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Preliminary communication

ELECTROCHEMICAL SYNTHESIS AND MOLECULAR STRUCTURE OF COORDINATIVELY UNSATURATED PLATINACYCLOBUTANES

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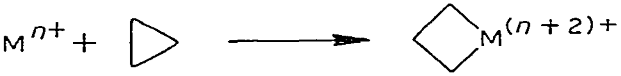
Summary

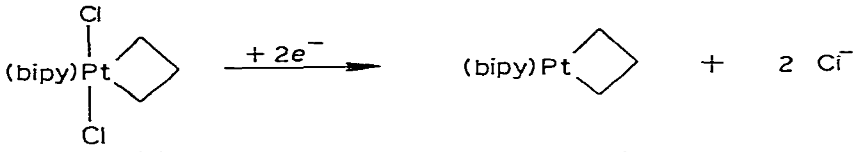
The 16-electron platinacyclobutane (bipy)Pt(C_3H_6) (II) is electrochemically synthesized from the platinum(IV) analog, (bipy)$PtCl_2(C_3H_6)$. II undergoes ready ligand substitution of bipyridine to afford a series of platinacycles with unusually large Pt splittings of the β-protons in the NMR spectrum but an X-ray crystal structure of II shows the molecular framework to be planar. II is further reduced to the paramagnetic platinacycle anion (bipy)Pt$(C_3H_6)^-$ in a reversible one-electron process.

Oxidative addition of cyclopropanes potentially represents a general method for the synthesis of a variety of metallacyclobutanes, i.e.:



(1)

Unfortunately, it is presently restricted to a variety of platinum(IV) complexes [1]. Although the series of coordinatively saturated, 18-electron platinacyclobutanes (where M = (bipy)$PtCl_2$, $(py)_2PtCl_2$, etc.) have been explored extensively [2] they do not show the properties characteristic of intermediates relevant to olefin metathesis, dimerization and related catalytic processes [3]. In this report we wish to present the convenient synthesis and structural characterization of the novel 16-electron platinacyclobutane in eq. 2 by electrochemical methods, e.g.:



(2)

(I) (II)

Coupled with the liberation of ethylene upon thermal decomposition, this series of platinacyclobutanes offers a promising avenue for studying the behavior of coordinatively unsaturated, 16-electron metallacyclobutanes.

The cyclic voltammogram in Fig. 1 of (bipy)$PtCl_2(C_3H_6)$ (I) in acetonitrile solution exhibits an irreversible cathodic wave at the peak potential E_p −1.35 V, followed by a totally reversible couple at E_0 = −1.67 V vs. NaCl-SCE. The controlled potential electrolysis at −1.35 V, requires the passage of 2.03 ± 0.05 electrons per platinum, in accord with the electrochemical reaction in eq. 2. The platinacyclobutane II was recovered in greater than 85% yields from the electrolyzed solution by precipitation with toluene. Recrystallization from acetonitrile afforded orange crystals which were characterized by elemental analysis, proton NMR spectroscopy (Table 1) and X-ray crystallography.

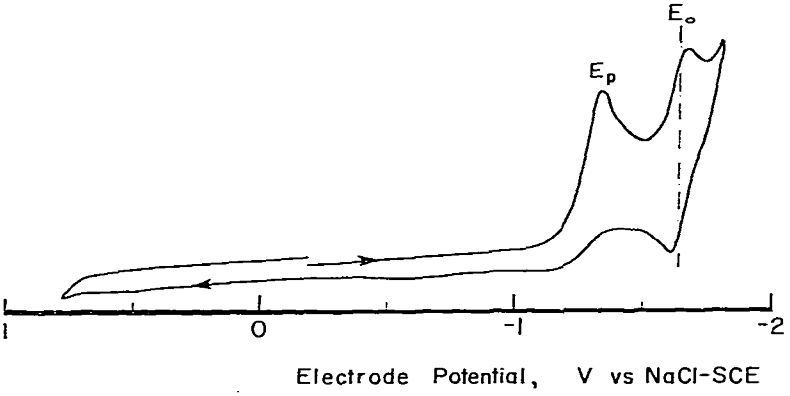
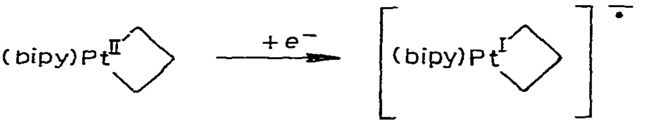


