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Bridge-splitting kinetics, equilibria and structures of *trans*-biscyclooctene complexes of platinum(II) †

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Received 4th March 2003, Accepted 17th April 2003
First published as an Advance Article on the web 13th May 2003

Cyclooctene (C_8H_{14}, cot) complexes of platinum(II) have been synthesised and characterised by means of multinuclear NMR, UV-Vis spectroscopy and X-ray crystallography. The bridge-splitting equilibrium constants of the dinuclear, chloride-bridged *trans*-$[PtCl_2(cot)]_2$, **1**, in dichloromethane solvent at 298 K with MeOH, MeCN and cot, yielding *trans*-$[PtCl_2(cot)(MeOH)]$, **2**, *trans*-$[PtCl_2(cot)(MeCN)]$, **3**, and *trans*-$[PtCl_2(cot)_2]$, **4**, were determined by UV-Vis measurements as $K_{12} = 0.0169 \pm 0.0015$, $K_{13} = 9.7 \pm 0.9$ and $K_{14} = 2.05 \pm 0.06$ mol^{-1} dm^3, respectively. Substitution of one cyclooctene from **4** by MeOH gives $K_{42} = 0.110 \pm 0.009$ and by MeCN $K_{43} = 2.25 \pm 0.03$. The bis-cyclooctene complexes **1** and **4** react quantitatively with chloride to give $[PtCl_3(cot)]^-$, **5**. The kinetics for bridge-splitting of **1** with MeOH, MeCN and cot was studied by conventional and cryo-stopped-flow spectroscopy. Second-order rate constants at 298 K are 0.128 ± 0.003, 4.93 ± 0.02 and 0.0637 ± 0.0009 mol^{-1} dm^3 s^{-1}, respectively. The corresponding activation parameters are $\Delta H^{\neq} = 43.7 \pm 1.8$, 42.0 ± 0.8 and 39.6 ± 0.9 kJ mol^{-1} and $\Delta S^{\neq} = -115 \pm 6$, -91 ± 3 and -135 ± 3 J K^{-1} mol^{-1}, indicating associative activation with a relatively large $-T\Delta S^{\neq}$ contribution to $\Delta G^{\neq}$. Crystal and molecular structures of **1**, **4**, and the tetraphenylphosphonium salt of **5** have been determined, indicating a moderate ground-state *trans* influence of cyclooctene. The molecular structure of **4** with two C=C double bonds coordinated *trans* to each other and perpendicular to the platinum coordination plane, features a significant Pt–C bond lengthening compared to cyclooctene complexes with chloride or nitrogen *trans* to cyclooctene, leading to high reactivity and thermodynamic instability. Equilibrium data confirm that the thermodynamic stability of a cyclooctene coordinated *trans* to another cyclooctene is much lower than *trans* to a ligand with less π-back-bonding capacity.

Introduction

Substitution processes *trans* to alkenes in platinum(II) complexes are extremely fast due to their large kinetic *trans* effect.[1] We have previously studied such fast exchange[2] and substitution[3] processes quantitatively using NMR and cryo-stopped-flow spectroscopy. During this work we prepared the cyclooctene analogues of Zeise's ethene complexes, *viz.* the chloride-bridged dinuclear complex *trans*-$[PtCl_2(cot)]_2$, **1**, and the monomeric $[PtCl_3(cot)]^-$, **5**. Splitting of **1** with cyclooctene results in the mononuclear complex *trans*-$[PtCl_2(cot)_2]$, **4**, so far the only example of a mononuclear *trans*-bis-alkene platinum(II) complex stable at ambient conditions.[4,5] It is expected to display unusual reactivity properties due to the mutual labilization of the two *trans* alkene ligands. It is relevant as a model for the unstable *trans*-$[PtCl_2(C_2H_4)_2]$, which has been proposed to exist as a possible short-lived intermediate in the reaction mechanism for ethene exchange at $[PtCl_3(C_2H_4)]^-$.[2,6] The bis-ethene complex was first reported by Chatt and Wilkins 50 years ago as an unstable yellow solid that could be precipitated from acetone at −80 °C.[7,8] It has also been identified as an elusive compound in THF[9] and chloroform solution.[2,10]

Substitution reactions *trans* to cyclooctene proceed more slowly than those *trans* to ethene, due to the steric and electronic properties of the cyclooctene. Cyclooctene complexes are more stable than their ethene analogues at ambient conditions,[3] facilitating mechanistic investigations of their reactions. Cyclooctene is also easier to handle in quantitative experiments than the volatile ethene. The aim of the present study was to elucidate the structure–reactivity properties of the three cyclooctene complexes **1**, **4**, and **5** in order to gain more information on binding modes and reaction mechanisms that would be applicable also to ethene complexes. Equilibria and kinetics for bridge-splitting and substitution processes have been studied and structures determined. Scheme 1 gives an overview of the system studied and the notation used.

Experimental

Chemicals

Methanol (Riedel-de Haën), acetonitrile (Merck) and dichloromethane (Riedel-de Haën) solvents were of analytical grade and were freshly distilled from CaH_2 under a dinitrogen atmosphere prior to use. Cyclooctene (C_8H_{14}, cot) (Acros) was dried over molecular sieves and PPh_4Cl (Aldrich) was dried under vacuum before use. K_2PtCl_4 (Johnson Matthey Chemicals Ltd.) was used directly.

