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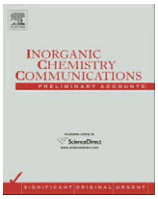

Bridge-splitting of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$ by weak nucleophiles: Crystal and molecular structure of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(MeCN)]$

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ABSTRACT

Bridge-splitting of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$, **1**, by L in dichloromethane yields *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(L)]$ (L = THF, **2**, or MeCN, **3**) with bridge-splitting equilibrium constants of 0.0289 ± 0.0007 and 3601 ± 215 mol^{-1} dm^3, respectively, as determined by UV/Vis measurements. The reaction of **3** in MeCN with Cl^- is essentially quantitative. The crystal structure of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(CH_3CN)]$ is reported.

Zeise's anion, $[PtCl_3(\eta^2\text{-}CH_2{=}CH_2)]^-$, and the chloride-bridged dinuclear complex, *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$, **1**, represent the earliest well documented organometallic complexes [1]. Reaction of **1** with ethene in acetone at −80 °C results in the formation of a yellow unstable complex, *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)_2]$ [2]. This species has been postulated as a short-lived intermediate in the reaction mechanism for ethene exchange at $[PtCl_3(\eta^2\text{-}CH_2{=}CH_2)]^-$ [3,4], and in non-co-ordinating solvents like chloroform, it is formed as a product of bridge-splitting of **1** by ethene. Upon standing at room temperature under an ethene atmosphere the white, moderately stable compound, *cis*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)_2]$, can be obtained [5].

We previously reported [6] on the bridge-splitting kinetics, equilibria and structures of the remarkably stable cyclooctene (cot) derivatives of Zeise's dimer. Due to the gaseous nature of ethene, and the increase in reactivity, studies of **1** are considerably more complicated. We succeeded in obtaining values for the bridge-splitting equilibrium constants, according to Scheme 1, for MeOH [4] and ethene [5] and now extended this work to illustrate the quantitative experimental studies between **1** and THF and CH_3CN. These solvents are representative of weak nucleophiles enabling the investigation of these highly reactive systems using simple, conventional UV–Vis measurements [7].

The spectroscopic data were fitted [8] to appropriate equations [9] for quantitative determination of the equilibrium constants as shown in the inserts of Figs. 1 and 2, respectively, for THF and MeCN.

Figs. 1 and 2 clearly illustrate the difference in coordinating ability of the THF and MeCN ligands. Moreover, the reaction of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(MeCN)]$ with subsequently added Cl^- in MeCN (solution of **1** in MeCN), proceeds essentially quantitatively to **4**.

By comparing the bridge-splitting equilibrium constants for *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$ with L, to form *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(L)]$, of 0.13 ± 0.01 (MeOH) [4], 6.8 ± 0.6 $(CH_2{=}CH_2)$ [5], 0.0289 ± 0.0007 (THF) and 3601 ± 215 (MeCN) mol^{-1} dm^3, the difference in the coordinating ability of the various nucleophiles to the Pt(II) metal centre is quantitatively defined.

Bridge-splitting equilibrium constants in dichloromethane at 298.2 K for the cyclooctene analogues of Zeise's dimer, *trans*-$[PtCl_2(cot)]_2$, with various nucleophiles are 0.0169 ± 0.0015 (MeOH) [4], 2.05 ± 0.06 (cot) and 9.7 ± 0.9 (MeCN) mol^{-1} dm^3, while with Cl^- the reaction is quantitative [6]. A sequence of bridge-splitting efficiency of MeOH < cot < MeCN < Cl^- was established from this study which is in agreement with the current results for the very reactive ethene based derivatives. In the same study we also reported the crystal structure of the remarkably stable *trans*-$[PtCl_2(cot)_2]$ obtained by bridge-splitting of *trans*-$[PtCl(cot)]_2$ with cyclooctene in dichloromethane as mentioned above. In contrast, the ethene analogue is too reactive/unstable to be isolated, and it isomerises to the more stable *cis*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)_2]$ upon concentration of the solutions [5].

In comparison, the bridge-splitting in chloroform of the styrene analogue of Zeise's dimer, *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CHC_6H_4)]_2$, with

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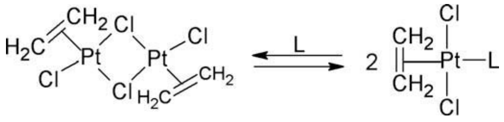

Scheme 1. Bridge-splitting equilibrium of **1** with nucleophiles L to form *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(L)]$ (L = THF, **2**, or MeCN, **3**, Cl^-, **4**, MeOH, **5** and $CH_2{=}CH_2$, **6**).

ethanol and styrene yielded equilibrium constants of 0.0110 and 0.0235 $mol^{-1}\ dm^3$, respectively [10].

The significantly enhanced stability of the ethene complexes, as demonstrated by the larger equilibrium/formation constants, as compared to the corresponding cot and styrene counterparts, may be attributed to a more efficient back bonding capacity of ethene. This effect is supported by previous kinetic studies on the substitution of Cl^- *trans* to a range of olefins in $[Pt(\eta^2\text{-olefin})Cl_3]^-$ where the stability of the five-coordinate transition state (and subsequently the reaction rate) increased with the π-accepting capability of the olefin [11]. Based on our previous work [11] and the results discussed above a sequence of back bonding capacity of styrene < cot ~ $CH_2{=}CHSiMe_3$ < $CH_2{=}CHCH_2OH$ ~ $CH_2{=}CH_2$ is proposed.

