Kinetics and Mechanism of Halogen-bridge Cleavage in Dimethylaminomethylphenyl-*C*^{1},*N* Pallada- and Platina-cycles by Pyridines. Pressure Effects, and Crystal Structures of the *N,N-cis* Reaction Product, its *N,N-trans* Orthometallated Analogue and a Dimer of Similar Reactivity†

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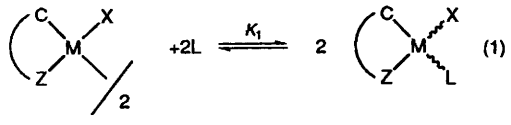
An ambient and high-pressure stopped-flow kinetic study of the halogen-bridge cleavage reaction in the pallada- and platina-cycles $[\{M(o\text{-}C_6H_3RCH_2NMe_2)X\}_2]$ (M = Pd or Pt; R = H, 4-MeO, 5-Me or 5-F; X = Cl or I) by a series of substituted pyridines in chloroform as solvent revealed that it is a fast, associatively driven second-order process, with strong steric rather than electronic demands. Substituent effects and activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$) were in full accord with the proposed associative mechanism. The Pd dimers transformed into *N,N-trans* monomers of the type $[Pd(o\text{-}C_6H_3RCH_2NMe_2)X(py)]$ (py = pyridine). In contrast, the Pt counterparts afford *N,N-cis* species $[Pt(o\text{-}C_6H_3RCH_2NMe_2)X(py)]$ under the same conditions. The geometry of the *N,N-cis* complex $[Pt\{o\text{-}C_6H_3(4\text{-}MeO)CH_2NMe_2\}X(py)]$, as well as of the *N,N-trans* platinacycle $[Pt\{o\text{-}C_6H_4C(Me)=NOH\}Cl(py)]$, has been confirmed by X-ray crystallography. The most striking structural differences in the *N,N-cis* and *N,N-trans* related platinacycles are the Pt–Cl and Pt–N(py) bond distances [2.300(1) and 2.408(5), 2.138(4) and 2.02(1) Å, respectively]. The crystal structure of *trans*-$[(Bu^n_3P)IPd(\mu\text{-}I)_2PdI(PBu^n_3)]$ has also been determined and used to account for its similar reactivity to $[\{Pd(o\text{-}C_6H_4CH_2NMe_2)I\}_2]$ in the bridge-splitting reaction.

Cleavage of halogen bridges (X) in cyclometallated Pd^{II} and Pt^{II} (M) complexes by various donor ligands (L) including pyridines, equation (1) (Z = N,P,S, *etc.*), is a classical reaction



(1)

widely used, for example, for the synthesis of monomeric metallacycles from the corresponding dimers, for the structural characterization of cyclometallated species, and for the separation of enantiomers.[1] In addition, reactions of type (1) are postulated as key pre-equilibria in synthetically important insertion reactions of alkenes,[2] alkynes[3] and other unsaturated molecules[4] into the Pd–C bonds of dimeric palladacycles. Although the overall monomerization reaction (1) is well known, limited mechanistic information is available on this and related reactions. Bridge cleavage on Pd^{II} and Pt^{II} complexes was studied kinetically by Pearson and Muir[5] for the example shown in equation (2)

$$[Br_2Pt(\mu\text{-}Br)_2PtBr_2]^{2-} + 2py \longrightarrow 2[PtBr_3(py)]^- \quad (2)$$

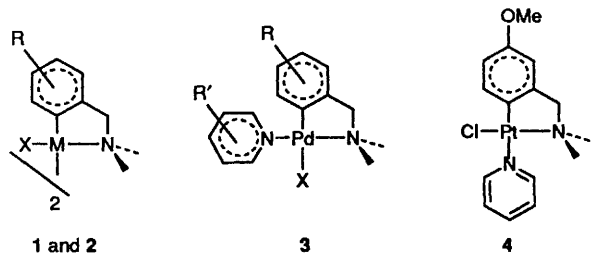
(py = pyridine). Muir and Cancio[6] measured the rates of reactions of this dimer with alkenes,[6a] ethanolamine and ethylenediamine.[6b] Elding and Olsson[7] investigated the reaction of $[I_2Pd(\mu\text{-}I)_2PdI_2]^{2-}$ with iodide. And recently, Cusumano *et al.*[8] reported kinetic data for reaction (3) (X = H or 2,6-Ne_2)

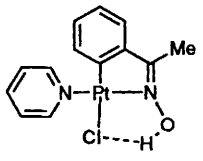
$$[(Pr^n_3P)IPd(\mu\text{-}I)_2PdI(PPr^n_3)] + 2X\text{-}py \longrightarrow 2[PdI_2(PPr^n_3)(X\text{-}py)] \quad (3)$$

in chloroform as the solvent.

Bridge-splitting processes are mechanistically unique, since they are, in a certain sense, at the interface of substitution[9] and addition[9] reactions at metal centres, and this is an insufficiently investigated area in mechanistic inorganic/organometallic chemistry. Cyclometallated halide-bridged complexes with a Pd–C or Pt–C σ bond, which has a strong *trans*-labilizing effect,[9] are interesting for comparing both the role played by σ C- and P-donor ligands in the bridge-splitting reaction and the reactivity of related Pd^{II} and Pt^{II} derivatives. The influence of the M–C bond on the reactivity of square-planar complexes has a long history,[10] but there is no indication of decreasing

† *Supplementary data available* (No. SUP 57064, 4 pp.): a complete list of pseudo-first-order rate constants at 19.2–48.7 °C. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.





	M	R	X
1a	Pd	H	Cl
1b	Pd	5-Me	Cl
1c	Pd	4-MeO	Cl
1d	Pd	5-F	Cl
1e	Pd	H	I
2f	Pt	H	Cl
2g	Pt	4-MeO	Cl

Scheme 1 In complex **3**, R and X are as for **1** and R′ = H, 4-Me, 3-MeCO, 4-CN, 2,4- or 2,6-Me_2

research activity in this area.[11] The cyclometallated complexes investigated in this study are shown in Scheme 1. Dimers **1** and **2** have been used to obtain kinetic data on their interaction with substituted pyridines [equation (1)] as a function of temperature and pressure. Note that bridge-cleavage reactions have not been studied kinetically under pressure. The platinum monomer **4** was used for the structural characterization of the reaction product, and by way of comparison the structure of the aryl oxime complex **5** was determined since it appeared to be a geometric alternative of compound **4**. An X-ray diffraction study of *trans*-[$(Bu^n_3P)IPd(\mu\text{-}I)_2PdI(PBu^n_3)$] **6** was also performed to account for the kinetic data for reaction (3)[8] which appeared to be very similar to those for complexes **1** found in this work.