Preparation of complexes

trans-$[PtCl_2(C_2H_4)]_2$ was prepared from K_2PtCl_4 *via* $[PtCl_3(C_2H_4)]^-$ according to literature procedures.[8] Complex **1** was prepared by treating *trans*-$[PtCl_2(C_2H_4)]_2$ with 2.2 molar equivalents of cyclooctene in dichloromethane. Using a larger excess of cyclooctene resulted in formation of **4**. Complexes **2** and **3** were prepared *in situ* by reacting **1** with excess MeOH (*ca.* 1000×) or MeCN (*ca.* 100×), respectively, as specified in the ESI (stability constant determinations). † Crystals of **1**, **4** and PPh_4**[5]** suitable for crystallography were grown as described below.

† Electronic supplementary information (ESI) available: observed pseudo-first order rate constants for bridge splitting reactions, absorbance *versus* added ligand concentrations for equilibrium constant determinations and complete crystallographic details in CIF format. See http://www.rsc.org/suppdata/dt/b3/b302482m/

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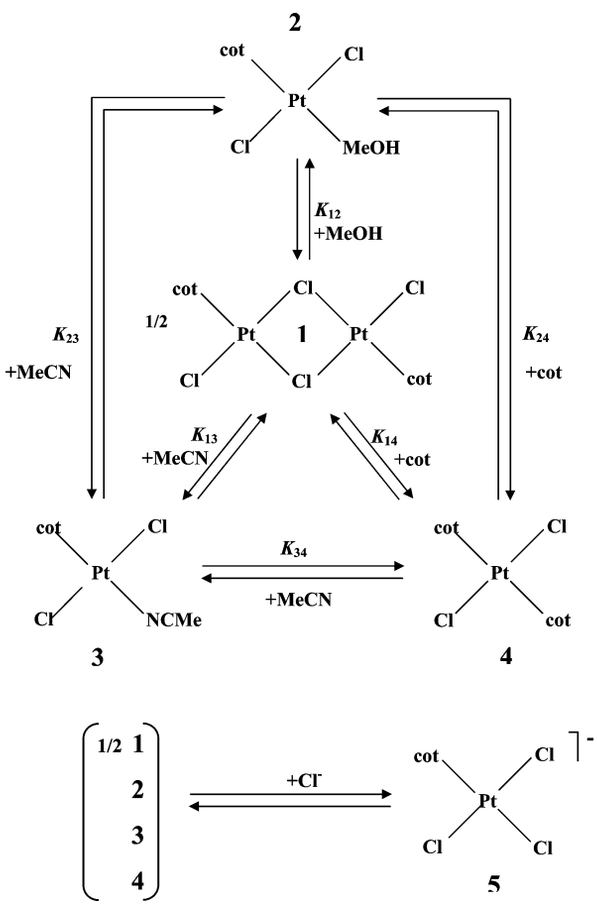
DOI: 10.1039/b302482m

Table 1 Crystallographic data and refinement parameters for **1**, **4** and PPh_4**[5]**

	1	**4**	PPh_4**[5]**
Empirical formula	$C_{16}H_{28}Cl_4Pt_2$	$C_{16}H_{28}Cl_2Pt$	$C_{32}H_{34}Cl_3PPt$
Formula weight	752.36	486.37	751.00
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/Å	8.2310(16)	5.8407(12)	11.227(2)
b/Å	5.9600(12)	7.4886(15)	14.746(3)
c/Å	20.991(4)	10.069(2)	18.901(4)
α/°	90	84.01(3)	90
β/°	99.68(3)	88.45(3)	107.18(3)
γ/°	90	73.59(3)	90
V/Å^3	1015.1(3)	420.17(15)	2989.5(10)
Z	2	1	4
μ/mm^{-1}	14.287	8.653	5.035
Collected reflections	7730	4315	31554
Independent reflections	2168	2547	9316
R_{int}	0.0877	0.0343	0.0647
Observed reflections [$I > 2\sigma I$]	1887	2542	5336
R ($I > 2\sigma I$)	0.0650	0.0428	0.0354
wR ($I > 2\sigma I$)	0.1622	0.1129	0.0675
R (all data)	0.0734	0.0429	0.0914
wR (all data)	0.1668	0.1131	0.0777



Scheme 1 Reaction scheme and notation for equilibrium constants.

***trans*-[$PtCl_2(C_8H_{14})$]$_2$, 1.** ^{1}H NMR: 1.45 (m, 8H), 1.55 (m, 4H), 1.83 (m, 4H), 2.01 (m, 4H), 2.29 (m, 4H), 5.47 (m, 4H). ^{195}Pt NMR: −2434, −2453. ε^{248} 17505, ε^{271} 7370, ε^{353} 760 cm^{-1} mol^{-1} dm^3.

***trans*-[$PtCl_2(C_8H_{14})(MeOH)$], 2.** ^{195}Pt NMR: −2696 (7.1 mmol dm^{-3} of **1**, 4 mol dm^{-3} MeOH in $CDCl_3$). ε^{286} 1088, ε^{342} 285 cm^{-1} mol^{-1} dm^3.

***trans*-[$PtCl_2(C_8H_{14})(MeCN)$], 3.** ^{195}Pt NMR: −2892 (6.3 mmol dm^{-3} of **1**, 38 mmol dm^{-3} MeCN in $CDCl_3$). ε^{248} 3722, ε^{270} 2567, ε^{301} 1290 cm^{-1} mol^{-1} dm^3.