Slow evaporation of the dichloromethane solution of **1** containing acetonitrile yielded crystals of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(MeCN)]$, **3**, suitable for X-ray analysis [12] (Fig. 3).

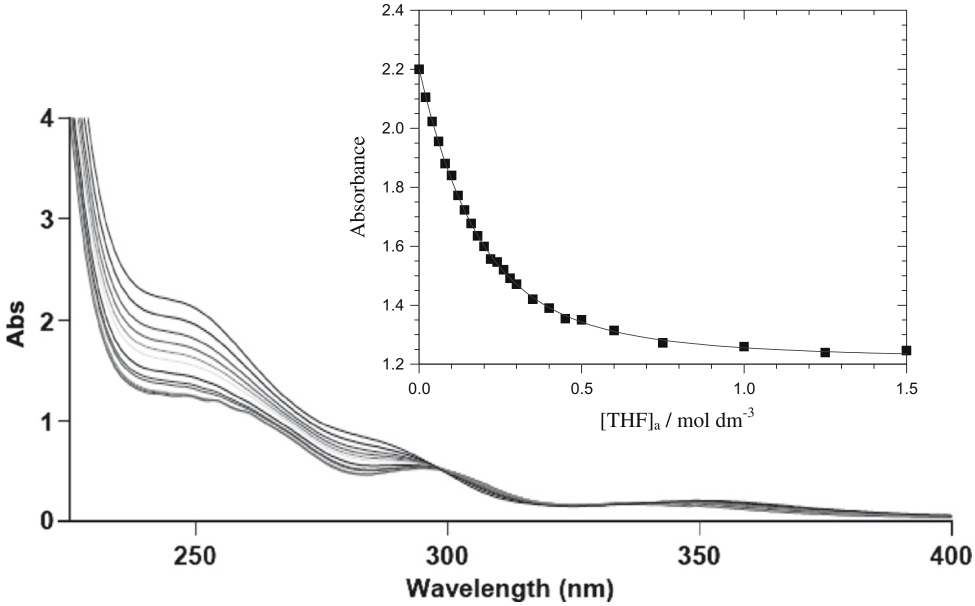

Fig. 1. UV–Vis spectral changes observed for the bridge-splitting reaction of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$ (**1**) ([Pt] = 0.303 $mmol\ dm^{-3}$) by THF in dichloromethane at 298 K. The insert shows the least-squares fit at 245 nm yielding $K_{THF} = 0.0289 \pm 0.0007\ mol^{-1}\ dm^3$.

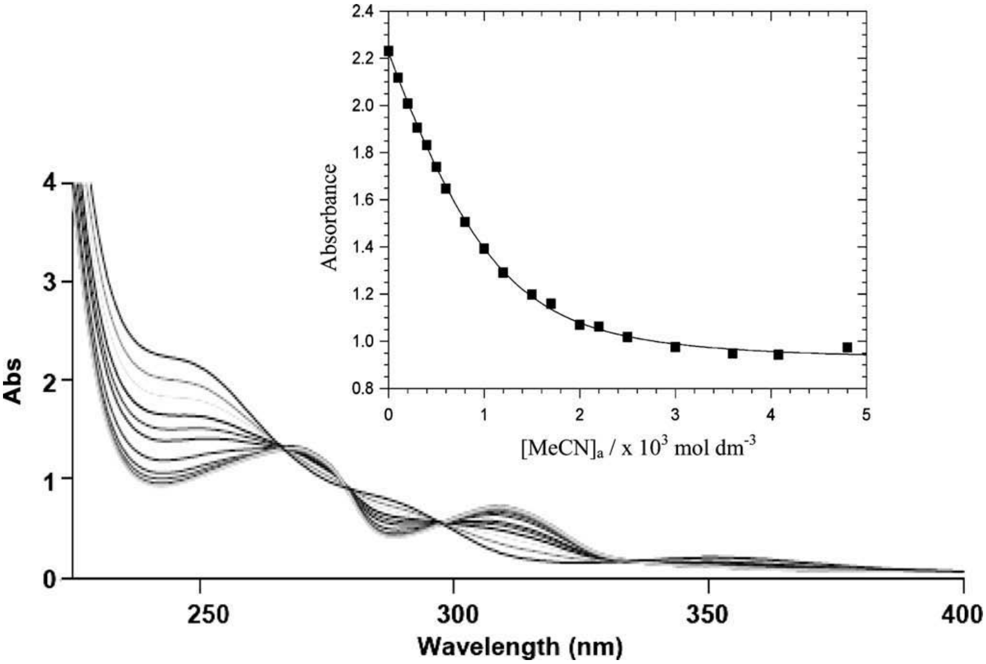

Fig. 2. UV–Vis spectral changes for the bridge-splitting reaction of *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)]_2$ (**1**) ([Pt] = 0.303 $mmol\ dm^{-3}$) by MeCN in dichloromethane at 298 K. The insert shows the least-squares fit at 245 nm yielding $K_{MeCN} = 3601 \pm 215\ mol^{-1}\ dm^3$.

