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A Stable, Mononuclear, Cationic Pt(III) Complex Stabilised by Bulky N-Heterocyclic Carbenes

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The thermally stable, paramagnetic Pt(III) complex [PtI₂(IPr)₄][BAR Finder] has been prepared by oxidation of the Pt(II) complex [Pt₂I₆(IPr)₂] with iodine in the presence of NaBAR Finder. X-ray crystallographic studies revealed the mononuclear nature of this species with a square-planar geometry. EPR and DFT studies pointed out to a metal-centred radical.

Platinum compounds in closed-shell oxidation states of (0), (II), and (IV) abound in literature, but less is known about their (I) and (III) open-shell counterparts. Although dinuclear Pt(III) species are well known, the scarcity of well characterised paramagnetic mononuclear Pt(III) species is noteworthy, despite of being postulated as transient intermediates in several chemical transformations including oxidation of platinum alkyls and aryls, and anticancer activity of cis-platin and carboplatin. In 1984, Usón et al. reported the first crystallographically characterised anionic, mononuclear Pt(III) complex [Pt(C₂H₄I)₂]⁻. Since then only a few reports have appeared on the full characterisation of mononuclear Pt(III) complexes. In most of the cases, the isolation was possible by using ligands that can easily delocalise the unpaired electron or preventing their dimerisation by blocking the axial coordination sites in their octahedral complexes. Bond and Colton reported that a bulky pincer phosphine ligand allowed for the spectroscopic (electron paramagnetic resonance, EPR) characterisation of a “moderately stable Pt(III) cation”, although the authors were not able to isolate it in a pure form as a consequence of its fast disproportionation into uncharacterised Pt(II) and Pt(IV) species. Some of us have isolated very recently a paramagnetic, mononuclear Pt(III) alkyl complex [PtBr(IPr'')(IPr)][BAR Finder] stabilised by bulky N-heterocyclic carbene (NHC) ligands IPr (where IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and IPr' indicates a cyclometallated ligand) that is an intermediate in the formation of a C–Br bond. The X-ray structure of this complex exhibited an unprecedented see-saw geometry. According to computational studies, such structure was not due to steric constraints but to the effect of the alkyl group in trans to the bromine ligand. In this report we have succeeded in the isolation and characterisation, including X-ray diffraction and EPR studies, of the first mononuclear, cationic, square-planar Pt(III) complex stabilised by NHCs, particularly IPr ligands. In fact the use of NHCs for the stabilisation of third-row radical complexes is limited to two other examples recently published, in one of them electron delocalisation on the imidazol ring has been proved.

The complex trans-[PtMeI(IPr)]⁺ 1 reacts with I₂ to yield, almost quantitatively, the pale-yellow bis-iodide derivative trans-[Pt₂I₂(IPr)₂] 2, formed after rapid reductive elimination of methyl iodide without detecting any Pt(IV) intermediates (Scheme 1). Compound 2 has been spectroscopically and crystallographically characterised (see ESI).

Scheme 1 Synthesis of mononuclear, cationic Pt(III) species 3.

When complex 2 is reacted with half-equivalent of I₂ in the presence of NaBAR Finder (NaBAR Finder = sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate) in dichloromethane an intense blue solution is formed almost immediately (Scheme 1). The ¹H NMR spectrum of the crude reaction mixture reveals the formation of a single product showing only broad signals in the range of ~7.3 to 7.9 ppm for the carbene ligands that hints at the presence of a paramagnetic species in solution, from which it has been possible to isolate the Pt(III) complex 3. It should be pointed out that addition of either I₂ or NaBAR Finder alone to 2 was not productive, recovering unaltered the reactants. Only when the three reagents are mixed together the formation of 3 is achieved. Therefore,
variation of the concentration of iodide through precipitation as NaI is key for the reaction to proceed. Complex 3 is fairly air-stable and partially decomposes at r.t. to uncharacterised complexes after a few days or weeks (in solution and in the solid state) but it can be kept indefinitely unaltered at 5 °C.

The X-band EPR spectrum (at 16 K) of a polycrystalline sample of complex 3 dispersed in n-hexane is shown in Fig. 1. It corresponds to low spin (S = ½) Pt(III) entity with a markedly orthorhombic effective g-tensor. Their principal values, g₁ = 1.069(5), g₂ = 1.280(5) and g₃ = 3.612(5), deviate largely with respect to the free electron g-value (gₑ = 2.0023).

It hints at one unpaired electron residing on a metal orbital, that is, suggesting a Pt(III) oxidation state, and excluding a ligand-centred radical. The signal at g₃ = 3.612(5) (Fig. 1) shows hyperfine coupling (see Fig. S6 in ESI) to two equivalent ¹²⁷I nucleus (natural abundance 100%, I = 5/2). Moreover, these eleven signals show satellites (see Fig. S6 in ESI) due to coupling with ¹⁹⁵Pt (¹⁹⁵Pt, natural abundance 33.3%, I = 1/2). With respect to the signals at high-field (g₁ and g₂) the lack of resolution hampered the observation of coupling to the ¹²⁷I and ¹⁹⁵Pt nuclei.