***trans*-[$PtCl_2(C_8H_{14})_2$], 4.** ^{1}H NMR: 1.42 (m, 8H), 1.64 (m, 8H), 2.15 (m, 8H), 5.58 (m, 4H). ^{195}Pt NMR: −2747. ε^{277} 6372, ε^{340} 1182 cm^{-1} mol^{-1} dm^3.

PPh_4[$PtCl_3(C_8H_{14})$], PPh_4[5]. ^{1}H NMR: 1.40 (m, 3H), 1.64 (m, 3H), 2.10 (m, 3H), 2.40 (m, 3H), 4.99 (tm, 2H, $^{2.5}J_{PtH}$ 70 Hz), 7.60–7.70 (m, 8H), 7.76–7.84 (m, 8H), 7.86–7.94 (m, 4H). ^{195}Pt NMR: −2681. ε^{340} 313, ε^{342} 232 cm^{-1} mol^{-1} dm^3.

NMR measurements

All NMR spectra were recorded at 295 K in $CDCl_3$ on a Varian Unity 300 spectrometer operating at 299.78 and 64.27 MHz for the ^{1}H and ^{195}Pt nuclei, respectively. ^{1}H spectra were calibrated on the residual $CHCl_3$ peak at 7.25 ppm relative to TMS. ^{195}Pt NMR spectra were recorded with a WALTZ-16 proton decoupling sequence. Peak resonances are reported in ppm relative to $PtCl_6^{2-}$ (1 g H_2PtCl_6 in 3 cm^3 1.0 mol dm^{-3} HCl containing 50% D_2O, $\delta = 0$ ppm) as external reference.

X-Ray crystallography data collection and refinement

Crystals of **1** were grown from dichloromethane and those of **4** from a dichloromethane solution of **1** containing a few drops of cyclooctene. Crystals of PPh_4**[5]** were obtained by treating any of complexes **1**, **2**, **3** or **4** with PPh_4Cl in dichloromethane. Data were collected on a Siemens SMART CCD diffractometer using MoKα (0.71073 Å) and ω-scans at 293(2) K. After completed collection, the first 50 frames were repeated to check for decay, which was not observed. All reflections were merged and integrated using SAINT[11] and were corrected for Lorentz, polarization and absorption effects using SADABS.[12] The structures were solved by the heavy atom method and refined through full-matrix least-squares cycles using the SHELXL97[13] software package with $\Sigma(|F_o| - |F_c|)^2$ being minimised. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites using a riding model. The high platinum content in the crystals of **1** (52%) resulted in a large μ value, which complicated the absorption corrections and resulted in a fairly high residual electron density. However, this was located within 1.3 Å of the metal centres indicating no physical meaning. The DIAMOND[14] Visual Crystal Structure Information System software was used for the graphics. Crystal data and details of data collection and refinement are given in Table 1.

CCDC reference numbers 205486–205488.

See http://www.rsc.org/suppdata/dt/b3/b302482m/ for crystallographic data in CIF format.

Equilibrium measurements

Series of solutions of complex **1** in dichloromethane containing the same total concentration of platinum and varying concentrations of methanol, acetonitrile or cyclooctene, respectively, were prepared and their UV-Vis spectra were recorded in 1.00 cm quartz cells at 298.2 K on a Cary 300 Bio UV-Vis spectrophotometer. Solutions were aged long enough to ensure that equilibrium was established before measurement. Least-squares fits of the appropriate equations to the absorbance/concentration data (*vide infra*) were performed using the SCIENTIST[15] non-linear least-squares minimising programme. Absorbance/concentration data and wavelengths are given as ESI.†

Kinetic measurements

For rapid reactions, the bridge splitting of **1** with methanol, acetonitrile and cyclooctene were monitored using a Hi-Tech SF-61DX-2 diode-array stopped-flow system equipped with a Hi-Tech Ltd. (Salisbury, UK) Cryo Flow temperature unit described previously.[3] Slower reactions were followed by use of the Cary 300 Bio UV-Vis spectrophotometer. The Cary cell compartment was flushed with dry nitrogen to minimize condensation on the cell's windows at low temperature. Based on the equilibrium measurements, the following wavelengths were selected for the kinetics: 275 nm (MeOH), 300 nm (MeCN) and 280 nm (cot). Ligand concentrations were sufficiently large to ensure pseudo first-order reaction conditions and complete conversion of the reactants to products. In all cases, single exponential kinetics was observed. To determine activation parameters, reactions were studied between −10 and 25 °C for MeOH, −5 and 25 °C for CH_3CN, and between 5 and 32 °C for cyclooctene. Data were collected and observed pseudo first-order rate constants were calculated using the Hi-Tech software package KinetAsyst2.[16] All least-squares fits were performed using the SCIENTIST[15] non-linear minimising programme. Complete experimental data with experimental errors are given as ESI.†

Results and discussion

Preparation and characterization of complexes

Complexes **1**, **4** and and the tetraphenylphosphonium salt of **5** were conveniently prepared and isolated as solids while complexes **2** and **3** could only be prepared *in situ* by bridge splitting of **1** with methanol or acetonitrile, respectively. Compound **4** seems to be the only structurally characterized mononuclear platinum(II) complex so far containing two monodentate alkene ligands coordinated *trans* to each other.[17]

