CYCLOPENTADIENYL–METAL COMPLEXES
II. MASS SPECTROMETRIC AND GAS PHASE KINETIC STUDIES ON THE THERMAL STABILITY AND THE STRUCTURE OF $(CH_3)_3Pt\text{-}\pi\text{-}C_5H_5$

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SUMMARY

Gaseous cyclopentadienyltrimethylplatinum(IV) decomposes apparently homogeneously at 165° in a Teflon reactor with a halflife of about 10^3 seconds. Methane and platinum are major products and the primary reaction step has been shown to involve separation of a methyl radical. These results together with mass spectrometric, single crystal X-ray diffraction, and low temperature NMR data clearly demonstrate the multicenter bonding of the cyclopentadienyl ligand to platinum. The noble gas 18-electron configuration of the platinum atom is probably responsible for the surprising thermal stability of the title compound when compared with $Pt(CH_3)_4$, which is non-existent. The bond dissociation energy $(CH_3)_2(\pi\text{-}C_5H_5)Pt\text{-}CH_3$ can be estimated at 39 ± 5 kcal/mole. The mass spectrometric fragmentation pattern is discussed and vapor pressure measurements gave $\log p$ (mm) $=(7.38\pm0.45)-(2540\pm140)/T(°K)$ resulting in a heat of vaporization of 11.62 ± 0.65 kcal/mole.

INTRODUCTION

The widespread interest in the reactivity and structure of cyclopentadienyl–metal complexes is apparent from the rapidly increasing number of scientific contributions in this field. (For leading references see ref. 1). One of the most frequently disputed questions concerns the nature of the metal to cyclopentadienyl bonding, and involves distinguishing between 2-center (σ, or bihapto) and multicenter (σ–π, or multihapto) bonding. In a previous publication the relationship between the observed thermal stabilities of $R_xM(C_5H_5)$ complexes (R = alkyl) and the dissociation energies of the two-center metal–carbon σ-bonds was discussed[1]. Because of the extra stabilization energy generated in the cyclopentadienyl radical, $(CH_3)_xM$–σ-C_5H_5 bonds are about 30 kcal/mole weaker than the corresponding $(CH_3)_xM$–CH_3 bonds[1]. For several alkyl metal compounds, σ-bonded cyclopentadienyl structures can therefore *a priori* not be expected to be stable at room temperature. It appears now to be established[2-5], that earlier reports on the preparation[6] and structure[7] of $Pt(CH_3)_4$ were in error and were actually dealing with $(CH_3)_3PtOH^2$. On the other hand $(CH_3)_3$-PtC_5H_5 has been prepared by Robinson and Shaw[8] and both π-bonding[8] and σ-bonding[9] have been suggested for the cyclopentadienyl ligand. Bond energy considera-

tions, however, suggest that $(CH_3)_3Pt\text{-}\sigma\text{-}C_5H_5$ should not exist. This paper describes kinetic, mass-spectroscopic, NMR and single-crystal X-ray diffraction data which demonstrate that the cyclopentadiényl ring in the title compound is, in fact, π-bonded.

EXPERIMENTAL

General

Kinetic measurements were carried out in the gas phase using a Teflon-coated stainless-steel reaction cell[10] and a static reaction system described previously[11]. Mass spectra were recorded on a CEC 21-104 mass spectrometer at 74 eV and NMR spectra on a Varian HA-60 instrument. Molecular weight determinations were carried out on a vapour phase "osmometer" obtained from Knauer-Corporation, Berlin, DDR, and IR analyses on a Grubb–Parson "Spectromaster" spectrophotometer.

Preparation of $(CH_3)_3PtC_5H_5$

$(CH_3)_3PtC_5H_5$ has been prepared from $(CH_3)_3PtI$ and cyclopentadienylsodium[8]. It was purified by repeated recrystallization from methanol and by sublimation in vacuo at room temperature. Recrystallization yielded colourless fine needles while slow sublimation resulted in bricks of several mm in length. $(CH_3)_3PtI$ was prepared from anhydrous $PtCl_4$ and methylmagnesium iodide[6] followed by recrystallization from benzene.

RESULTS AND DISCUSSION

A. Identification and physical properties of $(CH_3)_3Pt\text{-}\pi\text{-}C_5H_5$

The melting point was found to be 108.5°, in constrast with the value of 65°C reported by Shaw et al.[8]. More recently Semion et al.[12] also reported a higher value for the m.p., namely 104–104.5°. Considering that all other physical properties are in agreement and consistent with the formula $(CH_3)_3PtC_5H_5$ it can be concluded that the higher melting point is the correct one.