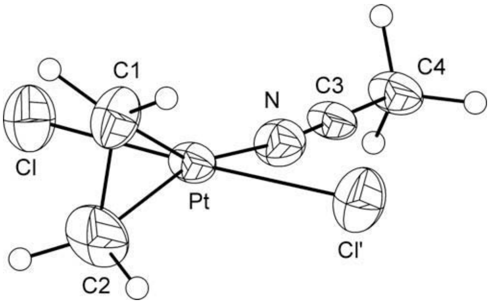

Fig. 3. Molecular diagram of **3** showing the numbering scheme and thermal displacement ellipsoids at 30% probability level, hydrogen atoms are of arbitrary size. The disorder in the hydrogen atoms of the MeCN ligand is omitted for clarity. Selected geometrical parameters include distances Pt–Cl 2.292(5), Pt–C1 2.09(2), Pt–C2 2.13(2), Pt–N 2.017(18), C1=C2 1.43(4) Å; angles Cl–Pt–N 88.94(11)° and torsion angle C1=C2–Pt–Cl 99.4(11)°.

The molecules of **3** are situated on a mirror plane running through C1, C2, Pt, N, C3 and C4. The *trans* orientation is obvious, while the Pt–C and Pt–Cl bonds compare favourably with those observed in Zeise's anion [13]. The relatively short Pt–N bond distance is indicative of the low ground state *trans* influence of ethene. In general, amines, and most notably pyridines, form stable *trans* reaction products when reacted with Zeise's anion in polar solvents, and some studies in this regard has been reported [14,15]. It was found that prolonged standing of **3** resulted in isomerisation to the more stable *cis*-[$PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(MeCN)$] isomer.

Acknowledgements

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Appendix A. Supplementary material

CCDC 730772 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.06.010.

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[4] R.M. Plutino, S. Otto, A. Roodt, L.I. Elding, Inorg. Chem. 38 (1999) 1233.
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[6] S. Otto, A. Roodt, L.I. Elding, Dalton Trans. (2003) 2519.
[7] THF (Merck), acetonitrile (Merck), and dichloromethane (Riedel de Haen) were dried and distilled under a dinitrogen atmosphere prior to use. A series of solutions with the same total concentration of platinum as (**1**) in dichloromethane were prepared containing varying amounts of THF and acetonitrile, respectively. The UV–Vis spectra were recorded in a 1.00 cm quartz cell on a Cary 300 Bio UV–Vis spectrophotometer at 298.2 K. Solutions were aged sufficiently long to ensure that equilibrium was established before the measurements were made. Absorbance/concentration data and wavelengths are available as ESI.
[8] SCIENTIST, Program for Least-Squares Parameter Optimization, MicroMath Scientific Software, Salt Lake City, UT, 1990.
[9] Overall reaction for THF (**2**):*trans*-$[PtCl_2(C_2H_4)]_2 + 2L \overset{K_L}{\rightleftarrows} 2$ *trans*-$[PtCl_2(C_2H_4)(L)]_{(\mathbf{2})}$ $K = [\mathbf{2}]^2/[\mathbf{1}][L]^2$ $A_{obs} = C_{Pt}(\varepsilon_1 + \varepsilon_2/[\mathbf{2}])$; $[\mathbf{1}] = C_{Pt} - [\mathbf{2}]/2$ $[L]_{add} = [\mathbf{2}] + [L]$; $[\mathbf{2}]^3K - 2[\mathbf{2}]^2(KC_{Pt} + K[L]_{add} - 1) + [\mathbf{2}](4KC_{Pt}[L]_{add} + K[L]^2_{add}) - 2KC_{Pt}[L]^2_{add} = 0$
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[12] Crystal data for **3**: $C_4H_7Cl_2NPt$, $FW = 335.10$, colourless rectangle, $0.10 \times 0.06 \times 0.05$ mm, Orthorhombic, *Pnma*, $a = 9.6170(19)$, $b = 8.7530(18)$, $c = 9.5890(19)$ Å, $V = 807.2(3)$ Å^3, $Z = 4$, $D_c = 2.757$ g cm^{-3}, $F(0\,0\,0) = 600$, $T = 293(2)$ K, Bruker Smart CCD, rotating anode Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $\theta = 3.00$–$27.09°$, $\mu = 17.952$ mm^{-1}, $R_{int} = 0.1456$, $T_{min}/T_{max} = 0.080/0.321$, ω-scans, 6624 collected reflections, 958 unique, 580 observed ($I > 2\sigma(I)$), $R_1 = 0.0519$ and $wR_2 = 0.1185$ ($I > 2\sigma(I)$), $S = 0.912$, 49 parameters, $\Delta\rho_{max} = 2.243$ e Å^{-3}, $\Delta\rho_{min} = -1.471$ e Å^{-3}, structure solution by the Patterson and subsequent Fourier methods.
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