In the ^{1}H NMR spectra of complexes **1**, **2**, **3** and **4** all resonances were broad and no coupling of the alkene protons to the Pt nucleus could be observed, suggesting that the complexes are in fast exchange with free ligand (cot, CH_3CN or MeOH). The $^{2,5}J_{PtH}$ of 70 Hz for **5** is in good agreement with the 64 Hz recorded for the analogous ethene complex.[3]

Solid state structures

Molecular diagrams showing the numbering schemes and thermal ellipsoids for **1**, **4** and **5** are given in Fig. 1. Selected geometrical parameters are summarised in Table 2. In all compounds, the cyclooctene molecules are coordinated to the metal centres through the double bonds in a 'side-on' fashion as predicted by the Dewar–Chatt–Duncanson model forming an angle very closely perpendicular to the coordination plane.[18] The cyclooctene molecules adopt a twisted chair conformation in all cases. The dihedral angles between the coordination plane and that formed by the Pt–C(1)–C(2) moieties are 89.8(3), 88.2(6) and 88.9(2)° for complex **1**, **4**, and **5**, respectively, indicating that the perpendicular coordination mode is virtually not influenced by different packing modes.

Table 2 Selected bond lengths (Å) and angles (°) for **1**, **4** and PPh_4[**5**]; symmetry related atoms primed

Bond/angle	**1**	**4**	PPh_4[**5**]
Pt–Cl(1)	2.340(3)	2.3068(18)	2.3632(12)
Pt–Cl(1′)	2.371(3)	2.3068(18)	
Pt–Cl(2)	2.265(4)		2.3022(12)
Pt–Cl(3)			2.2913(12)
Pt–C(1)	2.132(13)	2.259(6)	2.160(4)
Pt–C(2)	2.143(13)	2.287(6)	2.161(4)
C(1)–C(2)	1.41(2)	1.375(8)	1.399(6)
Cl(1)–Pt–Cl(1′)	83.84(12)	180	
Cl(1)–Pt–Cl(2)	173.74(12)		90.68(5)
Cl(1)–Pt–Cl(3)			86.81(5)
Cl(2)–Pt–Cl(3)			177.16(4)
Cl(1)–Pt–C(1)	96.2(4)	86.04(17)	160.96(12)
Cl(1)–Pt–C(2)	96.5(4)	86.19(18)	161.19(12)
Cl(2)–Pt–C(1)	89.8(4)		88.80(12)
Cl(2)–Pt–C(2)	89.4(2)		87.64(13)
Cl(3)–Pt–C(1)			94.00(12)
Cl(3)–Pt–C(2)			94.30(13)
Cl(1′)–Pt–C(1)	157.0(4)	93.96(17)	
Cl(1′)–Pt–C(2)	164.5(4)	93.81(18)	
C(1)–C(2)–Pt–Cl(1)	91.8(8)	88.5(4)	
C(1)–C(2)–Pt–Cl(2)	90.7(8)		90.0(3)
C(1)–C(2)–Pt–Cl(3)			91.1(3)

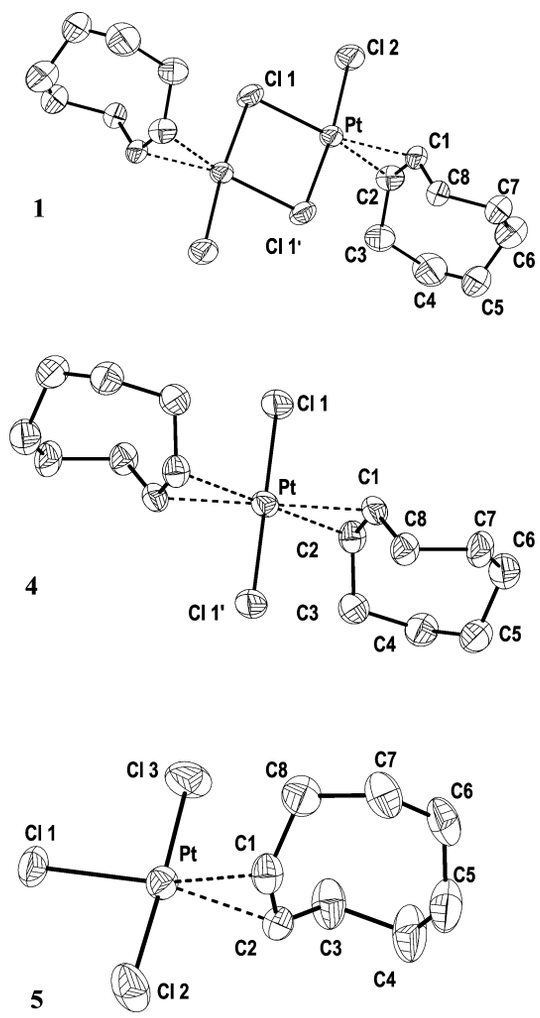


Fig. 1 Molecular diagram of **1**, **4** and **5** showing the numbering scheme and thermal ellipsoids (30% probability level).

