Reactivity of Co-ordinated Ligands. Part XXIV.[1] Cyclopentadienyl Cyclo-enyl Complexes of Platinum(II)

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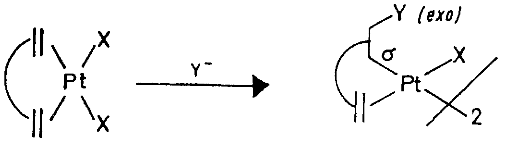
The preparation of the complex $[(C_7H_8)Pt(\sigma\text{-}C_5H_5)_2]$ is reported. The ^1H n.m.r. spectrum of this complex indicates that the cyclopentadienyl rings are σ-bonded to platinum and that they display fluxional behaviour in solution but with an activation energy too low to permit ' freezing-out ' at accessible temperatures. In solution the complex rearranges with time to form a σ–π complex, having a π-cyclopentadienyl ring co-ordinated to platinum and a cyclopentadienyl attached to the dienyl ligand. Both *endo*- and *exo*-isomers may possibly be formed in this rearrangement, for which a concerted mechanism with a cyclic transition state is proposed. Other similar complexes of cyclo-octatetraene, cyclo-octa-1,5-diene, and dicyclopentadiene have also been prepared but have not been subjected to detailed study.

It is now well established that the addition of nucleophilic reagents (Y^-) to complexes of the type $[(\text{diene})PtX_2]$ (1) leads to derivatives (2) in which the Y^- group has added uniquely to give the *exo*-isomer with respect to metal.[2] Here we report the preparation of the complex $[(nbd)Pt(\sigma\text{-}C_5H_5)_2]$, (3) (nbd = norbornadiene) which undergoes a ready rearrangement to give two new products each of the same basic formulation, *i.e.* $C_{17}H_{18}Pt$, and which may be the *exo*- and *endo*-isomers (4) and (5) of the complex $[(C_7H_8{\cdot}C_5H_5)Pt(\pi\text{-}C_5H_5)]$. As such this work provides some evidence that where prior attack on the metal has been established *endo*-addition to the co-ordinated olefin may occur.



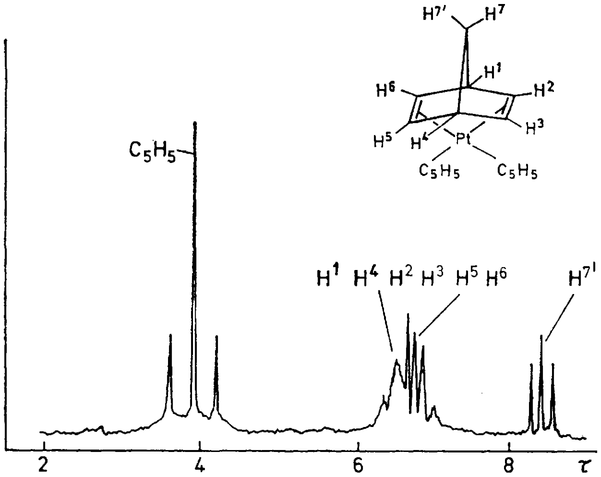
(1) (2)

RESULTS AND DISCUSSION

Addition of cyclopentadienylthallium to a stirred solution of $[(nbd)PtCl_2]$ in ether gives quantitative yields of a yellow solid of composition $C_{17}H_{18}Pt$ (3). Related complexes of cyclo-octatetraene, cyclo-octa-1,5-diene, and dicyclopentadiene may be prepared similarly but are not considered further here. Compound (3) was readily identified as $[(nbd)Pt(\sigma\text{-}C_5H_5)_2]$.

The mass spectrum was particularly simple, showing a parent ion at *m/e* 417 and other peaks at *m/e* 417, 352, 325, 287, and 260 mass numbers corresponding to the ions: $C_7H_8Pt(C_5H_5)_2^+$, $C_7H_8Pt(C_5H_5)^+$, $Pt(C_5H_5)_2^+$, $C_7H_8Pt^+$, and $Pt(C_5H_5)^+$ respectively.

The ^1H n.m.r. spectrum (see Figure) at room temperture is also simple showing a triplet at τ 6·63 ($J_{Pt\text{-}H}$ = 50·2 Hz) which may be assigned to the olefinic protons (H^2, H^3, H^5 and H^6), a multiplet centred at τ 6·48 assignable to the bridgehead protons at H^1 and H^4, a triplet at τ 8·39 due to the methylene bridge protons $H^{7,7'}$ and finally a triplet ($J_{Pt\text{-}H}$ = 40·6 Mz) of relative intensity 10 due to the cyclopentadienyl protons of the $\sigma\text{-}C_5H_5$ groups.