Experimental

Ligands, Palladium and Platinum Complexes **1** *and* **2**, *Solvents.*—Sources and preparations of all the Pd^{II} dimers are described in ref. 3. ^{1}H NMR ($CDCl_3$) (values in parentheses are the relative intensities of the corresponding signals; they are related to the ratio of the *ab–hg* and *ab–gh* isomers): **1a** δ 2.84(4) and 2.86(3) (2 s, NMe), 3.93 (s, CH_2), 6.84–6.99 (m, H^3–H^5), 7.14(4) and 7.19(3) (2 d, H^6, J_{HH} 7.5); **1b** δ 2.24(4) and 2.27(3) (2 s, 5-Me), 2.82(3) and 2.85(4) (2 s, NMe), 3.89 (s, CH_2), 6.74–6.77 (m, H^3–H^4), 6.95(4) and 7.01(3) (2 s, H^6); **1d** δ 2.82(1) and 2.85(2) (2 s, NMe), 3.90 (s, CH_2), 6.63–6.79 (m, 1 H), 6.79–6.92 (m, 2 H); **1e** δ 2.91(3) and 2.94(1) (2 s, NMe), 4.01 (s, CH_2), 6.78–7.04 (m, H^3–H^5), 7.63(3) and 7.71(1) (2 d, H^6, J_{HH} 7.0 Hz). The synthesis of the Pt^{II} dimers is described in detail elsewhere.[12] Spectroscopic data for **2f**: ^{1}H NMR [$(CD_3)_2SO$] δ 2.79 (s, Me, J_{PtH} 34.0), 4.01 (s, CH_2, J_{PtH} 40.6), 6.78–7.15 (m, H^3–H^5), 7.78 (dd, H^6, J_{HH} 8.0 and 1.1, J_{PtH} 44.9 Hz); ^{13}C NMR (CD_2Cl_2) δ 75.3 and 75.5 (CH_2), 121.1 (C^3), 124.3 (C^4), 125.0 and 125.2 (C^5), 127.5 and 128.6 (C^2), 131.2 and 131.8 (C^6), 147.4 (C^1) (the signal from Me is obscured by the solvent); ^{13}C NMR [$(CD_3)_2SO$] δ 51.3 (Me), 73.7 (CH_2, J_{PtC} 53), 121.1 (C^3, J_{PtC} 35), 123.0 (C^4, C^5), 124.8 (C^2, J_{PtC} 58), 133.5 (C^6, J_{PtC} 54 Hz), 146.8 (C^1). Compound **4** was prepared from **2g** and py.[3] All the substituted pyridines were purchased from Aldrich. Only 4-methylpyridine was a Fluka reagent. The pyridines were either distilled or recrystallized before kinetic measurements. Chloroform (HPLC grade) used as solvent was purchased from Aldrich and utilized as received.

Preparation of Chloro{2-[1-(*hydroxyimino*)*ethyl*]*phenyl*-C^1,N}(*pyridine*)*platinum*(II) **5**.—A solution of K_2PtCl_4 (200 mg, 0.48 mmol) in water (10 cm^3) was mixed with a solution of acetophenone oxime (85 mg, 0.63 mmol) in methanol (10 cm^3) and the resulting mixture kept at room temperature for 2 d.[13] The precipitated brownish black material was separated by filtration, washed with water and dried. The filtrate was extracted with chloroform. The dry product was dissolved in the extract and purified on a small chromatographic column filled with silica gel (mesh 40 × 100) and $CHCl_3$ as eluent. The yellow solution of [Pt{*o*-$C_6H_4C(Me)$=NOH}Cl{PhC(Me)=NOH}] obtained was concentrated to 1 cm^3, pyridine (150 cm^3) was added, and the final product was precipitated by addition of excess of *n*-hexane. Orange crystals of **5**, soluble in benzene, chloroform and acetonitrile, were obtained. Yield 45 mg, 17%. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, Me, J_{PtH} 8.7), 6.35 (dd, H^6, J_{HH} 7.3 and 1.2, J_{PtH} 50.0), 6.83–7.21 (m, H^3–H^5), 7.44 [m, $H^{3',5'}$ (py)], 7.90 [m, $H^{4'}$ (py)], 8.89 [dd, $H^{2',6'}$ (py), J_{HH} 6.7 and 1.4, J_{PtH} 44.5], 10.11 (s, OH, J_{PtH} 7.6 Hz). ^{13}C NMR (CD_2Cl_2): δ 11.3 (Me, J_{PtC} 30), 123.9 (C^4), 125.9 (C^3, J_{PtC} 39), 126.5 [$C^{3',5'}$ (py)], 127.0 (C^2), 129.6 (C^5, J_{PtC} 58), 130.2 (C^6, J_{PtC} 61), 138.7 [$C^{4'}$ (py)], 140.0 (C^1, J_{PtC} 1146), 143.6 (C=N, J_{PtC} 43), 154.1 [$C^{2',6'}$ (py), J_{PtC} 10 Hz].

Synthesis of trans-*Di*-μ-*iodo-bis*[*iodo*(*tri*-n-*butylphosphine*)-*palladium*(II)] **6**.—The allylic complex [PdCl(η^3-2-PhC_3H_4)-(PBu^n_3)] (53 mg, 0.116 mmol), which was prepared as described previously for the PPh_3 analogue,[14] was dissolved in chloroform (1 cm^3). The solution was mixed with a solution of LiI (47 mg, 0.348 mmol) in acetic acid (1 cm^3) and pure acetic acid (3 cm^3) added. The reaction mixture was kept for 22 h at 80 °C to form brownish red needle-like crystals of [$(Bu^n_3P)IPd(\mu\text{-}I)_2PdI(PBu^n_3)$] (21.1 mg, 32%). No attempt was made to isolate more material from the mother-liquor. ^{1}H NMR (CD_2Cl_2): δ 0.88 (t, Me, J_{HH} 6.5), 1.37 (m, $MeCH_2$), 1.48 (m, $EtCH_2$), 2.09 (dt, $PrCH_2$, J_{PH} 11.2 Hz). ^{31}P NMR (CD_2Cl_2): δ 36.54 (*versus* 85% H_3PO_4).