The molecular diagram of **1** shows its *trans* configuration, as expected for an analogue of Zeise's dimer (Fig. 1). Even though

Table 3 Bond lengths (Å) in dinuclear chloride-bridged cyclopentene, -heptene and -octene complexes, *trans*-$[PtCl_2(alkene)]_2$

Alkene	Pt–Cl_b [a]	Pt–Cl_t [b]	Pt–C	C(1)–C(2)	Ref.
C_5H_8	2.320(5) 2.349(5)	2.264(6)	2.20(2)	1.40(2)	19
C_7H_{12}	2.328(6) 2.362(6)	2.257(6)	2.14(2) 2.10(2)	1.38(3) —	19
C_8H_{14}	2.340(3) 2.371(3)	2.265(4)	2.132(13) 2.143(13)	1.41(2)	This work

[a] Cl_b = bridging. [b] Cl_t = terminal.

several halide-bridged dinuclear alkene complexes have been prepared, only three crystal structure determinations of such complexes seem to have been reported, *viz.* the cyclopentene, cycloheptene and tetramethylallene analogues.[19,20] The structural parameters of the cyclopentene, -heptene and -octene complexes given in Table 3 show that there is a gradual increase of the Pt–Cl(bridging) distances from cyclopentene to -octene, corresponding to a gradual weakening of the chloride double bridge in this order. In **1**, the terminal Pt–Cl(2) bond distance *trans* to bridging chloride, 2.265(4) Å, is significantly shorter than the two bridging Pt–Cl(1) bond distances, 2.371(3) Å *trans* to cyclooctene, and 2.340(3) Å *trans* to terminal chloride. It is also significantly shorter than the Pt–Cl distance *trans* to chloride in for example $PtCl_4^{2-}$, which is 2.317(2) Å (Table 5 below). The situation is similar in the cyclopentene and -heptene complexes, reflecting the ground state *trans* influence of the alkenes, and the weakened *trans* influence of the bridging chlorides compared to the terminal ones.

The data for complex **4** given in Table 2 agree well with those for an isostructural version of the compound reported recently, prepared by an alternative method.[4] Only two other structures of monomeric bis-alkene complexes have been found in the literature. They are both *cis* isomers, *viz.* *cis*-$[PtCl_2(CH_2CHC_6H_5)_2]$ and *cis*-$[PtCl_2(CH_2CH_2)_2]$.[21,22]

In Table 4, structural data for free and coordinated cyclooctene in platinum(II) complexes are presented. There is a substantial and significant lengthening of the Pt–C bond distances, from *ca.* 2.14 to 2.16 Å in the complexes with cyclooctene *trans* to chloride or nitrogen,[23] to *ca.* 2.27 Å in **4**, where the two cyclooctene ligands are *trans* to each other. Thus, as expected, there is a significant labilisation of the cyclooctene in the ground state of **4**, since the two *trans*-cyclooctene ligands share the same orbitals. This ground-state destabilisation will contribute to the observed thermodynamic instability and the extreme reactivity of the *trans*-alkene complexes in solution. It is also obvious that the C(1)–C(2) bond distances in the complexes are significantly longer than in free cyclooctene,[24] reflecting a weakening of the C(1)–C(2) double bond due to back donation of electrons from the metal center to the antibonding orbitals of the alkene and loss of electrons in the bonding C–C orbital. This effect is smaller for **4** than for the complexes with chloride or nitrogen *trans* to cyclooctene.

The crystal structure of $[PPh_4]$**5** is related to the previously reported $[Bu_4N]$**5**.[3] Although the Pt–Cl(1) and Pt–C bond distances are significantly longer than in the tetrabutyl ammonium salt, the C(1)–C(2) bond distance remains nearly the same (Table 4).

In Table 5, Pt–Cl bond distances *trans* to different ligands L in complexes $[PtCl_3(L)]^-$ are reported.[3,25–33] There is a progressive increase from 2.266(2) in $[PtCl_3(MeCN)]^-$ to 2.382(4) Å in $[PtCl_3(PEt_3)]^-$. The increase in bond length might indicate a moderate increase of ground state *trans* influence in the series:

$$MeCN < CO < py < Cl^-, CH_2CHSiMe_3 < Me_2SO < NH_3 < CH_2CHOEt < alkene < PEt_3$$

But this over-all effect is small, and packing effects in the crystal lattice might well contribute to some of the observed changes. For instance, the Pt–Cl bond distances in PPh_4**[5]** and Bu_4N**[5]** differ by 0.04 Å, from 2.363(1) to 2.324(2) Å, whereas that in the potassium salt of Zeise's anion is intermediate,

Table 4 Bond lengths (Å) in cyclooctene complexes of platinum(II)

Complex	L′ [a]	Pt–L_T	Pt–C [a]	C(1)–C(2)	Ref.
'Free' cot	—	—	—	1.22(4)	24
$[PtCl(Me_2NCH_2C_6H_4)(cot)]$	N	2.139(9)	2.15(1) 2.16(1)	1.38(2)	23
$[PtCl_2(cot)]_2$ (**1**)	Cl	2.371(3)	2.13(1) 2.14(1)	1.41(2)	This work
$Bu_4N[PtCl_3(cot)]$	Cl	2.324(2)	2.139(4) 2.147(4)	1.391(7)	3
$PPh_4[PtCl_3(cot)]$ (PPh_4**[5]**)	Cl	2.363(1)	2.160(4) 2.161(4)	1.399(6)	This work
trans-$[Pt(cot)_2Cl_2]$ (**4**)	cot	2.287(6) 2.259(6)	2.259(6) 2.287(6)	1.375(8)	This work

[a] Ligand/donor atom *trans* to cot.

