

# An unprecedented process involving normal and redox transmetallation reactions between Hg and Pt affording the unexpected $\text{K}[\text{Pt}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_6(\mu\text{-Cl})_3]$ complex: the key role of X-ray powder diffraction in unravelling its nature and structure†

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$[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  reacts with  $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$  (2 : 1 molar ratio) to give  $\text{K}[\text{Pt}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_6(\mu\text{-Cl})_3]$  (**1**); the intermediate  $[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}_2(\text{CH}_2=\text{CH}_2)]^-$  has been detected in solution and isolated as a  $\text{Me}_4\text{N}^+$  salt; the process occurs through successive normal and redox transmetallation reactions and an *ab initio* X-ray powder diffraction study of **1** has proven to be essential to establish its nature.

We are involved in the synthesis of ketonyl metal complexes  $[\text{M}]\text{CH}_2\text{C}(\text{O})\text{R}$  ( $\text{M} = \text{Au}(\text{III}), \text{Tl}(\text{III}), \text{Pd}(\text{II}), \text{Pt}(\text{II})$ ).<sup>1,2</sup> This type of complex is proposed as an intermediate in numerous organic transformations.<sup>3</sup> Most reported acetylonyl complexes  $[\text{Pt}(\text{II})]\text{CH}_2\text{C}(\text{O})\text{Me}$  have been obtained through methods that inevitably lead to species also containing phosphines, pyridine derivatives, Me or Ph ligands.<sup>4,5</sup> The only acetylonyl platinum complex containing an easily exchangeable ligand is  $[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2(\text{COD})]$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ), which has recently been reported in low yield.<sup>5</sup> We have reported the synthesis of  $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ , which allows preparation of acetylonyl palladium complexes choosing freely any additional ligand.<sup>2</sup> The same method that uses  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  to transmetallate the acetylonyl ligand, is here reported to give Pt(II) and Pt(IV) acetylonyl chlorocomplexes. There is only one isolated acetylonyl Pt(IV) complex,  $\text{NH}_4[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}_4(\text{NH}_3)]$ ,<sup>6</sup> which was obtained, in low yield, by irradiating an acetone solution of  $\text{Na}_2[\text{PtCl}_6]\cdot 6\text{H}_2\text{O}$ . An acetylonyl Pt(III) complex has been prepared by reacting a platinum blue with  $\text{HNO}_3$  and acetone.<sup>7</sup> We have widely used organomercury compounds to prepare organocomplexes of Au,<sup>8</sup> Pd,<sup>9</sup> Pt,<sup>10</sup> Rh,<sup>11</sup> Sn,<sup>12</sup> and Tl<sup>13</sup> through normal ( $[\text{M}]\text{-Cl} + [\text{Hg}]\text{-R} \rightarrow [\text{M}]\text{-R} + [\text{Hg}]\text{-Cl}$ ) or redox ( $[\text{M}^{n+}] + [\text{Hg}(\text{R})\text{Cl}] \rightarrow [\text{M}^{(n+2)+}](\text{R})\text{Cl} + \text{Hg}; [\text{M}^{n+}] + [\text{HgR}_2] \rightarrow [\text{M}^{(n+2)+}]\text{R}_2 + \text{Hg}$ ) transmetallation reactions.

The room temperature reaction between  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  and  $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$  (2 : 1 molar ratio; see ESI†) gives a grey precipitate from which **1**, a colourless and poorly soluble compound, was extracted with MeCN. Using different solvents and conditions, **1** always crystallized as small crystals not suitable for a single crystal X-ray diffraction study. In similar cases, it is very convenient to try to solve the structure using X-ray powder

