathways, in particular with the possibility of obtaining dinuclear or polynuclear species. In this context, it is interesting to mention the results of a recent work on chelation kinetics of bidentate phosphane ligands on five-coordinate $[Ru(CO)_4(\eta^1\text{-}P-P)]$ complexes, where the rates of ring closing (10^4 k_{obs}/s^{-1} at 60 °C, in *n*-heptane) are as follows: dppm (11.2), dppe (4.44), dppp (6.73), dppb (5.75). This stands in striking contrast with the strong dependence of the rates on ring size observed for the square-planar $[PtPh_2(CO)(\eta^1\text{-}P-P)]$ complexes (Table 3 and ref.[28]).

The nucleophilic power of the uncoordinated end of the chelating ligand is also a factor of major importance in controlling the rates of ring closure (k_3), as suggested by the data collected in Table 3. The differences in reactivity are the same as those found in the n^0_{Pt} nucleophilicity scale which controls the rates of bimolecular substitution reactions on platinum(II).[45] An attractive example comes from the comparison of the rates of ring closure by dppp, ppye, and $ppNMe_2$ with a 6-membered ring. As a matter of fact, the difference of velocity between dppp and ppye encompasses at least five orders of magnitude, in line with the much greater nucleophilicity of PPh_2 compared to pyridine. In the case of $ppNMe_2$, steric congestion brought about by alkyl substitution on the donor nitrogen atom impedes ring closure.

The opposite role of k_3 and k_4 in octahedral and square-planar complexes stems from the different mode of activation (dissociative vs. associative). In light of the above considerations, elongation of the ring combined with the use of a weak donor atom at one end of the chelating ligand, would be a way of increasing the "hemilability" of hybrid ligands in square-planar complexes and their possible efficiency as catalysts.

Experimental Section

General Procedures and Chemicals: All solvents were dried according to standard procedures by distillation under oxygen-free nitrogen from appropriate drying agents (i.e. dichloromethane from barium oxide and diethyl ether from sodium benzophenone ketyl). Spectrophotometric grade dichloromethane was dried by distillation, degassed by several freeze-pump-thaw cycles and then stored over activated 4-Å molecular sieves. $CDCl_3$ was purchased from Cambridge Isotopes Laboratories (D 99.8%). Solid phosphane ligands (Aldrich Chemical Co) triphenylphosphane (PPh_3), bis(diphenylphosphanyl)methane (dppm), and 1,3-bis(diphenylphosphanyl)propane (dppp) were recrystallized from ethanol. 1,2-Bis(phenylthio)ethane (dpte), and 1,3-bis(phenylthio)propane (dptp) were recrystallized from toluene before use. 2-(Diphenylphosphanyl)pyridine (PPh_2Py) was purchased from Aldrich. The other bidentate hybrid ligands P−X {1-(diphenylphosphanyl)-2-(pyrid-2-yl)ethane (ppye),[46] 1-(dimethylamino)-2-(diphenylphosphanyl)-ethane ($peNMe_2$),[47] 1-(dimethylamino)-3-(diphenylphosphanyl)-propane ($ppNMe_2$),[47] [*o*-(dimethylamino)phenyl]diphenylphosphane ($PNMe_2$),[48] 1-(diphenylphosphanyl)-2-(thioethyl)-ethane (P−SEt),[49] 1-(diphenylphosphanyl)-2-(thiophenyl)-ethane (P−SPh),[49] (diphenylphosphanyl)(thiophenyl)methane ($P-CH_2SPh$)[50]} were prepared according to published methods.

Instrumentation: ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K with a Bruker AMX R-300 spectrometer operating with a broad-band probe at 300.13 and 121.50 MHz for ^1H and ^{31}P nuclei, respectively. Chemical shifts (δ) refer to $SiMe_4$ for ^1H and to external H_3PO_4 (85%) for $^{31}P\{^1H\}$ NMR. The temperature within the NMR tube was calibrated by use of the ethylene glycole method.[51] UV/Vis data were collected with a rapid-scanning Hewlett−Packard Model 8452 A spectrophotometer. Infrared spectra were recorded in dichloromethane solution using a Perkin−Elmer FT-IR model 1730 spectrometer. Microanalysis was performed by Redox Analytical Laboratories, Milan, Italy.