Fig. 1 X-band EPR spectrum measured a 16 K of a polycrystalline sample of complex 3 dispersed in n-hexane.

Magnetic measurements, susceptibility as a function of the temperature, and isothermal magnetization at 1.8 K were also carried out (see ESI). The values can be interpreted in agreement with the EPR derived data, which means that the spectrum in Fig. 1 is associated to the main component of the sample and it is not due to minority paramagnetic entities.

Crystals suitable for an X-ray diffraction study of complex 3 were grown by slow diffusion of a concentrated solution of 3 in dichloromethane into diethyl ether (Fig. 2). The molecule has crystallographically imposed twofold symmetry with the asymmetric unit containing two half cations and anions with the Pt and the B atoms on twofold axes, respectively (only one of the cations is shown in Fig. 2). The structure of this compound is almost identical to that of its precursor 2 (see ESI). The platinum atom in 3 exhibits a perfect square-planar environment, as found in derivative 2. The two bulky IPr ligands are in a trans arrangement, reducing steric constrains with a C1–Pt1–C1’_2 angle of 179.5(2)°. On the other hand, the angle formed by the I1–Pt1–I1’_2 moiety is almost linear (177.055(14)°). There are only slight dissimilarities in the structural parameters of 2 and 3, but it is particularly noteworthy the lengthening of the Pt–CᵢPr bonds by almost 0.04 Å. Moreover, the dihedral angle defined by the coordination plane around the platinum atom and the imidazole ring is 77.65° in complex 3 and 70.01° in derivative 2. We believe that these subtle differences are the result of a reduced π back-donation of the platinum atom to the NHC ligands, an effect previously observed for other systems. Finally, a shortening of around 0.06 Å is observed for the Pt–I bond distances on going from Pt(II) to Pt(III).

Fig. 2 ORTEP view of complex 3. Thermal ellipsoids are drawn at 30% probability level. The Br⁻ anion has been omitted for clarity. Atoms labelled as “_2” correspond to those at equivalent positions. Selected bond lengths (Å): Pt1–C1: 2.069(1); Pt1–I1: 2.5294(2); N1–C1: 1.366(5); N2–C2: 1.362(5).

To support the previous findings, the neutral Pt(II) 2 and cationic Pt(III) 3 complexes were optimised at DFT level using the BHHLYP functional13,14 (see ESI for computational details). Both species clearly exhibit square-planar structures with I–Pt–I and CᵢPr–Pt–CᵢPr angles of 180.0°. N–CᵢPr–Pt–I dihedral angles are also similar, 76.6° and 78.0° for 2 and 3, respectively. The calculated bond distance trends are in line with the experimental evidences: from 2 to 3, Pt–CᵢPr bond distances are slightly enlarged (from 2.076 Å to 2.099 Å) whereas Pt–I values are shortened (from 2.674 Å to 2.581 Å).

The calculated Mulliken spin density of 3 accounts for 41% on the platinum atom and 29% on each iodine atom. Significant contributions from the NHC moiety are not
observed. The shape of the singly occupied molecular orbital (SOMO, Fig. 3) indicates that the platinum atom participates with the d_{xy} orbital and the iodine atoms with the p_x ones. The strong electronic localisation on the platinum supports the EPR results and the partial contribution of iodine atoms agrees with the hyperfine coupling (Fig. 1).

In order to get some insight about the reversibility of the Pt(II) ⇆ Pt(III) process, cyclic voltammetry experiments in dichloromethane solutions of complex 2 have been undertaken. As shown in Fig. 4, the electrochemistry of this derivative shows both anodic and cathodic processes, which, if assumed to be a one-electron transfer, can be considered to be close to reversible in nature (peak-to-peak potential ~69 mV and ratio of the anodic to cathodic peak 0.98). This result confirms the noticeable stability of Pt(III) species 3, derived from Pt(II) complex 2, in solution.

In summary, the mononuclear, paramagnetic Pt(III) complex [PtH(OPr)]_2[BAr^6] (3) exhibits a square-planar structure according to X-ray diffraction studies and DFT calculations. EPR and DFT studies point out to a metal-centred radical and cyclic voltammetric data enhance the stability of such paramagnetic species. Further studies on the preparation of related systems based on different NHCs are currently underway.

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**Notes and references**


3. The corresponding SOMO of complex [Pt(Cl_2)]^2 was also computed, obtaining a platinum d^2 orbital (see ESI) in agreement with previous EPR studies.