The molecular weight was determined by mass spectrometry to 305 (required 305) and vapor phase osmometry (ΔT-measurement using triphenylphosphine as a standard) gave 315.

The IR absorption spectrum was identical with that reported previously by Shaw et al.[8] and indicates multicenter bonding for the C_5H_5 group.

The NMR spectra in $CDCl_3$ solutions show two absorptions at τ 9.17 and 4.50 with the expected relative intensities of 9/5 for the methyl and the cyclopentadienyl protons respectively. Coupling with [195]Pt (natural abundance 33 %) results in side bands with $J(CH_3)$ 80.9 Hz and $J(C_5H_5)$ 5.6 Hz. The NMR data are in agreement with those reported by Shaw et al.[8].

Vapor pressure data obtained from measurements in a conventional isoteniscope arrangement resulted with standard deviations in the relationship:

$$\log p \text{ (in mm)} = (7.38 \pm 0.45) - (2540 \pm 140)/T(°K)$$

yielding a Trouton's constant of 20.6, an extrapolated boiling point of $\sim 292°$ and a heat of vaporization $\Delta H_v = 11.62 \pm 0.65$ kcal/mole.

B. Structural data

The X-ray diffraction pattern of a single cystal of the $(CH_3)_3PtC_5H_5$ used in these studies has been analyzed in our laboratories by Adamson and Bart[13].

Crystals are orthorhombic with $a=11.631$, $b=7.180$ and $c=10.359$ Å. The space group was determined as *Pna2*, and the mean bond lengths (in Å) are Pt–C(Me) $=2.11$, Pt–C(Cp) $=2.32$, C(Cp)–C(Cp) $=1.43$. The platinum atom lies above a point approximately in the center of the 5-membered ring. No disordering was detected in the positions of the carbon atoms which is consistent with a π-bonded structure. A brief literature note[12], describing the X-ray structure analysis of this same compound has appeared.

C. Mass spectrum

The observed mass spectrum is schematically represented in Fig. 1. In the mass range scanned up to $m/e \approx 600$ no peaks could be detected with a higher mass than that of the parent molecular ion. As is to be expected for a transition metal–alkyl complex, the molecular ions are of low abundance. The elimination of methyl radicals is clearly
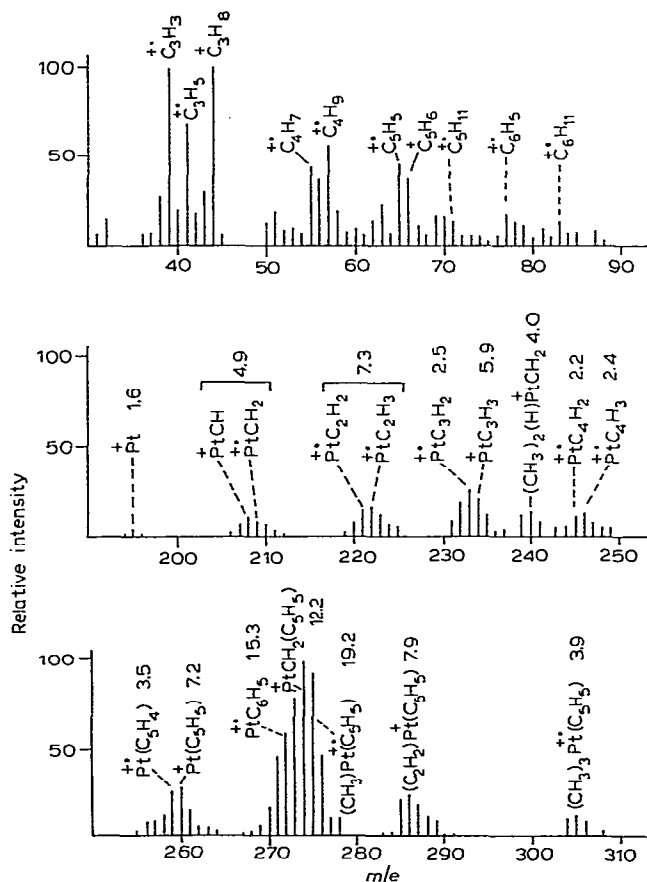

Fig. 1. Schematic representation of the mass spectrum of $(CH_3)_3Pt$-π-C_5H_5. Numbers indicate percentage of the total of platinum ions observed in the spectrum.