X-ray Data Collection and Structure Refinement of 18: Crystal data: $C_{28}H_{29}PPtS$ (623.63), monoclinic, $P2_1/c$ (no. 14), a = 12.230(3), b = 24.911(3), c = 16.493(2) Å, β = 90.789(15)°, V = 5025(1) $Å^3$, Z = 8, $D_{calcd.}$ = 1.649 Mg/m^3, $F(000)$ = 2448, μ (Mo-K_α) = 5.745 mm^{-1}, $R1$ = 0.044/0.070 and $wR2$ = 0.098/0.112 for 7123/9763 observed [$I > 2\sigma(I)$]/all independent reflections, GOF = 1.024. Air-stable, pale yellow crystals of **18** were obtained by slow diffusion of *n*-hexane into a concentrated dichloromethane solution of the complex. For the data collection, a prismatic single crystal (0.33 × 0.25 × 0.10 mm) was mounted on a Siemens P4 automated four-circle single-crystal diffractometer and measured with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). 12164

reflections were collected using the ω/2θ scan technique up to 2θ = 52°. No crystal decay was detected from the check reflections monitored every 197 measurements. Intensities were evaluated by profile fitting of a 96-steps peak scan among 2θ shells procedure[52] and then corrected for Lorentz polarisation effects. Absorption correction was applied by fitting a pseudo-ellipsoid to the azimuthal scan data of 20 suitable reflections with high χ angles.[53] Data collection and reduction were performed by XSCANS[54] and SHELXTL[55] packages. The accurate evaluation of the data set excluded the orthorhombic crystal system. The structure was solved by a combination of standard Direct Methods[56] and Fourier synthesis, and refined by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$ with the full-matrix least-squares technique based on all 9763 independent F^2 [R(int) = 0.0284], by using SHELXL97.[57] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model refinement among the "riding model" method with the X−H bond geometry and isotropic displacement parameter depending on the parent atom X. An empirical extinction parameter was included in the last refinement cycles. The last difference map showed the largest electron density residuals within 1 Å from the platinum atoms (max/min values 1.657/−1.437 eÅ^{-3}). The final geometrical calculations and drawings were carried out with the PARST program[58] and the XPW utility of the Siemens package, respectively.[59]

Synthesis of Complexes: The complexes *cis*-[$PtPh_2(CO)(SEt_2)$] (**1**),[60] [$PtPh_2(SEt_2)]_2$ (**2**),[60] and *cis*-[$PtPh_2(dmso)_2$] (**3**),[61] were synthesised according to literature methods. Complexes in which the heteronuclear P−X ligands are bound to the metal ion in a monodentate fashion were formed upon mixing equimolar amounts of complex **1** and of the appropriate ligand in $CDCl_3$ solution, taking advantage of the slow rate of ring closure. These reaction intermediates have been characterised in situ by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (T = 298 K).

***cis*-[$PtPh_2(\eta^1$-$Ph_2PPy)$(CO)] (4):** ^1H NMR($CDCl_3$): δ = 6.57 (m, 1 H), 6.65 (m, 2 H), 6.83 (m, 1 H, H^3-py), 6.90 (m, 1 H), 7.04 (m, 2 H), 7.13 (m, 1 H, H^5-py), 7.27 (m, 1 H, H^4-py), 7.53−7.44 (m, 14 H), 8.83 (m, 1 H, H^6-py).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.1 ($^1J_{PtP}$ = 1636 Hz). IR: ν_{CO} = 2070 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-ppye)(CO)] (5):** ^1H NMR ($CDCl_3$): δ = 2.55 (m, 2 H, CH_2), 2.74 (m, 2 H, CH_2−P), 6.77 (m, 2 H), 6.89 (m, 3 H), 7.04 (m, 4 H), 7.50 (m, 8 H), 7.63 (m, 6 H), 8.39 (m, 1 H, H^6-py). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 12.9 ($^1J_{PtP}$ = 1592 Hz). IR: ν_{CO} = 2066 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-$peNMe_2)$(CO)] (6):** ^1H NMR ($CDCl_3$): δ = 2.01 (s, 6 H, CH_3−N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 9.8 ($^1J_{PtP}$ = 1585 Hz). IR: ν_{CO} = 2062 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-$ppNMe_2)$(CO)] (7):** ^1H NMR ($CDCl_3$): δ = 1.43 (m, 2 H), 1.83 (m, 2 H), 1.94 (m, 2 H), 2.02 (s, 6 H, CH_3−N), 6.80 (m, 1 H), 7.05−6.90 (m, 7 H), 7.55−7.43 (m, 12 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.8 ($^1J_{PtP}$ = 1598 Hz). IR: ν_{CO} = 2071 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-$PNMe_2)$(CO)] (8):** ^1H NMR ($CDCl_3$): δ = 2.71 (s, 6 H, CH_3−N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.1 ($^1J_{PtP}$ = 1679 Hz). IR: ν_{CO} = 2064 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-$PCH_2SPh)$(CO)] (9):** ^1H NMR ($CDCl_3$): δ = 3.37 (m, $^2J_{PH}$ = 6, $^3J_{PtH}$ = 13 Hz, 2 H, CH_2−P), 6.77 (m, 1 H), 6.89 (m, 4 H), 7.00 (m, 5 H), 7.14 (m, 3 H), 7.47 (m, 8 H), 7.60 (m, 4 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 12.9 ($^1J_{PtP}$ = 1593 Hz). IR: ν_{CO} = 2068 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$-P−SPh)(CO)] (10):** ^1H NMR ($CDCl_3$):δ = 2.66 (m, 2 H), 2.26 (m, 2 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.4 ($^1J_{PtP}$ = 1570 Hz). IR: ν_{CO} = 2068 cm^{-1}.

