Synthesis and Properties of a Methyl Derivative of Zeise's Dimer

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A methyl(ethylene)platinum(II) complex $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ has been prepared and characterized; it forms complexes $[PtClMe(C_2H_4)L]$ where L = pyridine, Me_2S, or C_2H_4, undergoes exchange with unsaturated reagents (un) where (un) = PhCH=CHPh, $CH(CO_2Me)=CH(CO_2Me)$, or PhC≡CPh to give $[Pt_2(\mu\text{-}Cl)_2Me_2(un)_2]$, undergoes insertion with $CF_3C{\equiv}CCF_3$ to give, after treatment with pyridine, $[PtCl\{C(CF_3)=C(CF_3)Me\}(py)_2]$, and reacts with Zeise's dimer to give the unsymmetrical dimer $[Pt_2(\mu\text{-}Cl)_2ClMe(C_2H_4)_2]$.

Zeise's salt and dimer (**1**) are the oldest organometallic compounds, and their chemistry has been developed in great detail.[1] However, no alkyl derivatives have been prepared though such complexes contain mutually *cis* alkyl and ethylene ligands and are therefore of interest as the simplest models for intermediates in Ziegler–Natta polymerization.[2] We report the synthesis of a methyl derivative of Zeise's dimer, and an investigation of its properties. A summary is given in Scheme 1.

The complex $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ (**2**) was prepared by reaction of Zeise's dimer (**1**) in dichloromethane solution with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$,[3] followed by chromatography through Florisil to give pure (**2**). Highest yields (*ca.* 90%) are obtained if the solution is saturated with ethylene prior to mixing the reagents. *cis*-$[PtMe_2(SMe_2)_2]$ can also be used as a methylating agent in this reaction, but attempts with conventional methylating agents such as $SnMe_4$[4] gave only poor yields.

Complex (**2**) was characterized by elemental analysis, by chemical reactions (Scheme 1) and by n.m.r. spectroscopy.†

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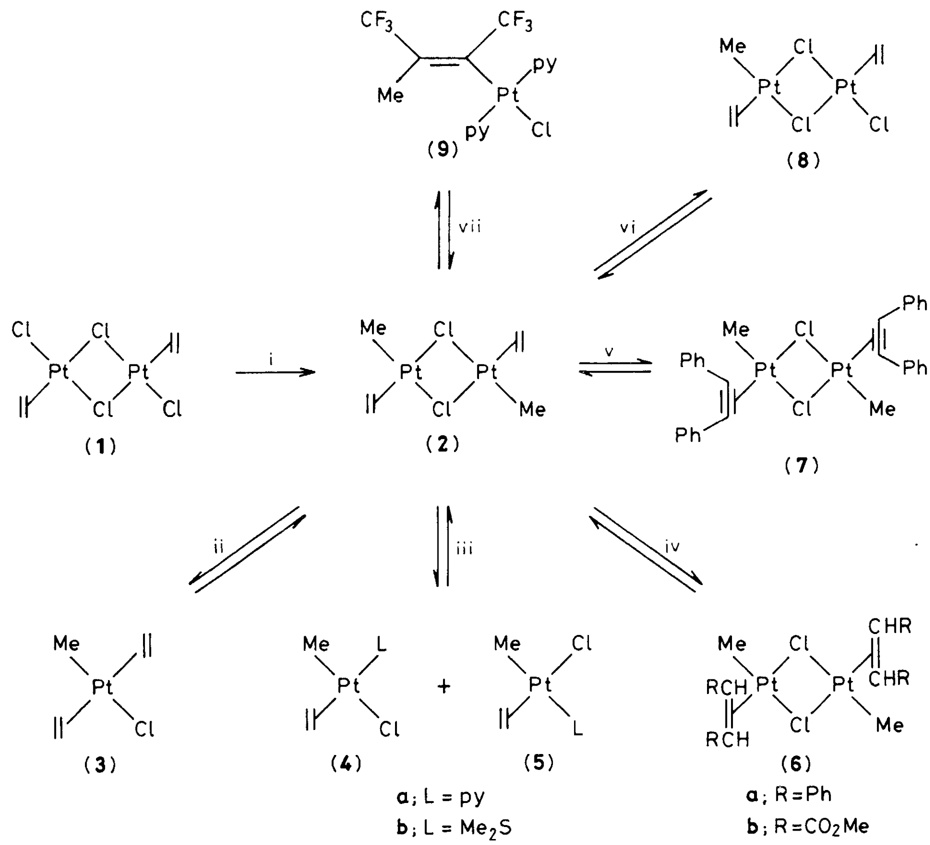
† *N.m.r. data.* ^1H (CD_2Cl_2) unless otherwise stated (δ, *J* in Hz). Compound (**2**): 0.52 [s, $^2J(PtH)$ 81, MePt], 3.73 [s, $^2J(PtH)$ 79, C_2H_4]; {$^{13}C\{^1H\}$ (CD_2Cl_2): −8.63 [s, $^1J(PtC)$ 682, MePt], 63.38 p.p.m. [s, $^1J(PtC)$ 254, C_2H_4Pt}. Compound (**4a**): 0.66 [s, $^2J(PtH)$ 72, MePt, 3.53 [s, $^2J(PtH)$ 72, C_2H_4]. Compound (**5a**): 0.41 [s, $^2J(PtH)$ 76, MePt], 4.12 [s, $^2J(PtH)$ not resolved, C_2H_4]. Compound (**3**) (at −60 °C): 0.32 [s, $^2J(PtH)$ 68, MePt], 3.62 [s, $^2J(PtH)$ not resolved, C_2H_4]. Compound (**6a**): 0.45 [s, $^2J(PtH)$ 86, MePt], 4.91 [s, =CH]; 3.73 [s, MeO]. Compound (**6b**): 0.42 [s, $^2J(PtH)$ 84, MePt], 5.96 [s, =CH). Compound (**7**): 0.90 [s, $^2J(PtH)$ 86, MePt], 7.44 and 8.06 [m, Ph). Note that the diphenylacetylene complex $[Pt_2Cl_4(PhCCPh)_2]$ is too unstable to be isolated. Compound (**8**): 0.59 [s, $^2J(PtH)$ 81, MePt], 3.81 [s, $^2J(PtH)$ 82, C_2H_4PtMe], 4.72 [s, $^2J(PtH)$ 72, C_2H_4PtCl]. Compound (**9**): 1.24 [s, MeC]: {^{19}F (CH_2Cl_2): 40.5 [q, $^5J(FF)$ 15, $^3J(PtF)$ 93, $PtC(CF_3)$]; 54.8 p.p.m. [q, $^5J(FF)$ 15, $PtCC(CF_3)$]}.