Kinetic and Other Measurements.—Spectrophotometric measurements were performed on Hitachi U-3200 and Shimadzu UV-250 spectrophotometers. Proton NMR spectra were run on CXP-200, AC 300, and AM 400 WB Bruker instruments. Carbon-13 and ^{31}P NMR spectra were recorded on the CXP-200 instrument. Chemical shifts are in δ, *J* in Hz. Kinetics of the bridge-cleavage reactions were studied on a Dionex D110 stopped-flow instrument, thermostatted within ±0.1 °C at ambient pressure. Kinetic experiments at elevated pressure (up to 100 MPa) were performed on a home-made high-pressure stopped-flow instrument.[15] The reactions of Pd complexes **1** were followed at 350 nm, the Pt complex **2g** at 325 nm. The concentrations were usually 3 × 10^{-4} and 6.5 × 10^{-4} mol dm^{-3}, respectively. Kinetic traces were analysed by using the OLIS KINFIT set of programs.

Crystal Structure Determinations.—Crystal data, data collection and processing parameters are reported in Table 1. Observed reflections were corrected for Lorentz and polarization effects. Absorption corrections were introduced by applying the DIFABS program.[16] Scattering factors for neutral atoms including *f* and *f*′ were taken from ref. 17. The positions of hydrogen atoms were refined using the 'rider' scheme and their isotropic thermal parameters fixed at U = 0.08 $Å^2$. Final full-matrix least squares gave the *R* and *R*′ values in Table 1. All calculations were performed with the SHELX 76 and 86 packages.[18,19]

Complex **4**. The structure was solved by the heavy-atom method and refined by full-matrix least squares in the isotropic

Table 1 Experimental datails for the X-ray diffraction analysis

Compound	**4**	**5**	**6**
Formula	$C_{15}H_{19}ClN_2OPt$	$C_{13}H_{13}ClN_2OPt$	$(C_{12}H_{27}I_2PPd)_2$
M	473.86	443.79	1125.1
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
a/Å	8.078(2)	15.428(4)	9.864(3)
b/Å	9.697(1)	8.110(2)	8.875(6)
c/Å	10.938(2)	21.110(6)	21.609(6)
α/°	66.24(1)	90	90
β/°	85.92(1)	90	93.96(2)
γ/°	85.31(1)	90	90
U/Å^3	780.9(2)	2641(1)	1887(1)
D_c/g cm^{-3}	1.947	2.162	1.980
Z	2	8	2
$F(000)$	432	1608	1064
Crystals	Light yellow drawn prisms	Light yellow drawn prisms	Brownish red needles
Crystal size/mm	0.22 × 0.18 × 0.38	0.22 × 0.23 × 0.33	0.26 × 0.08 × 0.83
μ(Mo-Kα)/cm^{-1}	92.4	109.2	42.8
Transmission factors (min., max.)	0.782, 0.999	0.698, 1.736	0.651, 1.859
Scan range/°	$2 < \theta < 34$	$2 < \theta < 30$	$2 < \theta < 27$
Scan mode	ω–2θ	ω	ω
ω Scan width/°	0.9 + 0.35 tan θ	1.2 + 0.35 tan θ	1.1 + 0.35 tan θ
Maximum allowed scanning time/s	50	60	60
Max., min. scan speed/° min^{-1}	8.2, 1.1	8.2, 1.2	8.2, 1.1
Reflections collected	$\pm h \pm k l$	$h k l$	$\pm h k l$
No. of unique reflections	5069	3196	3877
No. of independent observed reflections with $F > 4\sigma(F)$	4821	1783	1715
R	0.0315	0.0425	0.0439
R'	0.0337	0.0431	0.0439
Weighting scheme	$[\sigma^2(F) + 0.001\,306(F^2)]$	$[\sigma^2(F) + 0.000\,049(F^2)]$	Unit

Details in common: unit-cell determination, 25 randomly selected high θ reflections; Enraf-Nonius CAD4 diffractometer; λ 0.710 69 Å, graphite monochromatized; room temperature.

approximation. An absorption correction was made at this stage of refinement. Further refinement of the structure was carried out in the full-matrix anisotropic approximation. All hydrogen atoms were located in the Fourier difference synthesis. However, for further refinement, calculated idealized positions of these atoms were used. The final electron-density difference synthesis showed no peaks ≥2.9 or ≤ −2.4 e Å^{-3}, the largest lying close to the metal atom.

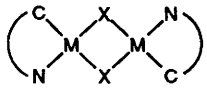
Complex **5**. The structure was solved by the heavy-atom method and refined by full-matrix least squares in the isotropic approximation. At this stage of the refinement, an absorption correction was employed. Further refinement of the structure was carried out in the full-matrix anisotropic approximation. The positions of all hydrogen atoms with the exception of that for the H atom at the oxime oxygen were calculated. The H atom at the oxime oxygen was localized in the Fourier difference synthesis. The final electron-density difference synthesis showed no peaks ≥1.8 or ≤ −1.2 e Å^{-3}, the largest lying close to the metal atom.

Complex **6**. The structure was solved by the heavy-atom method and refined by full-matrix least squares in the isotropic approximation. An absorption correction was used at this stage of the refinement. Further refinement of the structure was carried out in the full-matrix anisotropic approximation. The final electron-density difference synthesis showed no peaks ≥0.9 or ≤ −0.9 e Å^{-3}, the largest lying close to the metal atom.

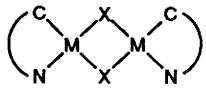
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Structure and Stability of Monomeric Products.—The Pd dimers of type **1** are a mixture of the *ab–hg* and *ab–gh* isomers as emphasised by their ^{1}H NMR spectra recorded at 300 MHz (see Experimental section). This is in contrast to previous studies on



ab-hg



ab-gh

such dimeric species (^{1}H NMR and X-ray structure analysis) from which it was concluded that they should only have the *ab–hg* geometry.[1,20] On the contrary, complex **6** is isomerically pure in solution and there is only one singlet in the ^{31}P NMR spectrum even at −100 °C. Halogeno- and acetato-bridge cleavage in Pd^{II} cyclometallated dimers by pyridine ligands affords monomeric species in which the donor atoms of the palladacycle and pyridine nitrogen are mutually *trans*.[1,21,22] This is usually true for the *N,N*-dimethylbenzylamine palladacycles **3**. There are, however, a few examples in the literature where this rule does not hold. In particular, a crystal-structure analysis shows that in the palladacycle [Pd{C_6H_4-C(Me)=N$C_{10}H_7$}Cl(4Me-py)] ($C_{10}H_7$ = α-naphthyl) the 4-methylpyridine (4Me-py) ligand occupies the position *trans* to the Pd–C bond.[23,*] Two geometric isomers, *viz. N,N-cis* and *N,N-trans*, were detected for [Pd{C_6H_3(4-MeO)CH=NPh}-Cl(py)] by ^{1}H NMR in $CDCl_3$.[24]