N.m.r. spectrum of $[(C_7H_8)Pt(C_5H_5)_2]$ in $CDCl_3$ at 25 °C

A σ-bonded cyclopentadienyl ring is expected to give an A_2B_2X type of n.m.r. spectrum and the appearance of a single signal indicates that each ring is probably undergoing a rapid tautomeric shift of the type observed with $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_5H_5)]$ (ref. 3) and a number of other $\sigma\text{-}C_5H_5$ complexes.[4] On cooling the sample to near −70 °C

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[1] Part XXIII, B. F. G. Johnson, J. Lewis, D. J. Thompson, and B. Heil, *J.C.S. Dalton*, 1975, 567.

[2] See *e.g.* P. M. Henry, *Accounts Chem. Res.*, 1973, **6**, 16.

[3] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.

[4] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, 1967, **89**, 2855; E. Maslowsky and K. Nakamoto, *Chem. Comm.*, 1968, 257; H. P. Fritz and C. G. Kreiter, *J. Organometallic Chem.*, 1965, **4**, 313; A. Davidson and P. E. Raketa, *J. Amer. Chem. Soc.*, 1968, **90**, 4479; F. A. Cotton and P. Legdzus, *ibid.*, p. 6232; B. Fuchs, M. Ishaq, and M. Rosenblum, *ibid.*, p. 5293.

the cyclopentadienyl absorption broadened considerably but even at the lowest attainable temperature of *ca.* −115 °C (Freon 21) no clear indication of an A_2B_2X spectrum was obtained. A methylcyclopentadienyl analogue (3a) was therefore prepared in an attempt to raise the coalescence temperature and although substantial broadening of the spectral lines was again observed, the limiting spectrum was not obtained. The activation energy associated with the line broadening was determined using the analysis of Piette and Anderson[5] for the fast-exchange limit case. If ΔH^* and ΔS^* are the activation parameters for the process, and T_2 is the transverse relaxation time in the fast-exchange limit, then the expression

$$\ln T(\pi\Delta v T_2 - 1) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} + \ln\frac{k}{hW_2T_2}$$

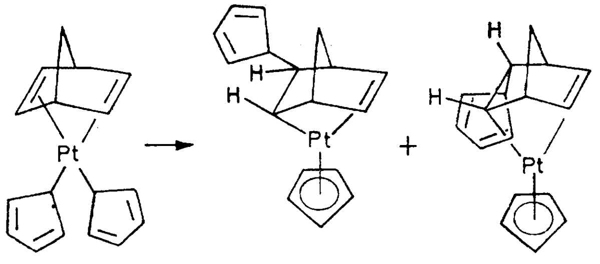
is readily obtained in which T is the absolute temperature, W_2 the second moment of the contributing resonances, and Δv the observed line width. If Δv_0 is the limiting line width, the substitution of $T_2 = 1/\pi\Delta v_0$ gives the more convenient expression:

$$\ln T\left(\frac{\Delta v}{\Delta v_0} - 1\right) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} + \ln\frac{k\pi\Delta v_0}{hW_2}$$

The plots of $\ln T\left(\frac{\Delta v}{\Delta v_0} - 1\right)$ with respect to $1/T$, using the methyl resonance in the methylcyclopentadienyl case were satisfactorily linear. ΔH^* Obtained from the slopes was found to be 2·2 ± 0·2 kcal mol^{-1} for the cyclopentadienyl case, and 3·1 ± 0·6 kcal mol^{-1} in the methylcyclopentadienyl complex. By taking representative values for the contributing chemical shifts, the respective values of W_2 were estimated to be $2{\cdot}02 \times 10^4$ and $3{\cdot}35 \times 10^2$ rad^2 s^{-2}. The corresponding intercepts, as estimates for the respective values of ΔS^* for the process gave −31 ± 12 and −34 ± 17 cal K^{-1} mol^{-1}. If these figures pertain to a true ring re-orientation process, then it is not difficult to understand why the process could not be stopped in the temperature range available to us. Such a large negative ΔS^* could be taken to imply a rather ordered transition state for the interconversion.

With time (4—5 h) the solution of (3) darkened, and the n.m.r. spectra changed considerably and is more complex than the initial cyclopentadienyl complex. Thus the resonance attributed to the σ-bonded cp in the initial complex is replaced by a new signal at τ 4·35. In addition new multiplets are observed at τ 5·50 and 5·75 and τ 5·90 and 6·20; a sharp triplet appears at τ 7·02 superimposed upon a multiplet, with additional multiplets at τ 7·8, 8·3, and 8·85. An unstable yellow solid may be separated from this solution and on the basis of analytical data and its mass spectrum has been identified as $C_{17}H_{18}Pt$. This mass spectrum showed an ion, assumed to be the parent, at *m/e* 417. However in this case the fragmentation was appreciably different to that of (3) exhibiting major peaks at *m/e* 352, 287, and 260 corresponding to the ions $C_7H_8Pt(C_5H_5)^+$, $C_7H_8Pt^+$, and $Pt(C_5H_5)^+$ and an unidentified peak at 253. No peak was found at 325 corresponding to the ion $Pt(C_5H_5)_2^+$.