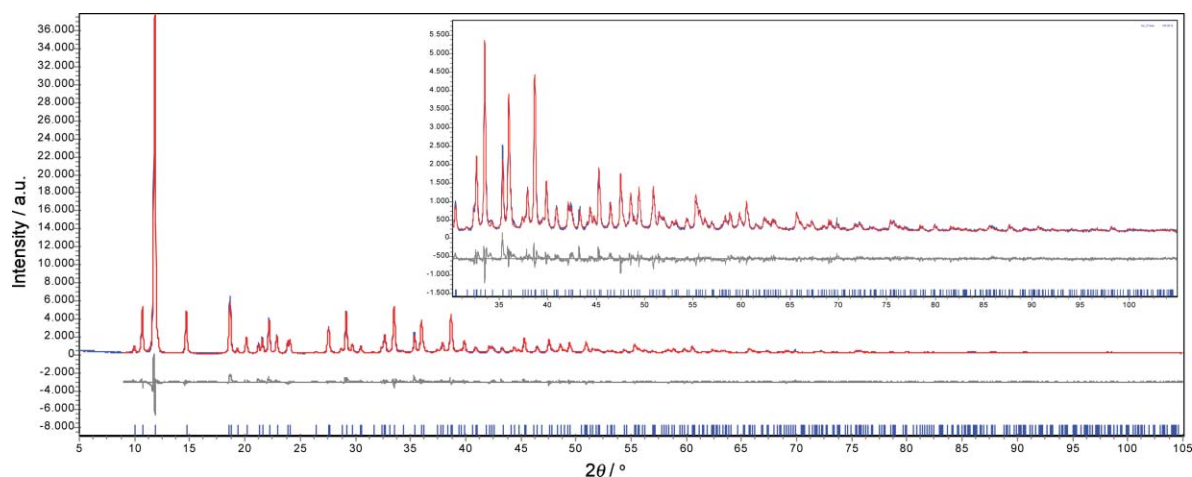
diffraction (XRPD).<sup>14</sup> In fact, this technique has allowed us to determine the correct connectivity of the  $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$  polymer,<sup>15</sup> tentatively (and incorrectly) assigned on the basis of spectroscopic data,<sup>2</sup> and to establish the actual nature of  $[\text{Rh}_3(\text{OH})_2(\text{COD})_3]\text{HF}_2$ ,<sup>16</sup> initially formulated as  $[\text{RhF}(\text{COD})]_x$ .<sup>17</sup> With the aid of *ab initio* XRPD methods, the structure of complex **1** was eventually solved (see Fig. 1 for observed, calculated and difference XRPD patterns),<sup>‡</sup> and found to be the  $\text{K}[\text{Pt}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_6(\mu\text{-Cl})_3]$  salt (Fig. 2). However, despite its simple formulation, we originally thought of a cubane  $[\text{Pt}_4\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_{12}(\mu_3\text{-Cl})_4]$  species, in analogy with most known  $\text{Pt}^{\text{IV}}(\text{alkyl})$  complexes  $[\text{Pt}_4\text{R}_{12}\text{X}_4]$  ( $\text{R} = \text{Me}, \text{Et}, \text{X} = \text{halogen}$ ).<sup>18</sup> Indeed, these two species of different nuclearity and nature would share similar elemental analyses, reactivity and some spectroscopic data (IR, NMR, ESI MS).

$\text{K}[\text{Pt}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_6(\mu\text{-Cl})_3]$  is an ionic species containing a dimetallic anion of (crystallographic)  $C_{3h}$  symmetry. Three chlorine atoms bridge a Pt...Pt vector similarly to that observed in the cation of the Pt(II) complex  $[\text{Pt}_2\{\eta^4\text{-C}_4\text{Pr}_4\}_2(\mu\text{-Cl})_3]^+$ .<sup>19</sup> Due to the intrinsic low precision of powder diffraction and to the occasional low quality of the single crystal determination of the latter complex, the pertinent bond parameters (although similar) are barely comparable. The octahedral coordination about each Pt atom is completed by three acetylonyl ligands whose orientation is dictated by the presence of the counterion: indeed,  $\text{K}^+$  is (octahedrally) linked to six oxygen atoms from six different anions generating a 3D ionic structure of the archetypal NiAs type (Fig. 2), and, as such, is responsible for the very low solubility of **1**.

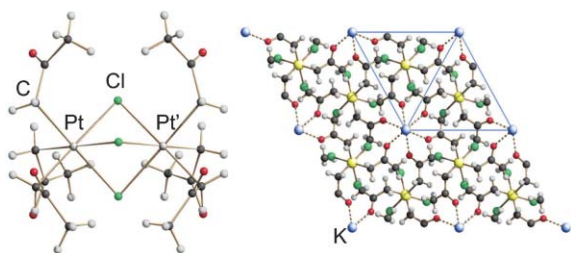
To elucidate the mechanism of formation of **1** we performed a study at different molar ratios and reaction times. The 1 : 1 reaction was followed by <sup>1</sup>H NMR in d<sup>6</sup>-acetone. After 15 min, the reaction mixture showed the presence of  $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$ ,  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$ , a platinum complex **2**, containing the  $\text{CH}_2\text{C}(\text{O})\text{Me}$  group and traces of **1** (see ESI†). After 30 min only traces of  $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$  were detected. As complex **2** could not be separated from the by-product  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$ , we repeated the reaction in the presence of  $\text{Me}_4\text{NCl}$  to transform  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$  into the starting mercurial ( $2[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}] + \text{Cl}^- \rightarrow [\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2] + [\text{HgCl}_3]^-$ ) thus requiring only a  $[\text{Pt}] : [\text{Hg}] = 2 : 1$  molar ratio. This reaction led to the isolation of  $\text{Me}_4\text{N}[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}_2(\text{CH}_2=\text{CH}_2)]$  (**2'**; see ESI†) whose NMR data agree with those of **2**. Therefore, we propose that the first step in the synthesis of **1** is a