Some of the 'Pd^{II}' equilibria of type (1) were characterized by their K_1 values. Deeming *et al.*[25] reported $K_1 = 2.2 \times 10^4$ and 0.77×10^4 dm^3 mol^{-1} for the interaction of **1a** with py or 2Me-py, respectively, in toluene as solvent at 30 °C. Later, Ryabov[26] measured K_1 for a series of ring-substituted acetato analogues of **1** and 2Ph-py in $MeCO_2H$ at different temperatures. All the values of K_1 show that equation (1) is strongly shifted to the right in the presence of an excess of pyridines, and under such conditions these monomerization

* In solution, however, this compound is a 4:1 mixture of the *N,N-cis* and *N,N-trans* isomers as in ref. 24.

reactions must be considered to be irreversible in a kinetic sense.

As in the Pd case, the Pt dimers of type **2** are a mixture of the *ab–hg* and *ab–gh* isomers as evidenced by the existence of two sets of signals in the ^{1}H NMR spectra in non-co-ordinating solvents.[12,27] The ^{13}C NMR spectrum of **2f** shows a similar double set. Note that there is a single set for **2f** in both the ^{1}H and ^{13}C NMR spectra recorded in a strongly co-ordinating solvent such as $(CD_3)_2SO$. These dimers also interact rapidly with pyridines, but the geometry of the complexes formed is not the same as in the Pd^{II} case. Complexes of type **3** and **4** or mixtures of them are produced depending on the reaction conditions and the nature of the pyridine ligand. For example, **2f** and **2g** react with py or 4Me-py in aprotic solvents to give *N,N-cis* species such as **4** (confirmed by an X-ray diffraction study, see below). The product with the *N,N-trans* geometry is produced when **2f** reacts with pyridine-3-sulfonic acid in aqueous medium. This monomerization is, however, accompanied by the aquation of the chloro ligand.[28]

Description of the Crystal Structures of **4**, **5** *and* **6**.—Figs. 1–3 show overall views of the molecules of **4**, **5** and **6**, respectively. Table 2 gives selected bond lengths and angles and Table 3 the atomic coordinates. The bond lengths and angles are in the range typical of compounds containing orthoplatinated phenyl rings and differently co-ordinated py ligands.[29] The structural features of complexes **4** and **5** are so similar that they may be treated with care as 'geometric isomers'. Thus, the effect of the strong donor, phenyl ring, on the py and chloro ligands can be observed. The σ-bound phenyl induces more than a 0.1 Å elongation of the Pt–N and Pt–Cl bonds *trans* to it. Other features of complexes **4** and **5** seem to be normal.

In complex **4**, the pyridine plane is rotated by 83° (*cf.* 56° in **5**) along the Pt–N(1) bond with respect to the Pt co-ordination plane and in the absence of agostic interactions[30] this is due to steric effects. The non-bonding contact between the α-pyridine carbon C(5′) and the C(10) methyl carbon at N(2), which equals 3.43 Å, is shorter than twice the van der Waals radius of carbon, while the other intraatomic contacts involving pyridine α-C–H hydrogens and other atoms (C···H, H···H, C···Cl and H···Cl) approach the sum of the van der Waals radii.

The geometric characteristics of **5** demonstrate that it is a 'phantom' of the similar Pd^{II} complex.[30] In fact many of the structural features are much the same, *e.g.* the M–C [1.98(1) and 1.983(5) Å], M–Cl [2.408(5) and 2.413(2) Å], M–N(py) [2.02(1) and 2.040(4) Å] and M–N(oxime) [2.00(1) and 1.993(5) Å]

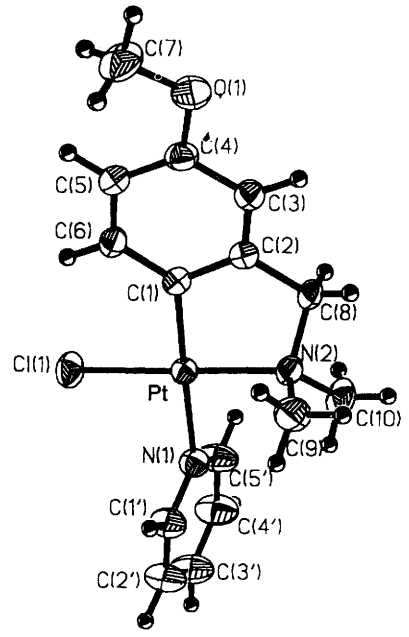


Fig. 1 Crystal structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level

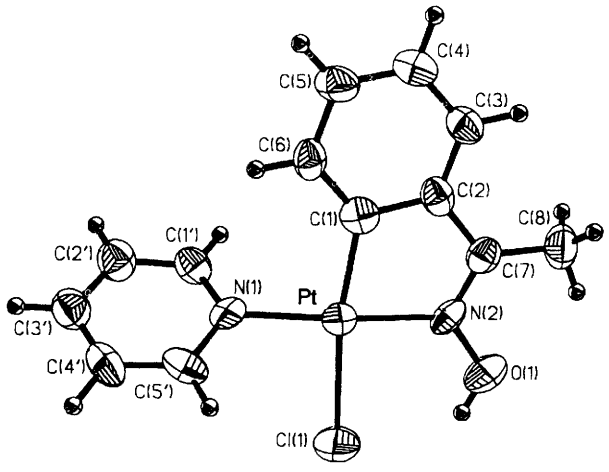


Fig. 2 Crystal structure of complex **5**. Thermal ellipsoids are drawn at the 50% probability level