Obviously this yellow material is some isomeric form (or mixture of isomeric forms) of complex (3). It seemed to us that a reasonable suggestion for structure of this compound is that shown in the Scheme and the n.m.r. spectrum of the material may be interpreted on this basis.



(3) (4) (5)

SCHEME Cyclopentadienyl-complex rearrangement reaction

In the n.m.r. spectrum, under high resolution, the π-cyclopentadienyl resonances were not singlets, but rather a pair of closely spaced lines each with associated ^{195}Pt sidebands. In addition, the tertiary proton H_X appeared as a pair of triplets ($J_{XA} = J_{XA'} = 8$ Hz) with a separation somewhat dependent on the solvent. In carbon tetrachloride, double irradiation of the complete low-field region, τ 4·2 and 4·9 (assigned to the cyclopentadienyl protons), produced nearly complete collapse of both triplets. The rearranged product thus appears to consist principally of two very similar species with slightly different cyclopentadienyl rings.

The possibility that the product was the result of a Diels–Alder condensation (leading to dimerisation of two cyclopentadienyl rings) was also considered. However, when the reaction was allowed to proceed in acetone, in the presence of tetrachloroethylene as a dienophile,* no significant difference was seen in the product n.m.r. spectrum after 24 h. It was therefore concluded that dimerisation could not be responsible for the appearance of the two π-cyclopentadienyl resonances.

We therefore propose that the product consists of a mixture of *endo-* and *exo*-substituted isomers, resulting from the different possible modes of addition of the cyclopentadienyl ring to the diene. Should this be the case then two mechanisms may be envisaged. The first involves ionic dissociation followed by direct addition to

$$[(C_7H_8)Pt(\sigma\text{-}C_5H_5)_2] \longrightarrow [(C_7H_8)Pt(\pi\text{-}C_5H_5)]^+ + C_5H_5^-$$

bonded olefin leading to the *exo*-product. The complex cation $[(C_7H_8)Pt(\pi\text{-}C_5H_5)]^+$ is known and treatment of this ion with $Tl(C_5H_5)$ leads to *exo*-$[(C_7H_8)(C_5H_5)Pt(\pi\text{-}C_5H_5)]$ as the sole product. In the second, alternative, mechanism the migration of one C_5H_5 group from the metal to the bonded olefin in a concerted way without the prior dissoci-

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* This dienophile was chosen because other more reactive proton-free dienophiles tended to react directly with the starting material, *e.g.* tetracyanoethylene.

[5] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, 1959, **30**, 899.

ation of the C_5H_5 ring is envisaged. In this case the formation of the *endo*-isomer may be understood. We cannot provide supporting evidence for this mechanism. Although *endo*-substituted complexes of this general type have not been previously reported, it may be that the unusual configuration of the cyclopentadienyl ring in the parent compound or transition state may make this possible.

EXPERIMENTAL

Preparation of $[(C_7H_8)Pt(\sigma\text{-}C_5H_5)_2]$.—Dichloro(norbornadiene)platinum (0·5 g) was suspended in ether (250 ml) under nitrogen, and the mixture cooled to 0 °C. Cyclopentadienylthallium (0·8 g) was added and the mixture stirred for 25 min. The resulting suspension was filtered, and removal of the solvent gave orange crystals which were dried *in vacuo* (Found: C, 48·7; H, 4·6. $C_{17}H_{18}Pt$ requires C, 48·9; H, 4·3%). The rearranged product could be obtained from a 10% solution of the initial form which had been left at room temperature for several days. The yellow product was washed with more solvent after being filtered off, and dried *in vacuo*. The n.m.r. spectrum was similar to a sample left to rearrange in the usual way (Found: C, 48·7; H, 4·4%).

The other dieneplatinum cyclopentadienides were prepared by essentially the same route.

N.m.r. Spectra.—These were recorded on a Varian HA 100 spectrometer at 100 MHz. For intensity recording purposes, the field homogeneity was optimised on the internal reference, and a sweep rate of 0·2 Hz s^{-1} was used. Field modulation was kept well below the saturation level to avoid distortion of peaks. For low-temperature work, sealed sample tubes were used, made up on a vacuum line with the Freon solvent distilled directly into the tube from a reservoir. Temperatures were measured using a precalibrated thermocouple inserted into a dummy sample, and are believed to be accurate to ±0·5 °C.

Mass Spectra.—These were recorded on an A.E.I. MS 12 spectrometer, using solid samples with a probe temperature of 40—70 °C.

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