the dominant reaction path initiating the overall fragmentation which is in agreement with a π-bonded cyclopentadienyl ligand. This is seen from the fact that the C_5H_5-containing Pt ions account for more than half of the metal ions observed. The formation of the most abundant metal ions ($CH_3\overset{+\cdot}{Pt}C_5H_5$ and $\overset{+}{CH_2}PtC_5H_5$) from the molecular ion involves a valence change from $+IV$ to $+II$. In agreement with literature data on ferrocene-like sandwich type cyclopentadienyl compounds[14,15] fragmentation of the C_5H_5 group occurs mainly by elimination of acetylene and to a smaller extent by elimination of H and CH_3.
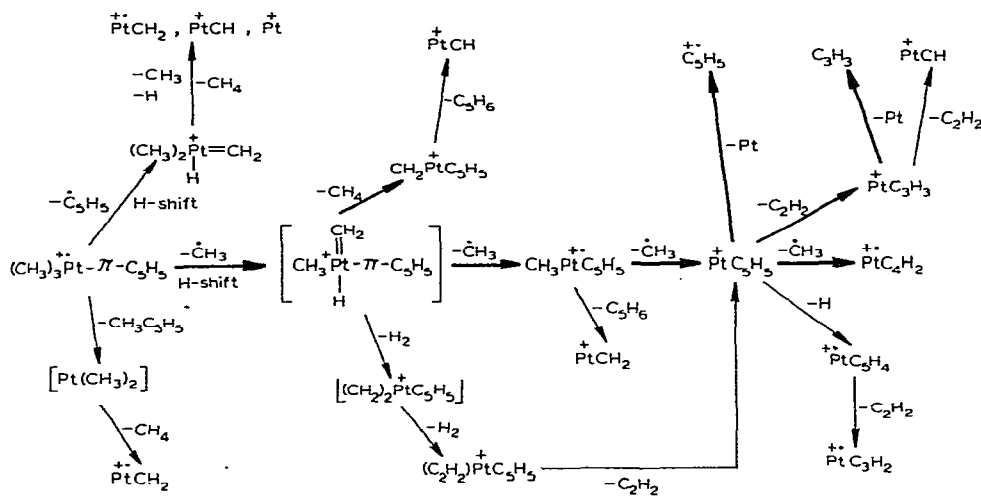
Fig. 2. Proposed scheme for the fragmentation of $(CH_3)_3\overset{+\cdot}{Pt}$-$\pi$-$C_5H_5$ in the mass spectrometer.

In Fig. 2 a scheme is proposed for the fragmentation of $(CH_3)_3\overset{+}{Pt}$-π-C_5H_5 in the mass spectrometer. The observed low molecular weight hydrocarbon ions probably originate primarily from organoplatinum ions. The relative size of the ionization potentials[16] for platinum (8.88 eV), $\overset{\cdot}{C}_3H_3$ (8.25 eV) and $\overset{\cdot}{C}_5H_5$ (8.69 eV) make a fragmentation according to:

$$\overset{+}{Pt}C_3H_3 \rightarrow Pt + \overset{+}{C}_3H_3 \tag{1}$$

$$\overset{+}{Pt}C_5H_5 \rightarrow Pt + \overset{+}{C}_5H_5 \tag{2}$$

possible. All other hydrocarbon ligands like CH_3 (9.9 eV), CH_2 (10.3 eV) and C_2H_2 (11.4 eV) have prohibitively high ionization potentials. Indeed the most abundant low molecular weight ions are $\overset{+}{C}_3H_3$ and $\overset{+}{C}_3H_8$ besides $\overset{+}{C}_3H_5$, $\overset{+}{C}_5H_5$ and $\overset{+}{C}_5H_6$. The high concentrations of the carbonium ions shown in Fig. 2 suggest that reactions (1) and (2) are important paths in the overall fragmentation pattern. Assuming that all $\overset{+}{C}_3$ and $\overset{+}{C}_5$ ions originate from $\overset{+}{Pt}C_3H_3$ and $\overset{+}{Pt}C_5H_5$, respectively, it can be concluded that at least one out of three parent molecular ions eventually emerges as a carbonium ion. The formation of $\overset{+}{C}_3H_8$ from $\overset{+}{C}_3H_3$ is not surprising in view of the

fact that hydrogen is being produced in the pyrolysis reaction. To a minor extent the small mass peaks in the range of C_1 to C_7 might also arise from the secondary ionization of products of the very fast thermal pyrolysis of the title compound in the inlet system of the mass spectrometer, kept at 250° and 2×10^{-6} mm Hg.