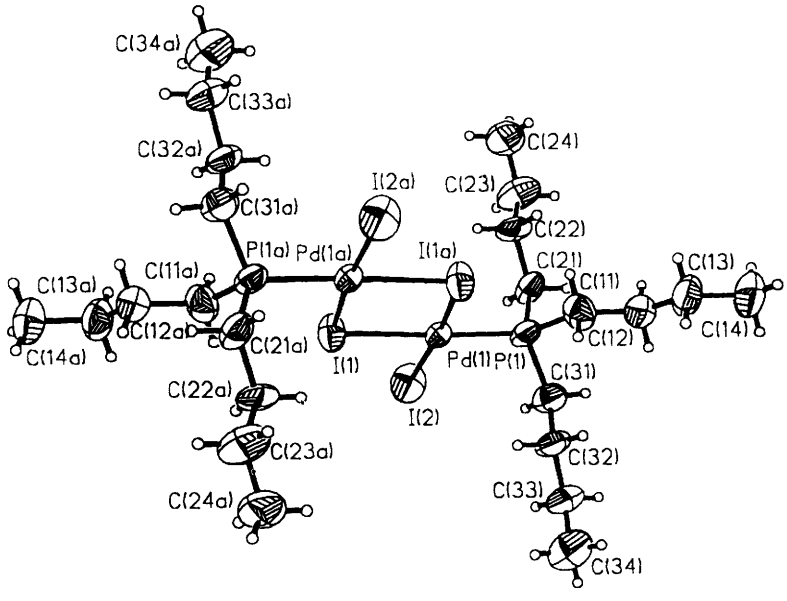


Fig. 3 Crystal structure of complex **6**. Thermal ellipsoids are drawn at the 50% probability level

Table 2 Selected bond lengths (Å) and angles (°) for complexes **4**, **5** and **6**

Complex **4**			
Pt–Cl(1)	2.300(1)	Pt–N(1)	2.138(4)
Pt–N(2)	2.073(4)	Pt–C(1)	1.980(5)
N(1)–C(1′)	1.330(8)	N(1)–C(5′)	1.342(8)
N(2)–C(8)	1.488(7)	N(2)–C(9)	1.506(9)
N(2)–C(10)	1.486(7)	O(1)–C(4)	1.371(7)
O(1)–C(7)	1.421(8)		
Cl(1)–Pt–N(1)	86.4(1)	Cl(1)–Pt–N(2)	175.8(1)
Cl(1)–Pt–C(1)	95.2(2)	N(1)–Pt–N(2)	96.5(2)
N(1)–Pt–C(1)	178.2(2)	N(2)–Pt–C(1)	81.9(2)
Pt–N(1)–C(1′)	121.6(4)	Pt–N(1)–C(5′)	120.0(4)
C(1′)–N(1)–C(5′)	117.7(5)	Pt–N(2)–C(8)	108.6(3)
Pt–N(2)–C(9)	107.7(4)	Pt–N(2)–C(10)	114.5(4)
C(8)–N(2)–C(9)	107.8(4)	C(8)–N(2)–C(10)	107.7(4)
C(9)–N(2)–C(10)	110.3(5)	C(4)–O(1)–C(7)	115.9(5)
Pt–C(1)–C(2)	115.2(4)	Pt–C(1)–C(6)	128.2(4)
O(1)–C(4)–C(3)	114.9(5)	O(1)–C(4)–C(5)	125.1(5)
Complex **5**			
Pt–Cl(1)	2.408(5)	Pt–N(1)	2.02(1)
Pt–N(2)	2.00(1)	Pt–C(1)	1.98(1)
N(1)–C(1′)	1.31(2)	N(1)–C(5′)	1.36(2)
N(2)–C(7)	1.31(2)	O(1)–N(2)	1.36(2)
Cl(1)–Pt–N(1)	92.6(3)	Cl(1)–Pt–N(2)	90.5(3)
Cl(1)–Pt–C(1)	170.2(4)	N(1)–Pt–N(2)	175.3(4)
N(1)–Pt–C(1)	96.7(5)	N(2)–Pt–C(1)	80.3(5)
Pt–N(1)–C(1′)	121.9(9)	Pt–N(1)–C(5′)	120.5(9)
C(1′)–N(1)–C(5′)	117(1)	Pt–N(2)–C(7)	117.9(9)
H(1)–O(1)–N(2)	119(1)	Pt–N(2)–O(1)	123.3(8)
Complex **6**			
Pd(1)–I(1)	2.666(2)	Pd(1)–I(1a)	2.593(2)
Pd(1)–I(2)	2.581(2)	Pd(1)–P(1)	2.256(4)
P(1)–C(11)	1.80(2)	P(1)–C(21)	1.80(2)
P(1)–C(31)	1.83(2)		
I(1)–Pd(1)–I(1a)	84.32(5)	I(1)–Pd(1)–I(2)	89.49(5)
I(1)–Pd(1)–P(1)	177.4(1)	I(1a)–Pd(1)–I(2)	173.81(6)
I(1a)–Pd(1)–P(1)	96.2(1)	I(2)–Pd(1)–P(1)	90.0(1)
Pd(1)–I(1)–Pd(1)	95.68(5)	Pd(1)–P(1)–C(11)	113.5(6)
Pd(1)–P(1)–C(21)	111.5(5)	Pd(1)–P(1)–C(31)	114.9(5)
C(11)–P(1)–C(21)	106.3(7)	C(11)–P(1)–C(31)	105.2(8)
C(21)–P(1)–C(31)	104.6(7)		

bond lengths for **5** and its palladium counterpart, respectively. There is an intramolecular Cl · · · H–O hydrogen bond in both complexes and the angle between the metal and pyridine planes is 56 and 52° for the Pt and Pd derivatives, respectively.

Complex **5** was synthesized by substituting pyridine for acetophenone oxime in the parent monomeric complex **7**, equation (4). A question that may arise is why **4** has the

$$[Pt\{o\text{-}C_6H_4C(Me)=NOH\}Cl\{PhC(Me)=NOH\}]\ \mathbf{7} + py \longrightarrow \mathbf{5} + PhC(Me)=NOH \quad (4)$$

N,N-cis geometry and **5** is *N,N-trans*? The simplest rationale is the hydrogen-bond pseudo-chelate effect found in **5** and related Pd^{II} complexes.[30] The hydrogen bond accounts for the ground-state stabilization of the *cis* arrangement of the chloro ligand and the oxime N donor centre. It is likely that this structural motif is always present in halogeno-oxime metal complexes including **7**. Correspondingly, the H^6 proton of the ortho-platinated ring of **7** is rather upfield, at δ 6.79 (J_{PtH} 38 Hz). There is no such ground-state stabilization in the parent dimers **2** and, hence, pyridine finds a local energy minimum moving *trans* to the Pt–C bond.