Fig. 1. Initial scan cyclic voltammogram of 1.0 X 10^{-3} *M* (bipy)$Pt(C_3H_6)$ in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate at a Pt microelectrode with a scan rate of 100 mV s^{-1}. The first irreversible cathodic wave labelled as E_p and the second reversible wave as E_0.

The second, reversible wave in Fig. 1 corresponds to the further one-electron reduction of platinacyclobutane II to the corresponding platinum(I) analog, i.e.:



(3)

Accordingly, the bulk electrolysis of an acetonitrile solution of (bipy)$Pt(C_3H_6)$ at −1.80 V vs. NaCl-SCE required the passage of 0.85 ± 0.05 electrons per platinum. The platinum(I) radical-anion is characterized by a deep red solution, showing an intense ESR absorption centered at $g = 1.97_2$. It is noteworthy that the cyclic voltammogram of this dark red solution exhibits a reversible oxidation wave centered at E_0 −1.67 V, which is the same as that of the second cathodic wave in Fig. 1. In other words, the platinum(I) anion-radical is directly related to (bipy)$Pt^{II}(C_3H_6)$ solely by the addition of an electron

TABLE 1

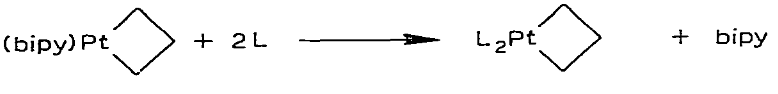
SPECTROSCOPIC DATA FOR THE SERIES OF PLATINACYCLOBUTANES II AND IV[a]

Platinacycle	$J(^{195}Pt—H)$		$J(^{31}P—H)$		$J(H_\alpha—H_\beta)$
	H_α	H_β	H_α	H_β	
$(bipy)Pt(C_3H_6)$	115 (8.71)	110 (6.68)	—	—	7
$(Ph_3P)_2Pt(C_3H_6)$	88 (9.73)[c]	112 (6.49)	*b*	*b*	*b*
$(Et_3P)_2Pt(C_3H_6)$	80 (9.65)[d]	94 (6.25)	5.5	4.3	8
$(Me_3P)_2Pt(C_3H_6)$	82 (9.53)	95 (6.26)	*b*	*b*	*b*

[a] ^1H NMR (220 MHz) spectra in $CHCl_3$. Coupling constants in Hz. Proton chemical shifts in τ relative to TMS given in parentheses. Ligand resonances (bipy, PR_3) not included. [b] Not resolved. [c] ^{31}P shift of 26.104 ppm relative to H_3PO_4. $J(^{195}Pt—^{31}P)$ 865 Hz. [d] ^{31}P shift of 8.136 ppm. $J(^{195}Pt—^{31}P)$ 869 Hz.

without attendant structural changes. The lifetime of the anion-radical III is estimated to be about 30 min at room temperature, judging from the decay of the ESR signal.

The platinacycle II is highly labile to substitution of the bipyridyl ligand. Thus treatment with a variety of phosphines leads to the bis-phosphine complexes in eq. 4, where L = PPh_3, PEt_3 [4], PMe_3. The displaced bipyridine is



(IV)

(4)

readily removed by sublimation, which allows the phosphine complexes to be obtained as colorless needles after recrystallization. Similarly, the addition of t-butyl isocyanide, carbon monoxide or phenylacetylene to II, resulted in the production of a series of new platinacyclobutane complexes, as witnessed by the changes in the NMR and IR spectra. Further discussion of these complexes will be deferred pending exhaustive characterization.

