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Review

Using electrospray ionisation mass spectrometry as a synthesis-targeting technique – An update on the chemistry of the platinum chalcogenide dimers $[Pt_2(\mu_2\text{-}E)_2(PPh_3)_4]$ (E = S, Se)

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ABSTRACT

Electrospray ionisation mass spectrometry (ESI MS) is a powerful analytical technique which, with appropriate application, can be used as the technique of choice for the investigation of coordination chemistry. This review summarises our development of the chemistry of the platinum(II) chalcogenide metalloligands $[Pt_2(\mu_2\text{-}E)_2(PPh_3)_4]$ (E = S, Se) using such a mass spectrometry-based approach.

William (Bill) Henderson was born in Darlington, UK, and grew up in Stockton-on-Tees (an important historical centre for sulfur chemistry with the invention of the friction match in the 1820s). He received a BSc in Chemistry with geochemistry and a PhD in organometallic chemistry (with Dr. Ray Kemmitt) from the University of Leicester. He the undertook postdoctoral research with the late Professor Du Shriver at Northwestern University, USA which included a period of catalysis research spent at Hokkaido University with Professor Masaru Ichikawa. In 1989 he returned to the UK, as a senior research scientist with Albright & Wilson Ltd (now Rhodia) in the West Midlands, before commencing at the University of Waikato in 1992, where he served 6 years as Chair of Department, and was promoted to Professor of Chemistry in 2005. His research interests cover a range of areas centred on coordination and organometallic chemistry, especially of the platinum group metals and gold, with ESI MS a cornerstone technique.

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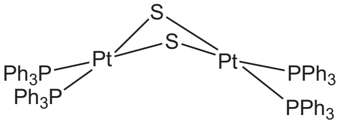
Contents

1. Introduction

The platinum(II) sulfido complex $[Pt_2(\mu_2\text{-}S)_2(PPh_3)_4]$ **1** has been known for some considerable time [1,2]; it is easily synthesised in good yield from the readily-prepared precursor *cis*-$[PtCl_2(PPh_3)_2]$ (and other routes) and has a varied and well-established reactivity, that has been reviewed on a number of occasions [3,4]. The selenide analogue $[Pt_2(\mu_2\text{-}Se)_2(PPh_3)_4]$ [5] has been less thoroughly investigated, but studies indicate that it has an equally interesting, and sometimes different, reactivity. There have also been extensive studies on the chemistry of analogous complexes containing $\{Pt_2(\mu_2\text{-}S)_2\}$ cores, but with alternative ligands in place of PPh_3, which offers the ability to tune reactivity; examples of ligands which have been explored include diphosphines such as $Ph_2P(CH_2)_2PPh_2$ (dppe) and $Ph_2P(CH_2)_3PPh_2$ (dppp) [6–14], $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (dppf) [15,16] and Ph_2Ppy (dppy; py = 2-pyridyl) [17,18].



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Our contribution [19] to the extensive field of metal–chalcogenide chemistry [20] has, in more recent years, often concerned the use of electrospray ionisation mass spectrometry (hereafter ESI MS) to the investigation of the chemistry of $[Pt_2(\mu_2\text{-}E)_2(PPh_3)_4]$ (E = S, Se). In this short review, examples of our qualitative application of ESI MS in exploring the chemistry of these systems are discussed.

2. Electrospray ionisation mass spectrometry (ESI MS)

Full details on the ESI MS technique are available in a multitude of review articles [21–26] and textbooks [27] focussing on inorganic and organometallic chemistry applications. The technique was developed in the 1980s by John Fenn (and co-workers) at Yale University, for which he was jointly awarded [28] the 2002 Nobel Prize in Chemistry. In essence, electrospray ionisation works by spraying (using an inert gas, typically nitrogen) a dilute solution of the analyte through a metal capillary held at a high potential (positive, if positive-ion mode is used, and *vice versa*). This produces a spray of charged liquid droplets, which are then evaporated using nitrogen to generate gas phase ions which are subsequently separated and detected (using one of a range of different detector types, including quadrupole, time-of-flight, or ultra high resolution ion cyclotron resonance mass analysers).

Electrospray ionisation is characterised by several desirable features. It is probably the 'softest' ionisation type, so inherent fragmentation is minimal; it is therefore ideally suited for the analysis of labile and/or thermally-sensitive materials, which of course includes many coordination complexes. In-source fragmentation can be achieved through collisions (e.g. with nitrogen gas molecules) effected by application of a suitable accelerating voltage. By investigating mass spectra under a range of fragmentation conditions, additional information about the complex can often be obtained by examination of the fragment ions formed. Furthermore, depending on the type of mass analyser used, there is effectively no upper mass limit; the time-of-flight (TOF) detector is