

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

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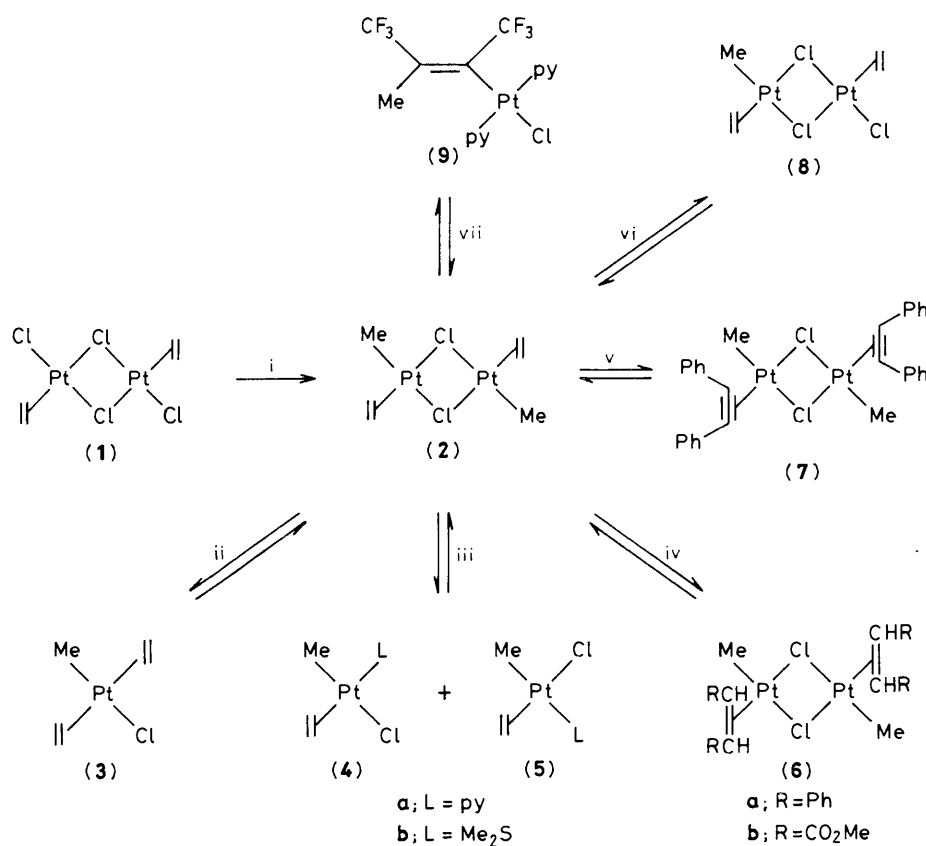
A methyl(ethylene)platinum(II) complex $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{C}_2\text{H}_4)_2]$ has been prepared and characterized; it forms complexes $[\text{PtClMe}(\text{C}_2\text{H}_4)\text{L}]$ where L = pyridine, Me_2S , or C_2H_4 , undergoes exchange with unsaturated reagents (un) where (un) = PhCH=CHPh , $\text{CH}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})$, or $\text{PhC}\equiv\text{CPh}$ to give $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{un})_2]$, undergoes insertion with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ to give, after treatment with pyridine, $[\text{PtCl}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Me}\}(\text{py})_2]$, and reacts with Zeise's dimer to give the unsymmetrical dimer $[\text{Pt}_2(\mu\text{-Cl})_2\text{ClMe}(\text{C}_2\text{H}_4)_2]$.

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 $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{C}_2\text{H}_4)_2]$ (**2**) was prepared by reaction of Zeise's dimer (**1**) in dichloromethane solution with $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$,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*- $[\text{PtMe}_2(\text{SMe}_2)_2]$ 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.[†]