***cis*-[$PtPh_2(\eta^1$- P−SEt)(CO)] (11):** ^1H NMR ($CDCl_3$): δ = 1.07 (t, 3 H, CH_3−CH_2−S), 2.24 (m, 4 H, CH_2 + CH_3−CH_2−S), 2.32 (m, 2 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.5 ($^1J_{PtP}$ = 1576 Hz). IR: ν_{CO} = 2066 cm^{-1}.

Chelate complexes with both dithioethers and hybrid P−X ligands were prepared by adding a stoichiometric amount of the ligand to compound **2** or **3** in dichloromethane solution. The compounds were precipitated in an almost quantitative yield by adding diethyl ether or *n*-hexane (1:1, v/v) and cooling to −30 °C. The off-white solids were washed with cold *n*-hexane and air-dried.

[$PtPh_2$(dpte)] (12): ^1H NMR ($CDCl_3$): δ = 3.03 (br. s, $^3J_{PtH}$ = 16.6 Hz, 4 H, CH_2−S), 6.81 (m, 2 H, H^4), 6.90 (dd, $^3J_{av}$ = 6.6, $^4J_{PtH}$ = 12.0 Hz, 4 H, $H^{3,5}$), 7.38 (d, $^3J_{H,H}$ = 6.6, $^3J_{PtH}$ = 76.0 Hz, 4 H, $H^{2,6}$), 7.41 (m, 6 H, $H^{m,m'}$ + H^p Ph−S), 8.00 (m, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 2.2 Hz, 4 H, $H_{o,o'}$ Ph−S). Yield: 95%. $C_{26}H_{24}PtS_2$ (595.68): calcd. C 52.42, H 4.06; found C 52.8, H 4.15.

[$PtPh_2$(dptp)] (13): ^1H NMR ($CDCl_3$): δ = 2.26 (m, 2 H, CH_2−CH_2−S), 3.28 (m, $^3J_{PtH}$ = 13.3 Hz, 4 H, CH_2−CH_2−S), 6.69 (m, 2 H, H^4), 6.78 (dd, $^3J_{av}$ = 7.1, $^4J_{PtH}$ = 11.5 Hz, 4 H, $H^{3,5}$), 7.23 (d, $^3J_{H,H}$ = 7.1, $^3J_{PtH}$ = 75.2 Hz, 4 H, $H^{2,6}$), 7.28 (m, 6 H, $H^{m,m'}$ + H^p Ph−S), 7.75 (m, $^3J_{H,H}$ = 7.1, $^4J_{H,H}$ = 2.7 Hz, 4 H, $H^{o,o'}$ Ph−S). Yield: 93%. $C_{27}H_{26}PtS_2$ (609.71): calcd. C 53.19; H 4.30; found C 53.6, H 4.27.

[$PtPh_2$(ppye)] (14): ^1H NMR ($CDCl_3$): δ = 2.36 (m, 2 H, CH_2), 3.59 (m, $^2J_{PH}$ = 25 Hz, 2 H, CH_2−P), 6.54 (m, 3 H), 6.85 (m, 1 H), 6.95 (m, 4 H), 7.08 (m, 2 H), 7.23 (m, 8 H), 7.40 (m, 4 H), 7.68 (m, 1 H), 8.55 (m, $^3J_{PtH}$ = 23 Hz, 1 H, H^6-py). $^{31}P\{^1H\}$ NMR ($CDCl^3$): δ = 16.4 ($^1J_{PtP}$ = 1886 Hz). Yield: 92%. $C_{31}H_{28}NPPt$ (640.61): calcd. C 58.12, H 4.41, N 2.19; found C 58.3, H 4.32, N 2.30.

[$PtPh_2$(peNMe$_2$)] (15): ^1H NMR ($CDCl_3$): δ = 2.34 (m, 2 H), 2.57 (s, $^3J_{PtH}$ = 18 Hz, 6 H, CH_3−N), 2.72 (m, 2 H), 6.60 (m, 1 H), 6.65 (m, 2 H), 6.82 (m, 1 H), 7.03 (m, 2 H), 7.20 (m, 2 H), 7.48−7.38 (m, 12 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.0 ($^1J_{PtP}$ = 1915 Hz). Yield: 89%. $C_{28}H_{30}NPPt$ (606.60): calcd. C 55.44, H 4.98, N 2.31; found C 55.6, H 5.07, N 2.42.