The structure of complex **6** is very similar to that of its recently reported analogue with $PPh_2(CH{=}CH_2)$ instead of tri-*n*-butylphosphine.[31] The major difference is a lower density for compound **6** reported here, *viz.* 1.980 *versus* 2.23 g cm^{-3}. Apparently, this is due to higher spatial requirements of the conformationally flexible Bu^n radicals. The bridging Pd–I bond lengths are 2.593(2) and 2.666(2) Å and those in the diphenylvinylphosphine complex 2.596(3) and 2.658(3) Å. The iodo

Table 3 Final atomic coordinates for non-hydrogen atoms for complexes **4**, **5** and **6**

	4		
Atom	*x*	*y*	*z*
Pt	0.013 39(2)	0.267 94(2)	0.494 74(1)
Cl(1)	−0.245 8(2)	0.200 5(2)	0.592 0(1)
N(1)	−0.085 9(6)	0.283 5(5)	0.313 3(4)
N(2)	0.254 4(5)	0.315 6(5)	0.418 9(4)
O(1)	0.406 3(6)	0.191 8(6)	0.981 9(4)
C(1)	0.112 4(6)	0.251 7(5)	0.660 9(4)
C(2)	0.275 6(6)	0.297 1(5)	0.645 3(4)
C(3)	0.372 4(6)	0.275 7(6)	0.751 5(5)
C(4)	0.302 4(7)	0.208 5(6)	0.882 4(5)
C(5)	0.139 5(7)	0.168 5(6)	0.902 2(5)
C(6)	0.045 1(6)	0.188 6(6)	0.792 9(5)
C(7)	0.358(1)	0.090(1)	1.112 5(6)
C(8)	0.336 1(6)	0.377 7(6)	0.501 9(4)
C(9)	0.346 8(7)	0.168 9(8)	0.433 3(7)
C(10)	0.266 6(8)	0.426 6(9)	0.277 8(5)
C(1′)	−0.113 3(8)	0.161 0(6)	0.293 2(6)
C(2′)	−0.197 2(9)	0.164 5(8)	0.187 2(7)
C(3′)	−0.257(1)	0.305 5(9)	0.093 7(7)
C(4′)	−0.230(1)	0.432 4(8)	0.113 7(7)
C(5′)	−0.145 0(9)	0.417 3(6)	0.224 8(6)
	5		
Atom	*x*	*y*	*z*
Pt	0.016 87(4)	0.134 73(5)	0.131 53(2)
Cl(1)	0.127 1(3)	0.343 6(5)	0.141 0(2)
O(1)	0.177 2(7)	0.043(2)	0.062 0(5)
N(1)	−0.062 9(7)	0.252(1)	0.192 2(4)
N(2)	0.094 2(7)	0.001(1)	0.075 3(5)
C(1′)	−0.093(1)	0.180(2)	0.243 0(6)
C(2′)	−0.149(1)	0.258(2)	0.286 5(7)
C(3′)	−0.170(1)	0.420(2)	0.276 5(7)
C(4′)	−0.134(1)	0.499(2)	0.225 1(8)
C(5′)	−0.082(1)	0.415(2)	0.184 1(7)
C(1)	−0.063(1)	−0.049(1)	0.110 6(6)
C(2)	−0.025(1)	−0.170(1)	0.070 0(6)
C(3)	−0.073(1)	−0.300(2)	0.046 7(7)
C(4)	−0.161(1)	−0.317(2)	0.062 7(7)
C(5)	−0.200(1)	−0.203(2)	0.101 9(8)
C(6)	−0.150(1)	−0.069(2)	0.126 7(6)
C(7)	0.064 1(9)	−0.139(2)	0.053 1(5)
C(8)	0.118(1)	−0.253(2)	0.016 4(7)
	6		
Atom	*x*	*y*	*z*
Pd(1)	0.058 4(1)	0.074 7(1)	−0.078 74(5)
I(1)	−0.058 0(1)	−0.170 5(1)	−0.034 62(5)
I(2)	0.047 6(2)	−0.047 4(2)	−0.187 4(1)
P(1)	0.147 5(4)	0.285 4(5)	−0.117 8(2)
C(11)	0.211(2)	0.417(2)	−0.059 2(7)
C(21)	0.023(1)	0.386(2)	−0.167 1(7)
C(31)	0.289(2)	0.254(2)	−0.166 4(7)
C(12)	0.276(2)	0.560(2)	−0.080 6(8)
C(22)	−0.104(1)	0.431(2)	−0.134 9(7)
C(32)	0.409(1)	0.179(2)	−0.131 1(8)
C(13)	0.336(2)	0.660(2)	−0.027 7(9)
C(23)	−0.209(2)	0.519(3)	−0.177 6(9)
C(33)	0.520(2)	0.130(2)	−0.171 7(9)
C(14)	0.402(2)	0.804(2)	−0.046(1)
C(24)	−0.329(2)	0.566(2)	−0.148(1)
C(34)	0.645(2)	0.056(3)	−0.138(1)

Table 4 Rate constants k_2 at 25 °C, and activation parameters for reactions of complexes **1** and **2g** with various pyridines in chloroform at 25 °C

Complex	Nucleophile	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a	py	(8.63 ± 0.16) × 10^3	15.5 ± 3.1	−118 ± 10
1b	py	(7.24 ± 0.28) × 10^3	19.9 ± 2.3	−104 ± 7
1c	py	(8.07 ± 0.26) × 10^3	17.9 ± 1.9	−110 ± 6
1d	py	(1.50 ± 0.03) × 10^4	18.0 ± 1.2	−105 ± 4
1e	py	(1.22 ± 0.02) × 10^4		
1c	4Me-py	(1.06 ± 0.03) × 10^4	16.4 ± 1.3	−114 ± 4
1c	3MeCO-py	(5.6 ± 0.4) × 10^3		
1c	4CN-py	(5.5 ± 0.2) × 10^3		
1c	2,4Me$_2$-py	(2.07 ± 0.02) × 10^3	12.4 ± 3.5	−140 ± 12
1c	2,6Me$_2$-py	25.1 ± 1.8	17.9 ± 0.2	−158 ± 1
2g	4Me-py	64 ± 1	44.4 ± 3.2	−61 ± 11
[(Pr$^n_3$P)IPd(μ-I)$_2$PdI(PPr$^n_3$)]*	py	(3.67 ± 0.11) × 10^4		
[(Pr$^n_3$P)IPd(μ-I)$_2$PdI(PPr$^n_3$)]*	2,6Me$_2$-py	26.5 ± 0.4		