[†] *N.m.r. data.* ¹H (CD_2Cl_2) unless otherwise stated (δ , *J* in Hz). Compound (**2**): 0.52 [s, ²*J*(PtH) 81, MePt], 3.73 [s, ²*J*(PtH) 79, C₂H₄]; {¹³C{¹H} (CD_2Cl_2): -8.63 [s, ¹*J*(PtC) 682, MePt], 63.38 p.p.m. [s, ¹*J*(PtC) 254, C₂H₄Pt]}. Compound (**4a**): 0.66 [s, ²*J*(PtH) 72, MePt, 3.53 [s, ²*J*(PtH) 72, C₂H₄]. Compound (**5a**): 0.41 [s, ²*J*(PtH) 76, MePt], 4.12 [s, ²*J*(PtH) not resolved, C₂H₄]. Compound (**3**) (at -60°C): 0.32 [s, ²*J*(PtH) 68, MePt], 3.62 [s, ²*J*(PtH) not resolved, C₂H₄]. Compound (**6a**): 0.45 [s, ²*J*(PtH) 86, MePt], 4.91 [s, =CH]; 3.73 [s, MeO]. Compound (**6b**): 0.42 [s, ²*J*(PtH) 84, MePt], 5.96 [s, =CH]. Compound (**7**): 0.90 [s, ²*J*(PtH) 86, MePt], 7.44 and 8.06 [m, Ph]. Note that the diphenylacetylene complex $[\text{Pt}_2\text{Cl}_4(\text{PhCCPh})_2]$ is too unstable to be isolated. Compound (**8**): 0.59 [s, ²*J*(PtH) 81, MePt], 3.81 [s, ²*J*(PtH) 82, C₂H₄PtMe], 4.72 [s, ²*J*(PtH) 72, C₂H₄PtCl]. Compound (**9**): 1.24 [s, MeC]: {¹⁹F (CH_2Cl_2): 40.5 [q, ³*J*(FF) 15, ³*J*(PtF) 93, PtC(CF₃)]}; 54.8 p.p.m. [q, ⁵*J*(FF) 15, PtCC(CF₃)]}.



Scheme 1. Reagents: i, [Pt₂Me₄(μ-SMe₂)₂]; ii, C₂H₄; iii, pyridine (py) or Me₂S; iv, RHC=CHR (*trans*-stilbene or dimethyl fumarate); v, PhC≡CPh; vi, (1); vii, pyridine, CF₃C≡CCF₃.

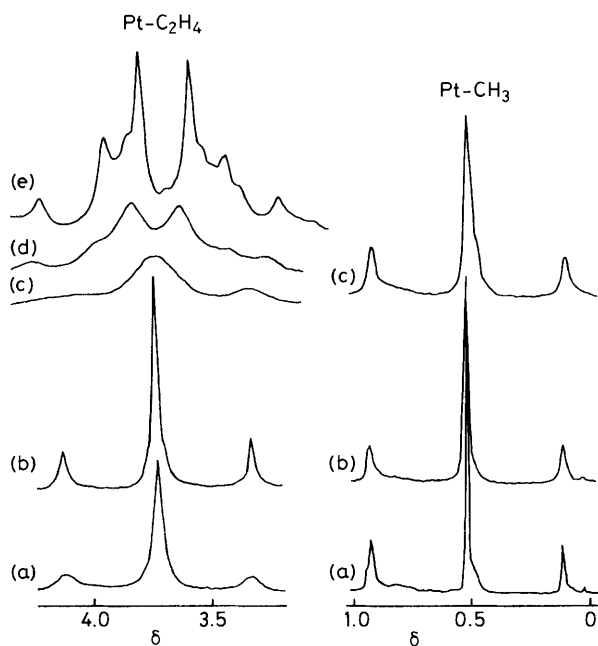


Figure 1. ¹H n.m.r. spectra of complex (2). (a) 20 °C, (b) -20 °C, (c) -65 °C, (d) -75 °C, and (e) -90 °C. The methyl resonance was unchanged from -60 to -90 °C and is not shown for the -75 and -90 °C spectra. *Added in proof:* a referee has suggested that the increased linewidths at low temperature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

Of particular significance is the observation of satellites around the C₂H₄ resonance in the ¹H or ¹³C n.m.r. spectra at room temperature, showing that rapid reversible dissociation of C₂H₄ does not occur. Rotation of the C₂H₄ about the Pt-C₂H₄ axis is slow below -65 °C (Figure 1). In contrast, Zeise's dimer gives a broad singlet without ¹⁹⁵Pt 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-C₂H₄ 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(SMe₂)₂] and [Pt₂(μ-Cl)₂Me₂(SMe₂)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 PtC₂H₄ resonances due to the unsymmetrical dimer (8) at 35 °C in the ¹H n.m.r. spectrum,† and at -80 °C each C₂H₄ 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 PtCl₂

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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