However one set of peaks centered at m/e 271 or 272 and having the appearance of a platinum ion cannot be readily explained. The formation of a $\overset{+}{Pt}C_6H_5$ ion from $(CH_3)_3 \overset{+}{Pt} C_5H_5$ is not apparent and there are no other indications for the presence of an impurity*.

D. NMR studies

As was to be expected for a multicenter bonded cyclopentadienyl ligand, the absorption bands at $-85°$ (in CS_2) and $-60°$ (in CS_2 and $CDCl_3$) were as sharp as those observed at room temperature. It is well known, however, that σ-C_5H_5 ligands also yield only one absorption for the ring protons because of a fast 1,5-metal transfer.

E. Kinetic measurements

Gaseous trimethylcyclopentadienylplatinum is surprisingly stable thermally if heterogeneous decomposition can be rigorously excluded. In previous studies[10,17] involving aluminum alkyls it has been shown that the use of reactors coated with Teflon minimizes wall reactions. Kinetic experiments were carried out between 115 and 165° in excess toluene. At 115°, less than 1 % conversion has been observed after 75 min. At 165° about one third of the material decomposed within 30 min. The amount of $(CH_3)_3$Pt-π-C_5H_5 recovered was identified after quenching of the reaction products by NMR spectroscopy using toluene as an internal standard. The NMR of the liquid product fraction did not reveal any other material besides the starting material. The decomposition apparently follows unimolecular kinetics, but the limited amount of material available did not allow for an extensive kinetic study.

The results of the kinetic studies are summarized in Table 1. Elemental pla-

TABLE 1

THERMAL DECOMPOSITION OF GASEOUS $(CH_3)_3$Pt-π-C_5H_5 IN A TEFLON REACTOR

Temp (°C)	Time (min)	Starting material		Products				Conversion [in % of $(PtCp)_o$]	$k_1{}^c \times 10^4$ (sec^{-1})
		$\left[\dfrac{(PtCp)}{T}\right]_0^{a,b}$		$\left[\dfrac{(PtCp)}{T}\right]_f^{a}$		Not condensed			
						(mmoles)	(CH_4/H_2)		
140.5	160	1.1	0.121	0.041		0.012		65.9	1.40
155.2	60	0.7	0.121	0.085		0.001	19	29.5	0.969
165.2	30	2.3	0.121	0.037		0.022	43	69.1	6.53
165.0	15	1.9	0.121	0.094		0.008	11	23.4	2.93
165.0	15	2.1	0.121	0.058				51.3	8.00
165.4	30	3.4	0.365	0.012		0.006		66.6	5.95

^{a} PtCp stands for $(CH_3)_3$Pt-π-C_5H_5, T for toluene, used as an internal standard, f indicates final, 0 initial concentrations. ^{b} Based on PMR analysis. ^{c} Rate constant for the unimolecular disappearance of $(CH_3)_3$-Pt-π-C_5H_5 with time.

* Note added in proof. King[20] also observed $C_6H_5\overset{+}{Pt}$ as a major fragment ion of the title compound.

tinum as well as CH_4 have been found as major products, and relatively small amounts of H_2 and C_2H_6 have been identified (gas-chromatography, mass spectrometry) as reaction products. The average rate constant (k_1) for the unimolecular decomposition at 165° is $\sim 6 \times 10^{-4}$ sec^{-1}. Assumption of the reasonable value of $\sim 10^{16}$ sec^{-1} for the preexponential factor [18,19] (based on the transition state formulation for unimolecular reactions) would result in an activation energy (E_1) of ~ 38.6 kcal/mole for splitting off CH_3 from $(CH_3)_3Pt\text{-}\pi\text{-}C_5H_5$. The lowest observed value for k_1 of $\sim 3 \times 10^{-4}$ sec^{-1} would yield a value for E_1 of 39.2 kcal/mole. Taking the approximations and the limited amount of experimental data into account a value of 39 ± 5 kcal/mole appears to be a reasonable estimate for E_1. Since the back reaction, the recombination of the radicals, would require practically no activation energy, this value would also be equal to the $\pi\text{-}C_5H_5(CH_3)_2Pt\text{-}CH_3$ bond dissociation energy.

The data presented in this work demonstrate unambiguously the multicenter bonding of the cyclopentadienyl ligand to the platinum atom. The surprising thermal stability of $(CH_3)_3Pt\text{-}\pi\text{-}C_5H_5$ when compared with the non existent compound $(CH_3)_3PtCH_3$ can be attributed to the noble gas 18-electron configuration of the platinum atom, as is also the case for $(CH_3)_3PtOH$.

ACKNOWLEDGEMENT

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