* Data taken from ref. 8.

bridges are thus noticeably asymmetric and, remarkably, match those in the azobenzene palladacycle di-μ-iodo-bis[2-(2,6-dimethylphenylazo)phenyl-C^1,N^2)palladium(II)] of 2.587(1) and 2.704(1) Å.[20d] The same difference in the Pd–Cl bond distances of bridging ligands of 0.128–0.154 Å was reported for complex **1c** and its 3-MeO and 5-MeO isomers.[20c]

Kinetics of Monomerization.—Monomerization of complexes **1**, which occurs on a stopped-flow time-scale, was studied in a large excess of incoming pyridines. The values of k_{obs} were calculated from the absorbance *versus* time traces. The kinetic fits were always good for complexes **1**, but worse for **2**. The observation of only one monoexponential trace points to the fact that despite the starting dimers **1** and **2** not being isomerically pure, this does not complicate the kinetics of the monomerization. Representative data shown in Fig. 4 demonstrate that the reaction is first-order in incoming pyridine [equation (5)] without a meaningful intercept, in agreement

$$k_{obs} = k_2[py] \quad (5)$$

with the practically irreversible nature of reaction (1). The second-order rate constants k_2 were found from the dependencies of k_{obs} on [X-py] obtained at different temperatures. The values of k_2 at 25 °C and the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) calculated from the temperature dependencies of k_2 in the range 19.2–48.7 °C are summarized in Table 4.

High-pressure Kinetic Studies.—Only the slower reactions could be measured using our high-pressure instrumentation. The kinetic data in the pressure range 10–100 MPa are summarized together with the calculated activation volumes in Table 5.

Table 5 The effect of pressure on the rate of monomerization

Complex	Nucleophile	Pressure/MPa	k_{obs}/s^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
1e	2,6Me$_2$-py[a]	10	1.53 ± 0.04	
		50	2.42 ± 0.07	−22.6 ± 2.9
		100	3.5 ± 0.2	
2g	4Me-py[b]	10	0.286 ± 0.007	
		30	0.341 ± 0.013	
		50	0.39 ± 0.03	−14.5 ± 1.3
		75	0.440 ± 0.007	
		100	0.49 ± 0.03	

[a] 0.066 mol dm^{-3}. [b] 0.0060 mol dm^{-3}, at 330 nm.

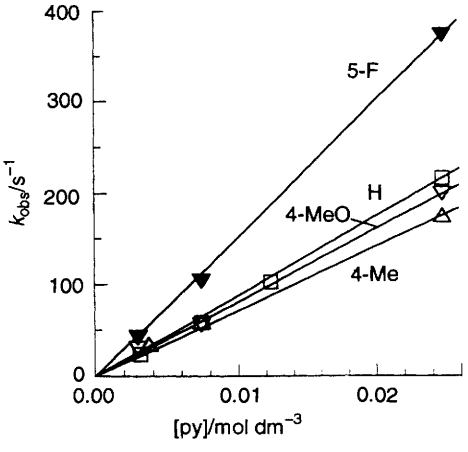


Fig. 4 Plots of k_{obs} *versus* py concentration for the monomerization of ring-substituted complexes **1**

Discussion

Among the kinetic data those worthy of comment are (*i*) the rate constants for **1** and *trans*-[(Pr$^n_3$P)IPd(μ-I)$_2$PdI(PPr$^n_3$)] are similar and the Pt dimer **2g** has a 100-times lower reactivity compared to its Pd counterpart **1c**; (*ii*) weak sensitivity to electronic effects; (*iii*) strong influence of steric crowding; (*iv*) very low activation enthalpies $\Delta H^{\ddagger}$; (*v*) large and negative activation entropies $\Delta S^{\ddagger}$ and volumes $\Delta V^{\ddagger}$.

Absolute Rates.—All the palladium complexes **1a**–**1e** react with pyridines at similar rates. Neither electron-donating/withdrawing groups nor the nature of the bridging halide significantly affect the values of k_2. For instance, the iodo dimer **1e** is only a factor of 1.4 more reactive than its chloro analogue **1a**. Halides may be considered as 'pseudo-leaving' ligands in the bridge-splitting reaction (1), since *there is* a cleavage of a halide–metal bond, but *there is no* dissociation of halide into the solvent bulk. It is, however, well documented that the rates of associative substitution reactions in square-planar complexes are weakly sensitive to the nature of the leaving ligand.[32] Thus, this observation is the first evidence for the associative character of the reactions.

The low 'electronic' sensitivity of the reactions provides reasons to estimate the effect of an organic σ-bound chelated backbone during bridge cleavage. Rate constants for the monomerization of **2g** and [Br$_2$Pt(μ-Br$_2$)PtBr$_2$]$^{2-}$, equation (2), were the first to be compared under similar conditions. The second-order rate constant for reaction (2) is 8.8 × 10^{-2} dm^3 mol^{-1} s^{-1} in acetone at 25 °C.[5] Hence, **2g** is more active than [Br$_2$Pt(μ-Br$_2$)PtBr$_2$]$^{2-}$ by a factor of *ca.* 10^3. The relative labilization by the platinacycle seems to be higher than the effect

of the non-chelated phenyl group in the classical substitution reaction (6), where the rate difference between L = Ph^- and Cl^- is only a factor of 40.[10a]

$$trans\text{-}[PtClL(PEt_3)_2] + py \longrightarrow trans\text{-}[PtL(py)(PEt_3)_2]^+ + Cl^- \quad (6)$$

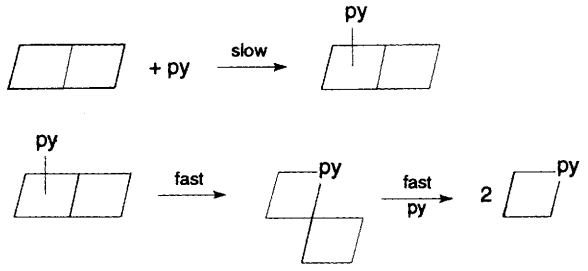
At the same time the reactivity of the Pd^{II} complex **1e** is very close to that of *trans*-$[(Pr^n_3P)IPd(\mu\text{-}I)_2PdI(PPr^n_3)]$ under exactly the same conditions (Table 4). Thus, the labilizing effects of the trialkylphosphine ligand and the chelated aryl σ-carbon bond are comparable and, as from the X-ray structural data, mostly of ground state in origin. In fact, the structural data reported here and elsewhere show that the in-plane aryl σ-carbon bond causes significant elongation of a metal–halide bond *trans* to it. Consequently, bridging fragments $M(\mu\text{-}X)_2M$ become markedly asymmetric and reactive. The bond distances in the Pd^{II} phosphine dimers $[(R_3P)XPd(\mu\text{-}X)_2PdX(PR_3)]$ indicate the same arrangement of this key structural fragment and account for the similar (and high) reactivity observed.