Table 5 Geometrical parameters for complexes of the type $[PtCl_3(L)]^-$

Complex	Pt–Cl/Å	Pt–L [a]/Å	C–C/Å	Ref.
$Et_4N[PtCl_3(MeCN)]$	2.266(2)	—	—	25
$Bu_4N[PtCl_3(CO)]$	2.289(3)	1.82(1)	—	26
$Et_4N[PtCl_3(py)]$	2.305(2)	—	—	27
$Bu_4N[PtCl_3(CH_2CHSiMe_3)]$	2.314(2)	2.13(3)	1.44(1)	3
$K_2[PtCl_4]$	2.317(2)	2.317(2)	—	28
$K[PtCl_3(Me_2SO)]$	2.318(5)	2.139(5)	—	29
$K[PtCl_3(NH_3)]$	2.321(7)	—	—	30
$Bu_4N[PtCl_3(CH_2CHOEt)]$	2.324(2)	2.14(2)	1.38(1)	31
$Bu_4N[PtCl_3(C_8H_{14})]$	2.324(2)	2.14(1)	1.391(7)	3
$K[PtCl_3(C_2H_4)]$	2.340(2)	2.131(5)	1.375(4)	32
$Ph_4P[PtCl_3(C_8H_{14})]$ (PPh_4**[5]**)	2.363(1)	2.161(5)	1.399(6)	This work
$Et_4N[PtCl_3(PEt_3)]$	2.382(4)	2.215(4)	—	33

[a] Average of the two Pt–C alkene bonds.

2.340 Å.[32] The important conclusion is that the ground state *trans* influence of the alkenes is moderate, compared to for instance the much larger *trans* influence of strongly σ-bonded aryl or silyl ligands, where Pt–Cl distances up to *ca.* 2.47 Å have been observed.[34]

Equilibria

More or less complete studies of the kinetics of bridge-splitting reactions of square-planar dinuclear complexes with amines,[35] alkenes,[36,37] iodide,[38] pyridines[39] and carbon monoxide[40] have been published earlier. In the present system we also observed equilibria between the dinuclear complex **1** and the monomeric complexes formed in the bridge-cleavage process, as shown in Scheme 1. The bridge-splitting reaction with the nucleophiles L = MeOH, CH_3CN, cyclooctene and chloride occurs according to eqn. (1) with complexes **2**, **3**, **4** and **5**, respectively, as products.

$$trans\text{-}[PtCl_2(cot)]_2 + 2L \rightleftarrows 2\ trans\text{-}[PtCl_2(cot)(L)] \quad (1)$$

In the case of chloride, the bridge cleavage is quantitative. In the other three cases, the equilibrium constants K, *viz.* K_{12}, K_{13} and K_{14} as defined in Scheme 1 can be calculated by least-squares fitting of eqns. (2)–(4) to the experimental concentration/absorbance data with C_{Pt} fixed and K, ε_1 (molar absorptivity of **1**) and ε_M (molar absorptivity of the monomeric product) as adjustable parameters. A denotes the observed absorptivity (equal to the absorbance since 1.00 cm cells were used).

$$K = [M]^2/([\mathbf{1}][L]^2) \quad (2)$$

$$A = \varepsilon_1[\mathbf{1}] + \varepsilon_M[M]/2 \quad (3)$$

$$[M]^3K - 2[M]^2(C_{Pt}K + K[L]_a - 1) + [M](4C_{Pt}[L]_aK + K[L]_a^2) - 2KC_{Pt}[L]_a^2 = 0 \quad (4)$$

In eqns. (2)–(4), C_{Pt} and [M] refer to the total starting concentration of **1** (as Pt_2) and the concentration at equilibrium of the monomeric product, respectively. The equilibrium concentrations of [**1**] = C_{Pt} – [M]/2 and [L] in eqns. (2) and (3) were calculated for each solution by use of eqn. (4). The concentration of L added is $[L]_a = [L] + [M]$.

The equilibrium constants K_{24} and K_{34} for the substitution processes of eqn. (5) were also calculated by least-squares fitting of eqn. (6) to the experimental absorbance/concentration data with an excess of cyclooctene added, keeping [cot] and C_M (total monomeric Pt concentration) fixed and K, ε_4 and ε_P as adjustable parameters. Here, ε_4 and ε_P denote the molar absorptivities of species **4** and of the product, respectively, at the specific wavelength.

$$trans\text{-}[PtCl_2(cot)_2] + L \rightleftarrows trans\text{-}[PtCl_2(cot)(L)] + cot \quad (5)$$

$$A = C_M(\varepsilon_4[cot] + \varepsilon_PK[L])/([cot] + K[L]) \quad (6)$$

From the values of K_{24} and K_{34} a value of K_{23} for the substitution process of eqn. (7) can also be derived.

$$trans\text{-}[PtCl_2(cot)(MeOH)] + MeCN \rightleftarrows trans\text{-}[PtCl_2(cot)(MeCN)] + MeOH \quad (7)$$

All equilibrium constants are given in Table 6. The agreement between K_{23}, K_{24}, and K_{34} calculated by the different methods is good. The magnitude of the equilibrium constant is highly dependent on the nature of the nucleophile and the solvent. Complexes **1** and **4** react quantitatively with a stoichiometric amount of chloride in the dichloromethane solvent.