† Electronic supplementary information (ESI) available: experimental details, analytical and spectroscopic data of **1** and **2'**. <sup>1</sup>H NMR spectrum of the 1 : 1 reaction mixture after 15 min in d<sup>6</sup>-acetone. See <http://www.rsc.org/suppdata/cc/b4/b416261g>

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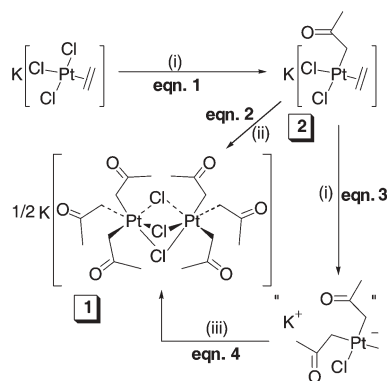
**Fig. 1** Rietveld refinement plot for **1**. The insert shows the high angle region at a magnified scale. Observed pattern (blue) and calculated pattern (red), peak markers and difference plot at the bottom.



**Fig. 2** Left: structure of the  $\text{K}[\text{Pt}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_6(\mu\text{-Cl})_3]^-$  anion;  $\text{Pt}\cdots\text{Pt}'$  3.289(2),  $\text{Pt}\text{-Cl}$  2.533(7),  $\text{Pt}\text{-C}$  2.20(2) Å. Right: crystal packing of **1**, viewed down [001], highlighting the octahedral coordination of the  $\text{K}^+$  ions [fragmented lines,  $\text{K}\cdots\text{O}$  2.50(2) Å].

normal transmetallation reaction giving  $\text{K}[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}_2\text{-(CH}_2=\text{CH}_2)]$  (**2**; eqn. 1, Scheme 1).

$^1\text{H}$  NMR spectra of the 2 : 1 ( $[\text{Hg}] : [\text{Pt}]$ ) reaction mixture showed the initial formation of **2** whose concentration decreased while the amount of **1** and free  $\text{CH}_2=\text{CH}_2$  increased. No other species were detected at room temperature or lower ( $-10\text{ }^\circ\text{C}$ ). We propose that, because  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$  and **2** were in contact in the 1 : 1 reaction and no reaction was observed, complex **2** must react with  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  to give (i) complex **1**, through a



**Scheme 1** Reagents: (i) +  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  –  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$ ; (ii) +  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$  –  $\text{Hg}$  –  $1/2\text{ KCl}$  –  $\text{CH}_2=\text{CH}_2$ ; (iii)  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$  –  $\text{Hg}$  –  $1/2\text{ KCl}$ .

redox transmetallation reaction (eqn. 2 in Scheme 1), or (ii) a complex “ $\text{K}[\text{Pt}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2\text{Cl}]$ ”, through a normal transmetallation reaction (eqn. 3 in Scheme 1), which would react quickly with  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$  to give **1** and  $\text{Hg}$  (eqn. 4 in Scheme 1). The formed  $\text{Hg}$  is responsible for the grey colour of the initial precipitate obtained in the reaction. We have verified that complex **2'** reacts with  $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$  to give **1**.

In conclusion, although organomercury compounds have been widely used to prepare organometallic complexes, this is the first example in which (i) successive normal and redox transmetallation reactions have been observed and (ii) an organomercury complex has been used in the synthesis of a Pt(IV) complex. Complex **1** is (i) the first organoplatinum(IV) complex containing three bridging halogens, (ii) the first fully characterized acetylonyl Pt(IV) complex and (iii) the first tris(ketonyl) metal complex ever isolated. Complexes **1** and **2'** can be used to prepare any tris(acetylonyl) Pt(IV) or monoacetylonyl Pt(II) complex, respectively, by simple replacement or bridge splitting reactions.

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## Notes and references

‡ Crystal data:  $\text{C}_{18}\text{H}_{30}\text{Cl}_3\text{K}_2\text{O}_6\text{Pt}_2$ , FW 878.04, hexagonal,  $P6_3/m$ ,  $a = 9.4729(2)$ ,  $c = 17.5707(5)$  Å,  $V = 1365.49(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 2.135\text{ g cm}^{-3}$ . Bruker AXS D8 diffractometer,  $\text{Cu-K}\alpha$ ,  $\theta : \theta$  scan,  $\Delta\theta = 0.02^\circ\text{ step}^{-1}$ ,  $t = 34\text{ s step}^{-1}$ ; indexing [GOF(25) = 41], structure solution (by simulated annealing) and (restrained) Rietveld refinement using TOPAS<sup>20</sup> (see Fig. 1). Final  $R_p$ ,  $R_{wp}$  and  $R_{\text{Bragg}} = 0.085, 0.111, 0.046$ , respectively. CCDC 253110. See <http://www.rsc.org/suppdata/cc/b4/b416261g/> for crystallographic data in .cif or other electronic format.

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