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Tetranuclear Platinum Complexes with μ-Hydrocarbyl Ligands

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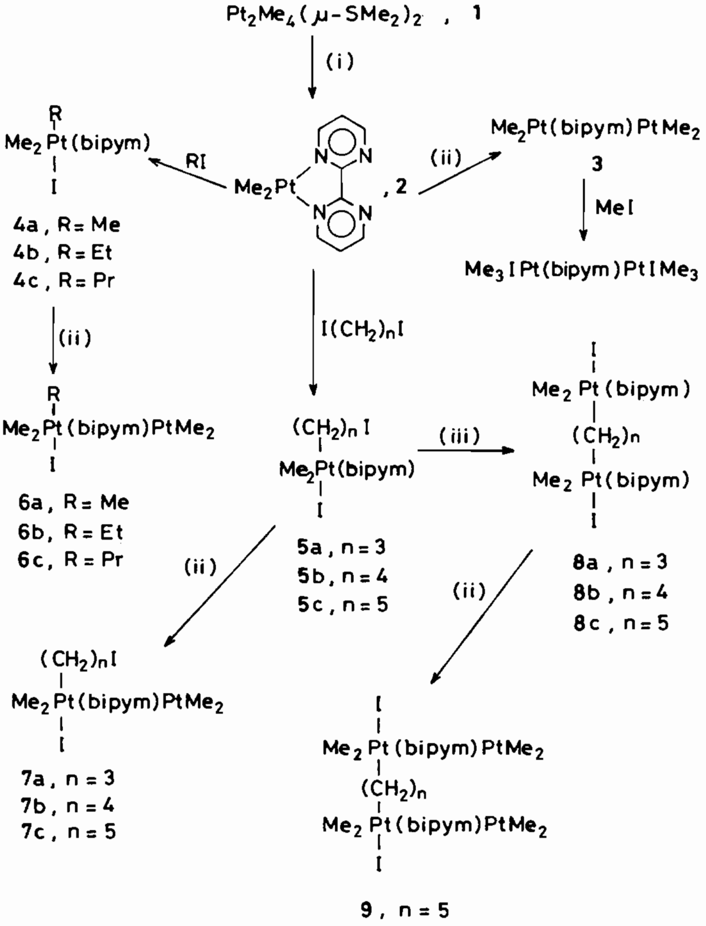
The recent interest in binuclear complexes with bridging hydrocarbyl ligands [1] prompts us to report a rational method for preparing tetranuclear complexes, including rare examples of mixed oxidation state Pt(II)–Pt(IV) complexes [2], which contain one or two μ-hydrocarbyl ligands. Some of the syntheses are shown in Scheme 1. The strategy is based on *trans* oxidative addition of α,ω-dihalogenoalkanes to dimethylplatinum(II) centres [3], with additional linking of platinum atoms by the bis(chelate) ligand 2,2′-bipyrimidine, bipym [4, 5]. Satisfactory C,H,N analyses were obtained for all new complexes.

The complex *1* (Scheme 1), with weakly bound Me_2S ligands [6], was used as a convenient source of $Me_2Pt(II)$ groups and gave *2* or *3* on reaction with bipym. Complex *3* is highly insoluble and so most syntheses used the more soluble *2* in acetone solution. Complex *2* reacted with alkyl iodides to give *4* and with excess α,ω-diiodoalkanes to give *5*[†]. Binuclear mixed oxidation state Pt(II)–Pt(IV) complexes were then prepared by linking a second $PtMe_2$ unit to the free nitrogen atoms of the bipym ligand of *4* or *5* to give *6* and *7*[†]. No intramolecular oxidative addition of the $Pt(CH_2)_n$–I group to the dimethylplatinum(II) centre of *7* occurred to give a μ-hydrocarbyl group, presumably because this would lead to ring strain. However, intermolecular oxidative addition between *5* and *2* did occur to give the



Scheme 1

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[†] Please see footnote overleaf.