The comparison of the bridge splitting equilibrium constants given in Table 6 shows that $K_{12} < K_{14} < K_{13}$. Including the fact that chloride splits the bridge quantitatively gives the following sequence of efficiency for the bridge-splitting ligands: MeOH < cot < MeCN < Cl^-. Similarly, if we compare pair-wise the equilibrium constants for the substitution reactions at the monomeric complexes, *i.e.* K_{24} and K_{23}, K_{34} and K_{32} and K_{43} and K_{42}, we arrive at the stability order MeOH < cot < MeCN for the competition between the ligands at the coordination site *trans* to cyclooctene. Summarizing, the qualitative order of thermodynamic stability for these cyclooctene complexes is: MeOH < cot < MeCN < Cl^-. These results confirm the conclusion from the structural study that the thermodynamic stability of a cyclooctene coordinated *trans* to another cyclooctene is much lower than *trans* to a ligand with less π-back-bonding capacity.

Table 6 Equilibrium constants K at 298 K in dichloromethane as defined in Scheme 1

K	Method	Value
K_{12}/mol^{-1} dm^3	Eqns. (2)–(4)	0.0169 ± 0.0015
K_{13}/mol^{-1} dm^3	Eqns. (2)–(4)	9.7 ± 0.9
K_{14}/mol^{-1} dm^3	Eqns. (2)–(4)	2.05 ± 0.06
K_{23}	$(K_{13}/K_{12})^{0.5}$	20 ± 2
K_{23}	K_{24}/K_{34}	20 ± 4
K_{24}	Eqn. (6)	9.1 ± 0.7
K_{24}	$(K_{14}/K_{12})^{0.5}$	11 ± 1
K_{34}	Eqn. (6)	0.444 ± 0.006
K_{34}	$(K_{13}/K_{14})^{0.5}$	0.46 ± 0.01

The equilibrium constant for the bridge splitting of the styrene analogue of Zeise's dimer, *trans*-$[PtCl_2(CH_2CHC_6H_4)]_2$, with styrene to form *trans*-$[PtCl_2(CH_2CHC_6H_4)_2]$ has been determined in chloroform as 0.0235 mol^{-1} dm^3.[41] This value is almost two orders of magnitude smaller than our value of K_{14} for splitting of **1** with cyclooctene given in Table 6. On the other hand, cleavage of the styrene complex with ethanol in chloroform, resulting in *trans*-$[PtCl_2(CH_2CHC_6H_4)(EtOH)]$, gave an equilibrium constant of 0.0110 mol^{-1} dm^3, which is close to our value of K_{12} for the splitting of **1** with methanol (Table 6). Thus, in the case of this styrene complex, the stability order is also alcohol < alkene, but the magnitude of the bridge splitting equilibrium constant is obviously highly dependent on the nature of the splitting alkene.

Bridge-splitting kinetics

For the experimental conditions used in the kinetics experiments, all traces showed well-defined first-order behaviour with the bridge-cleavage processes of eqn. (1) resulting in complete conversion to *trans*-$[PtCl_2(cot)(L)]$, L = MeOH, MeCN or cyclooctene, as shown in eqn. (1). The kinetics is monophasic, and the plots of observed rate constants *vs.* the concentration of the bridge-splitting nucleophile given in Fig. 2 are linear with negligible intercepts, corresponding to the simple rate law of eqn. (8).

$$k_{obs} = k_{1n}[L] \quad (8)$$

This is compatible with a two-step process with splitting of the first chloride bridge being rate-determining and with negligible reverse reactions and solvent paths. Rate constants at 298 K and activation parameters calculated from the Eyring plots in Fig. 3 are given in Table 7.

As illustrated in Fig. 4, the nucleophilic discrimination of **1** at 298 K is cot < MeOH < MeCN, or $k_{14} < k_{12} < k_{13}$, in relative numbers 1 : 2 : 80. In agreement with previous findings, acetonitrile is a good nucleophile,[42] whereas alkenes are known to be poor.[43] In the present case, the difference in nucleophilicity is mainly due to the different entropy contributions to the free energy of activation. The $-T\Delta S^{\neq}$ term varies in the order cot < MeOH < MeCN as 40 : 34 : 27 kJ mol^{-1} (Table 7).

Table 7 Second-order rate constants at 298 K and activation parameters for bridge splitting of **1** with neutral ligands L in dichloromethane solvent

L	k_{1n}	k_{1n}/mol^{-1}dm^{3}s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\%T\Delta S^{\neq}$ [a]
MeOH	k_{12}	0.128 ± 0.003	43.7 ± 1.8	−115 ± 6	44
MeCN	k_{13}	4.93 ± 0.02	42.0 ± 0.8	−91 ± 3	39
cot	k_{14}	0.0637 ± 0.0009	39.6 ± 0.9	−135 ± 3	50

[a] Contribution to $\Delta G^{\neq}$.