It is always interesting to compare the kinetic behaviour of related Pd^{II} and Pt^{II} centres. The ratio of the rate constants k_2 for **1c** and **2g**, which is 126 at 25 °C, is somewhat lower than normally expected (10^4–10^5) for substitution reactions when the reactivity of Pd^{II} and Pt^{II} complexes is compared.[9]

Electronic Effects.—Electron-poor palladacycles and electron-rich pyridines have an insignificant tendency to react faster. Although the pK_a values of the pyridines used vary over the range 1.90–6.03,[33] the values of k_2 only change by a factor of 1.9. This, however, seems to be normal, since rate constants in substitution reactions are usually poorly sensitive to the pyridine basicity.[34] The slope of the plot of log k_2 *versus* pK_a of the substituted pyridines is as low as +0.064. It is much lower than previously reported for substitution at Pt^{II},[35] but there is such a precedent in the literature.[36] The positive slope indicates that Pd^{II} is an electrophilic centre. The same result comes from the effect of substituents R in **1**. The electron-acceptor groups favour the reaction. The corresponding Hammett plot with $\rho = +0.67 \pm 0.06$ may be constructed on the assumption that there are two channels responsible for the electronic density on the metal, *viz. via* the Pd–C and Pd–N bonds, and hence $\sigma = \sigma(Pd\text{–}C) + \frac{1}{2}\sigma(Pd\text{–}N)$. The coefficient $\frac{1}{2}$ is due to the methylene group between the nitrogen and the phenyl ring. The slope may be compared with those where bridge cleavage was postulated as a rapid pre-equilibrium. Electronic effects have been investigated in several reactions of cyclopalladated compounds,[2,3] but the sign of ρ found here is opposite to that observed before. The insertion of styrene [2] and diphenylethyne [3] is characterized by negative values of ρ, which reflect the rate-limiting nucleophilic attack of the σ-bound Pd^{II} aryl carbon at the β carbon of the C=C or C≡C bond. The preceding bridge cleavage was considered to be a fast process. The present study confirms the correctness of this assumption. In fact, diphenylethyne reacts with **1a** at a second-order rate constant of 7.1×10^{-2} dm^3 mol^{-1} s^{-1} in $CHCl_3$ at 25 °C,[3] and this is 1.2×10^5 times slower than the reaction of **1a** with py!

Steric Effects.—In contrast to electronic effects, steric effects play a decisive role here. This has previously been noted,[22] but finds a quantitative support in this work. On going from 4Me-py to $2,4Me_2$-py and $2,6Me_2$-py, which are ligands of similar basicity, k_2 drops 5.1 and 424 fold, respectively. Since the introduction of steric hindrance in the vicinity of the donor centre decreases the reactivity, the reaction must be associative to a large extent. Interestingly, in the case of dissociative substitution at square-planar platinum(II) centres the rates are very similar for the same series of pyridines.[11a]

Activation Parameters.—Direct support for the associative nature of the bridge-cleavage reaction comes from the values of



Scheme 2

$\Delta H^‡$ and $\Delta V^‡$, Tables 4 and 5. At least in the Pd case, the values of $\Delta H^‡$ are too low, *viz.* 12–20 kJ mol^{-1}, to be associated with the breaking of any bond in the transition state. Correspondingly, the values of $\Delta S^‡$ are large and negative, probably reflecting the loss in entropy on going from the initial to the transition state in the associative process. The $\Delta S^‡$ values, −104 to −158 J K^{-1} mol^{-1}, are significantly negative and suggest that the transition state is ordered. We assume that the ordering may partly arise from the back donation from the metal into the apically co-ordinated py ligand in the transition state. In fact, if the back-bonding occurs into the antibonding π* orbitals of py, the d_{xz} or d_{yz} palladium orbitals must be involved. Hence, the orientation of apically co-ordinated py must be more or less rigorous.

The data in Table 4 indicate that the platinum complex **2g** is less reactive compared to the Pd complexes **1** because of the much higher $\Delta H^‡$ which may indicate that Pt–Cl bond breakage or at least its weakening plays a role in the transition state. The values of $\Delta V^‡$ for reactions of **1c** and **2g** with $2,6Me_2$-py and 4Me-py, respectively, do exhibit some differences. The very negative $\Delta V^‡$ for **1c** leaves no doubt that the reaction is truly associative.[37] The $\Delta V^‡$ for the Pt reaction is *ca.* 8 cm^3 mol^{-1} more positive, *viz.* −14.5 cm^3 mol^{-1}. This may partly be related to the smaller size of the entering group. There is no evidence for any crucial mechanistic differences between Pd and Pt orthometallated halogen-bridged dimers, but there are some structural and kinetic features that do affect the rate of the reactions.

Conclusion

Bridge cleavage in Pd^{II} and Pt^{II} dimers with a dimethylaminomethylphenyl-C^1,N backbone by pyridines is a rather fast, bimolecular, associatively driven reaction in which bond making plays the dominant role, Scheme 2. These statements are in full accord with the values of the rate constants, enthalpies, entropies, and volumes of activation. It is likely that the asymmetry of the bridging $M(\mu\text{-}X)_2M$ unit is responsible for the high reactivity. As in the anation reactions,[28b] the orthometallated C,N-backbone does not bring about the mechanistic associative/dissociative changeover. This may be due to the fact that the *in-plane* aryl ring, as CO in *cis*-$[PtPh_2(CO)(Et_2S)]$,[11a] is involved in the creation of a novel lowest unoccupied molecular orbital that is very appropriate for associative nucleophilic attack. The geometry of the complexes formed is, however, significantly different since it is *N,N-cis* and *N,N-trans* for the Pd^{II} and Pt^{II} cases, respectively. The crystallographic evidence presented for **4** and **5** demonstrates that both geometrical isomers may, in principle, exist in the Pt case in the solid state.

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