Scheme 1. *Reagents*: i, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$; ii, C_2H_4; iii, pyridine (py) or Me_2S; iv, RHC=CHR (*trans*-stilbene or dimethyl fumarate); v, PhC≡CPh; vi, (**1**); vii, pyridine, $CF_3C{\equiv}CCF_3$.

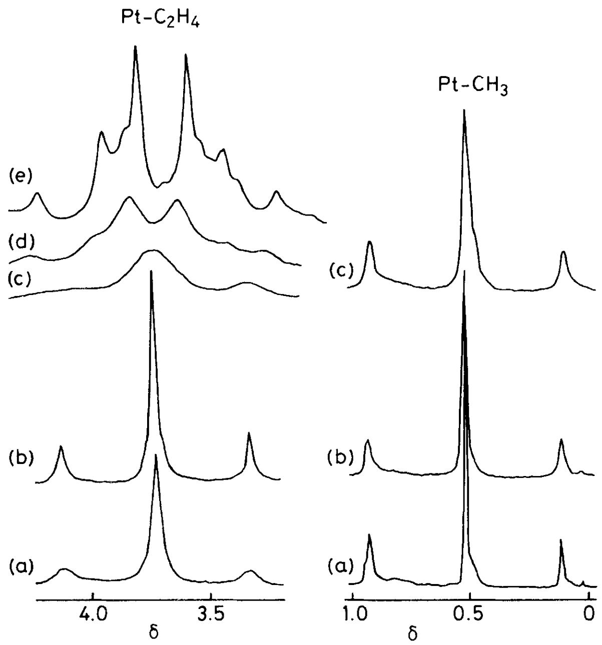


Figure 1. ^1H n.m.r. spectra of complex (**2**). (a) 20 °C, (b) −20 °C, (c) −65 °C, (d) −75 °C, and (e) −90 °C. The methyl resonance was unchanged from −60 to −90 °C and is not shown for the −75 and −90 °C spectra. *Added in proof*: a referee has suggested that the increased linewidths at low temperature may be due to chemical shift anisotropy relaxation of ^{195}Pt.

Of particular significance is the observation of satellites around the C_2H_4 resonance in the ^1H or ^{13}C n.m.r. spectra at room temperature, showing that rapid reversible dissociation of C_2H_4 does not occur. Rotation of the C_2H_4 about the Pt–C_2H_4 axis is slow below −65 °C (Figure 1). In contrast, Zeise's dimer gives a broad singlet without ^{195}Pt satellites at temperatures as low as −90 °C, indicating a very rapid exchange process. Clearly the strong σ-donor methyl group leads to stronger Pt–C_2H_4 backbonding in (**2**) and hence the ethylene is less prone to dissociation or rotation compared to Zeise's dimer.[5] Complex (**2**) decomposed over a period of *ca.* 2 weeks at room temperature in the dark, but formed a more stable derivative with pyridine characterized as a mixture of isomers (**4a**) and (**5a**).† With dimethyl sulphide at low temperature similar isomers were formed, but evaporation of the solution gave starting material and *trans*-$[PtClMe(SMe_2)_2]$ and $[Pt_2(\mu\text{-}Cl)_2Me_2(SMe_2)_2]$ by disproportionation. Similarly, with ethylene at low temperature (**3**) was formed,† but at higher temperatures the equilibrium favoured (**2**) and free ethylene. Species similar to (**3**) are also intermediates in the exchange reactions of (**2**) with alkenes and alkynes to give (**6**) and (**7**) respectively (Scheme 1).† A mixture of equimolar amounts of (**1**) and (**2**) gave one MePt and two PtC_2H_4 resonances due to the unsymmetrical dimer (**8**) at 35 °C in the ^1H n.m.r. spectrum,† and at −80 °C each C_2H_4 resonance split into an $[AB]_2$ multiplet.

An attempt was made to effect insertion of ethylene into the MePt bond of (**2**) by heating a solution to 50 °C with ethylene (10 atm., 20 h). Some low molecular weight polyethylene was formed, and (**2**) was recovered along with some Pt and $PtCl_2$

formed by decomposition. It is therefore clear that, even in this ideal system, insertion of C_2H_4 into the PtMe bond requires a high activation energy.[6] However, reaction with the activated alkyne, $CF_3C{\equiv}CCF_3$, led to rapid *cis*-insertion and the product was characterized as the pyridine complex (**9**).†

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