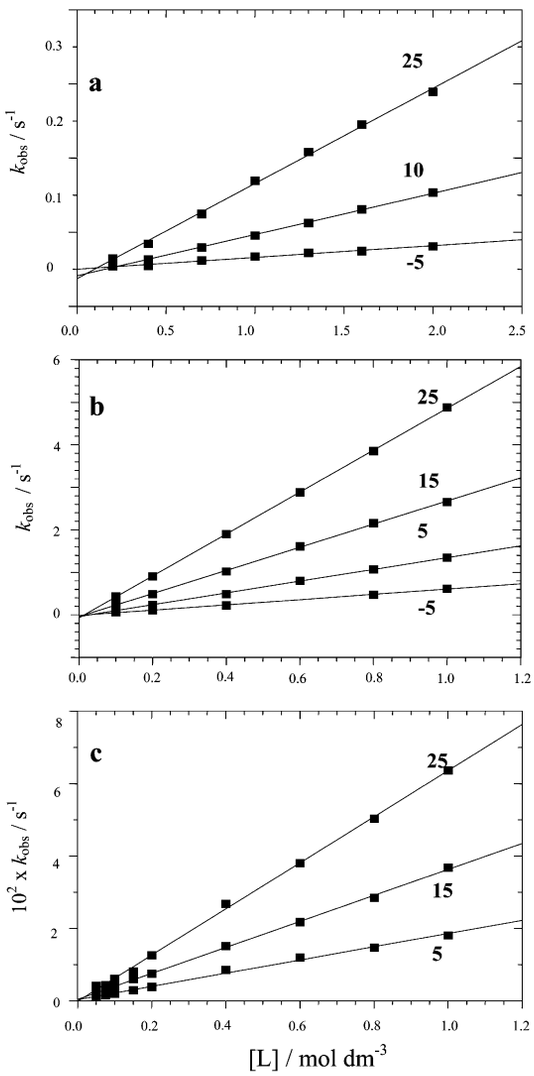


Fig. 2 Bridge splitting of **1** with MeOH (a), MeCN (b) and cyclooctene (c) in dichloromethane at various temperatures.

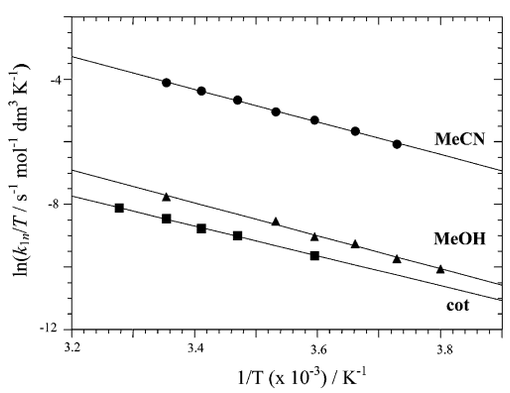


Fig. 3 Eyring plots for bridge splitting of **1** with MeOH, MeCN and cyclooctene in dichloromethane.

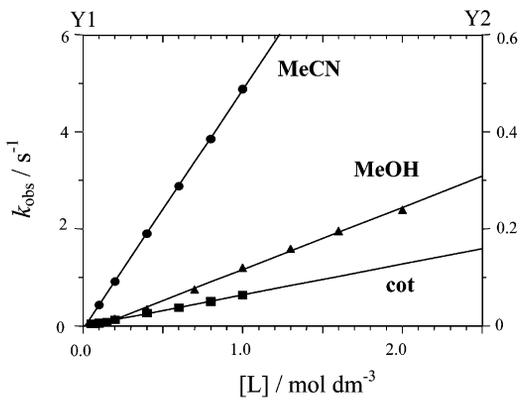


Fig. 4 Bridge splitting of **1** with MeOH (Y2), MeCN (Y1) and cyclooctene at 25 °C in dichloromethane.

The three bridge-splitting reactions proceed with the characteristic negative values of $\Delta S^{\neq}$ usually observed for associatively activated square-planar substitution reactions. As observed previously for substitution reactions *trans* to alkenes, the $-T\Delta S^{\neq}$ terms contribute relatively much (between 40 and 50%) to the overall free energy of activation.[2,3]

Conclusions

The chloride-bridged dinuclear complex *trans*-$[PtCl_2(C_8H_{14})]_2$ splits into monomeric complexes on addition of chloride, acetonitrile, cyclooctene and methanol. With chloride, bridge cleavage is quantitative, whereas equilibria between monomeric and dimeric complexes are established with the other three ligands. Bridge-splitting is fast with chloride and acetonitrile, much slower with methanol and cyclooctene. The bridge-splitting reactions are monophasic, but in principle two-step processes, with the splitting of the first bridge rate-determining. This step is characterised by largely negative entropies of activation, and a relatively large contribution from the entropy term to the overall free energy of activation. Splitting with cyclooctene results in the isolation of *trans*-$[PtCl_2(C_8H_{14})_2]$. The molecular structure of this complex with the two C=C double bonds coordinated *trans* to each other and perpendicular to the platinum coordination plane, features a significant Pt–C bond lengthening compared to cyclooctene complexes with chloride or nitrogen *trans* to cyclooctene. This weakening of the platinum–cyclooctene bond contributes to the high reactivity and relative thermodynamic instability of this compound, which can serve as a model for other monomeric *trans*-bis-alkene complexes that have been postulated as short-lived intermediates in chemical reactions. The cyclooctene complexes react slower than their ethene analogues.

Acknowledgements

Financial support from the Swedish Science Research Council (VR), the South African NRF and the Rand Afrikaans University, and the Swedish International Development Cooperation Agency (SIDA), including a post-doctoral fellowship at Lund University for S. O. is gratefully acknowledged. The Crafoord Foundation is thanked for funding of the diode array and cryo-stopped-flow units.

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