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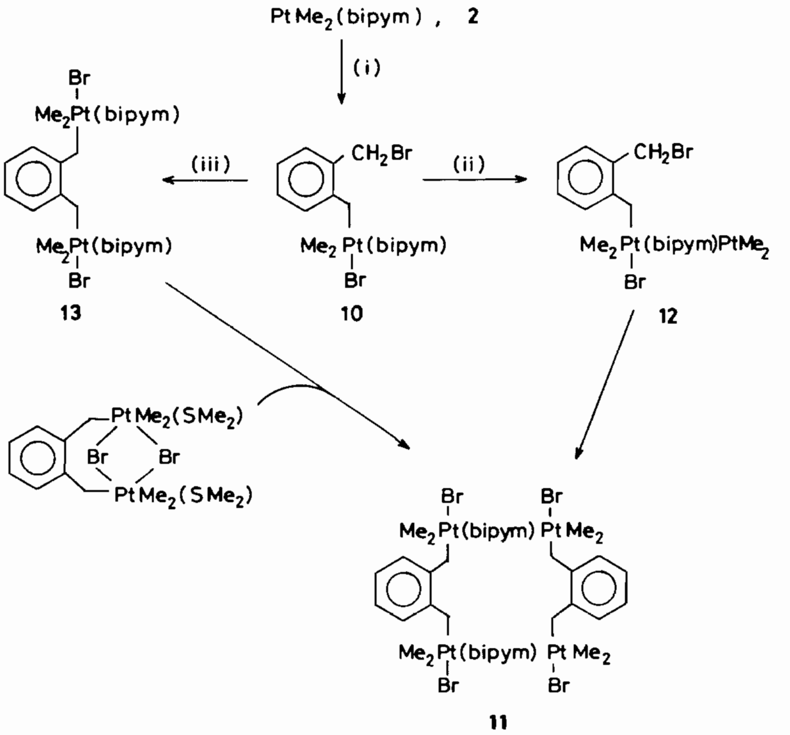
binuclear Pt(IV)–Pt(IV) complexes, *8*†, and the free nitrogen atoms of the most soluble derivative, *8c*, could again be linked to $PtMe_2$ units to give *9*†. Complex *9* thus contains both μ-hydrocarbyl and μ-bipym groups with two Pt(IV) and two Pt(II) centres.

An exception to the above reactivity pattern was observed with α,α′-dibromo-*o*-xylene which gave the expected product *10* on reaction with *2*, but which gave the product *11* after treatment with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. Complex *11* is clearly formed by intermolecular oxidative addition involving two molecules of *12*. The nuclearity of *11* was confirmed both by an independent synthesis involving combination of two platinum(IV) dimers as shown in Scheme 2 and from the mass spectrum, which contains a peak centred at m/e = 1424, with the expected isotope pattern for a Pt_4 species, corresponding to the molecular ion –4 bromine atoms. Complex *11*† is a remarkable tetranuclear complex having two μ-bipym ligands and to μ-hydrocarbyl ligands.

Thus far our studies have been confirmed to platinum complexes, but heteronuclear complexes containing platinum and other metals can clearly be prepared by analogous methods. Studies of the synthesis and reactivity of such complexes are in progress. Very few systems are known which allow a stepwise, rational synthesis of high nuclearity complexes as described above.



Scheme 2

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† Typical spectroscopic data: *4a*, ^1H NMR (CD_2Cl_2): 1.56 ppm [s, 6H, $^2J(PtH)$ 72 Hz, MePt *trans* to N], 0.67 ppm [s, 3H, $^2J(PtH)$ 72 Hz, MePt *trans* to I]; IR: 1567 and 1546 cm^{-1}. *5a*, ^1H NMR (CD_2Cl_2): 1.52 ppm [s, 6H, $^2J(PtH)$ 74 Hz, MePt *trans* to N], 2.86 ppm [t, 2H, $^3J(HH)$ 7 Hz, CH_2I]; IR: 1568 and 1547 cm^{-1}. *6a*, ^1H NMR (CD_2Cl_2): 1.63 ppm [s, 6H, $^2J(PtH)$ 76 Hz, $MePt^{IV}$ *trans* to N], 1.34 ppm [s, 6H, $^2J(PtH)$ 90 Hz, $MePt^{II}$], 0.70 ppm [s, 3H, $^2J(PtH)$ 70 Hz, $MePt^{IV}$ *trans* to I]; UV-vis: λ_{max} 570 nm; IR: 1559 and 1552 cm^{-1}. *7a*, UV-vis: λ_{max} 571 nm; IR: 1568 cm^{-1}. *8c*, ^1H NMR (CD_2Cl_2): 1.37 ppm [s, 12H, $^2J(PtH)$ 74 Hz, MePt]; IR: 1568 and 1546 cm^{-1}. *9*, UV-vis: λ_{max} 570 nm, IR: 1561 cm^{-1}. *10*, ^1H NMR (CD_2Cl_2): 1.63 ppm [s, 6H, $^2J(PtH)$ 72 Hz, MePt], 3.02 ppm [s, 2H, $^2J(PtH)$ 92 Hz, Pt-CH_2], 3.90 ppm [s, 2H, J(PtH) 6 Hz, CH_2Br]; IR: 1568 and 1550 cm^{-1}. *11*, ^1H NMR (C_5D_5N): 1.78 ppm [s, $^2J(PtH)$ 76 Hz, MePt]; IR: 1570 cm^{-1}. *11* was only sparingly soluble in pyridine and reacted slowly; the spectrum must be obtained immediately after dissolution.