The series of 16-electron platinacyclobutanes in Table 1 show rather unusual couplings of the ^{195}Pt and ^{31}P nuclei to the α- and β-protons of the $CH_2CH_2CH_2$ moiety in the ^1H NMR spectrum. Indeed in some cases, the coupling to the β-protons is even larger than the corresponding coupling to the α-protons. In addition, the β-protons in II and IV are markedly shifted (1.0–1.5 τ) to lower fields in comparison to the platinum(IV) analog $L_2PtCl_2(C_3H_6)$ [5] and the related platinum(II) metallacyclopentane $(Ph_3P)_2Pt(C_4H_8)$ [6]. (The proton—proton coupling is adequately described as an A_4X_2 system, and it results in the observation of a triplet and a quintet for the α- and β-methylene groups, respectively, after decoupling the ^{31}P nucleus.)

In light of the unusually strong platinum couplings to the β-protons in II and IV, a crystal structure of $(bipy)Pt(C_3H_6)$ was undertaken. The most striking feature of the molecular geometry shown in Fig. 2 is the almost complete planarity of the structure. Inspection of the bond angles in the platinacycle moiety (angle CPtC 70°, PtCC 96°, CCC 99°), indicates this 4-membered ring to be relatively strain-free, even in the absence of pucker. This conclusion is further supported by the observation of unexceptional carbon—carbon bond lengths of 1.53(1) Å. The absence of an unusual bonding interaction between

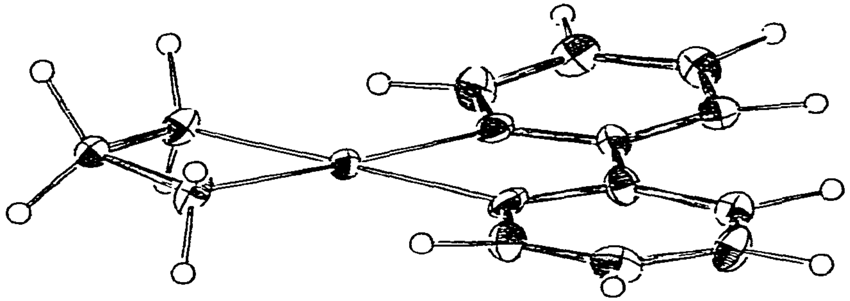
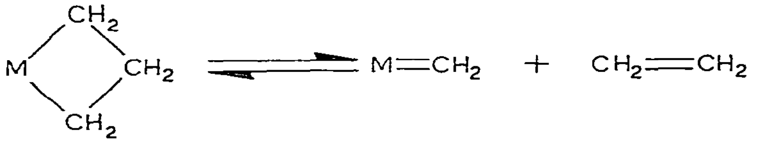


Fig. 2. ORTEP drawing of the molecular structure of (bipy)Pt(C_3H_6).

the platinum center and the β-hydrogens in the solid state*, contrasts with the unusually large chemical shift and β-coupling constants in the solution NMR data. These observations raise the possibility of a facile puckering motion allowed by a rather strain-free ring. The accurate structural data obtained for this class of metallacyclobutanes bears critically on the conformational energy change associated with ring puckering in metallacyclobutanes, which has been suggested as the dominant factor controlling the stereochemistry of the olefin metathesis reaction**, the key step being proposed as the reversible fragmentation in eq. 5.



(5)

In accord with this formulation, the mass spectrum of (bipy)Pt(C_3H_6) shows an intense carbene fragment (bipy)PtCH_2^+ (m/e = 365) and copious amounts of ethylene, together with the parent ion (m/e = 393). Furthermore, the thermal decomposition of (bipy)Pt(C_3H_6), either in the solid state or in solution, yields ethylene in addition various amounts of propylene and cyclopropane, dependent on the ligands and the experimental conditions, as we will elaborate later.

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*The hydrogens in I (Fig. 2) were located by a difference Fourier synthesis and refined smoothly with discrepancy indices $R(F)$ = 0.0367 and $R_w(F)$ = 0.0362. The crystal structure of II will be described in detail separately.

**For a review of these arguments see Grubbs in ref. 3a.