[$PtPh_2$(PNMe$_2$)] (16): ^1H NMR ($CDCl_3$): δ = 3.10 (s, $^3J_{PtH}$ = 17 Hz, 6 H, CH_3−N), 6.59 (m, 3 H), 6.85 (m, 1 H), 7.04 (m, 3 H), 7.14 (m, 2 H), 7.38 (m, 11 H), 7.53 (m, 2 H), 7.60 (m, 2 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 ($^1J_{PtP}$ = 1990 Hz). Yield: 90%. $C_{32}H_{30}NPPt$ (654.64): calcd. C 58.71, H 4.62, N 2.14; found C 58.8, H 4.70, N 2.21.

[$PtPh_2$(P−SPh)] (17): ^1H NMR ($CDCl_3$): δ = 2.38 (m, 2 H, CH_2−S), 2.99 (m, $^2J_{PH}$ = 24 Hz, 2 H, CH_2−P), 6.76 (m, 4 H), 6.92 (m, 2 H), 7.19 (m, $^3J_{PtH}$ = 76 Hz, 2 H, $H^{2,6}$ *trans* to S), 7.40 (m, 15 H), 7.99 (m, 2 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 41.6 ($^1J_{PtP}$ = 1803 Hz). Yield: 87%. $C_{32}H_{29}PPtS$ (671.69): calcd. C 57.22, H 4.35; found C 57.6, H 4.45.

[$PtPh_2$(P−SEt)] (18): ^1H NMR ($CDCl_3$): δ = 1.20 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3−CH_2−S), 2.49 (m, 2 H, CH_2−S), 2.66 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_3−CH_2−S), 2.80 (m, 2 H, CH_2−P), 6.72 (m, 3 H), 6.86 (m, 1 H), 7.02 (m, 2 H), 7.19 (m, $^3J_{PtH}$ = 74 Hz, 2 H, $H^{2,6}$ *trans* to S), 7.49−7.34 (m, 12 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 40.2 ($^1J_{PtP}$ = 1832 Hz). Yield: 90%. $C_{28}H_{29}PPtS$ (623.65): calcd. C 53.92, H 4.69; found C 54.1, H 4.61.

Kinetics

NMR Measurements: The ring-closure reactions were initiated as follows: $6{\cdot}10^{-3}$ mmol of the hemilabile ligand was dissolved in $CDCl_3$ (0.3 mL) in a 5-mm NMR tube which was immersed in a liquid nitrogen bath. After a few minutes, a [D]chloroform solution of *cis*-[$PtPh_2(CO)(SEt_2)$] ($6{\cdot}10^{-3}$ mmol, 0.2 mL) was added over the frozen solution of the ligand and the NMR tube was cooled again to allow the complex solution to freeze over that of the ligand. Then, the NMR tube was rapidly inserted into the probe of the spectrometer thermostated at 298 K. ^1H or $^{31}P\{^1H\}$ NMR spectra were recorded, immediately after the sample temperature reached an equilibrium value (i.e. stable lock signal), and at subsequent appropriate time intervals. The first recorded spectrum only showed signals relative to free sulfide at $\delta = 2.57$ and 1.27 and to the ring-open *cis*-[$Pt(Ph)_2(CO)(\eta^1$-P−X)] complex, indicating that the displacement of SEt_2 from **1** by the phosphorus end of all the bidentate ligands is too fast at 298 K to be monitored by ^1H NMR spectroscopy. The ring-closure process was followed by monitoring the decrease in intensity of the ^1H or $^{31}P\{^1H\}$ signals associated with the amount of unchanged *cis*-[$PtPh_2(CO)(\eta^1$-P−X)] and the matching increase of the signals due to the final chelate [$PtPh_2$(P−X)] product. Care was taken to choose well-defined and not overlapping resonances for the kinetic analysis (selected values of the chemical shifts and of the ^{195}Pt coupling constants for ring-open and chelate complexes are reported in Table 2. The peaks monitored during the kinetic runs are marked in bold).

UV/Vis Measurements: The reactions of ring opening of the chelate complexes *cis*-[$Pt(Ph)_2$(S−S)] (S−S = dpte and dptb) by dppm and dppp were carried out in CH_2Cl_2 at 298 K, with various concentrations of diphosphane. The kinetics were started by mixing known pre-thermostated volumes of complex and diphosphane solutions, located in a tandem quartz cell (1 cm path length), in the cell compartment of the spectrophotometer. The use of at least a tenfold excess of nucleophile over the complex ensured pseudo-first-order kinetics in all runs. The kinetics were usually followed over four half-lives by monitoring the spectral changes at suitable times. Rate constants were determined using ProFit (Cherwell Scientific Publishing Limited) data analysis software by fitting absorbance 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 optimized (A_0 = absorbance after mixing of reagents, A_∞ = absorbance at completion of the reaction).

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