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THE FLUXIONAL BEHAVIOUR OF $Pt_2(\eta^1,\eta^2\text{-}C_3H_5)_2(acac)_2$

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Summary

The ^1H NMR spectrum of $Pt_2(\eta^1,\eta^2\text{-}C_3H_5)_2(acac)_2$ has been examined and shown to be consistent with its solid state structure. Magnetization transfer measurements have shown pairwise exchange of the allylic protons, consistent with the platinum atoms reversing their bonding to each allyl group with $\Delta G^\ddagger$ 15.8 kcal mol^{-1}. An equilibrium is slowly established with $\Delta G^\ddagger$ 23.0 kcal mol^{-1} and ΔG° 0.43 kcal mol^{-1} between the dimer and $Pt(\eta^3\text{-}C_3H_5)(acac)$, which was not detected in the original work.

Recently, it has been shown that $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\eta^1,\eta^2\text{-}C_3H_5)]^+$ (I) is fluxional with the two iron atoms exchanging role between η^1- and η^2-bonding [1] (see Scheme 1). This interchange provides a route for intermolecular allyl exchange between two metals, but in the iron case, no evidence was found for dissociation to monomers. Usually, platinum forms η^3-allyls, but the parent unsubstituted allyl presents an exception to this rule. An X-ray structure determination of $Pt_2(\eta^1,\eta^2\text{-}C_3H_5)_2(acac)_2$ has shown the solid state structure to be II [2]. At the time that this compound was characterised, its low solubility prevented any solution state studies by NMR spectroscopy. With the greater sensitivity of modern NMR spectrometers, it is now possible to carry out an NMR investigation of its solution properties, and investigate dynamic processes occurring in the molecule.

A freshly prepared solution of II in CD_2Cl_2 shows the ^1H NMR signals expected for this structure with H^1 at δ 3.20, H^2 at δ 3.64, H^3 at δ 4.64, H^4 at δ 2.47, and H^5 at δ 1.75 ppm. The acetylacetonate signals are at δ 5.45 (CH), δ 2.04 and δ 1.91 ppm (CH_3) (see Fig. 1a). At room temperature, the signals are broadened by chemical exchange, but at 10°C, the HH coupling is clearly resolved and was shown by decoupling to be J_{13} 15, J_{23} 7.5, J_{34} 5, J_{35} 12, and J_{45} 9 Hz. At 400 MHz, the ^{195}Pt satellites are broad due to ^{195}Pt relaxation resulting from chemical shift anisotropy, but sharpen somewhat at 250 MHz, to give $J(^{195}Pt, {}^1H^1)$ 84, $J(^{195}Pt, {}^1H^2)$ 63, and $J(^{195}Pt, {}^1H^4)$ 92, 135 Hz. Magnetization transfer measurements were

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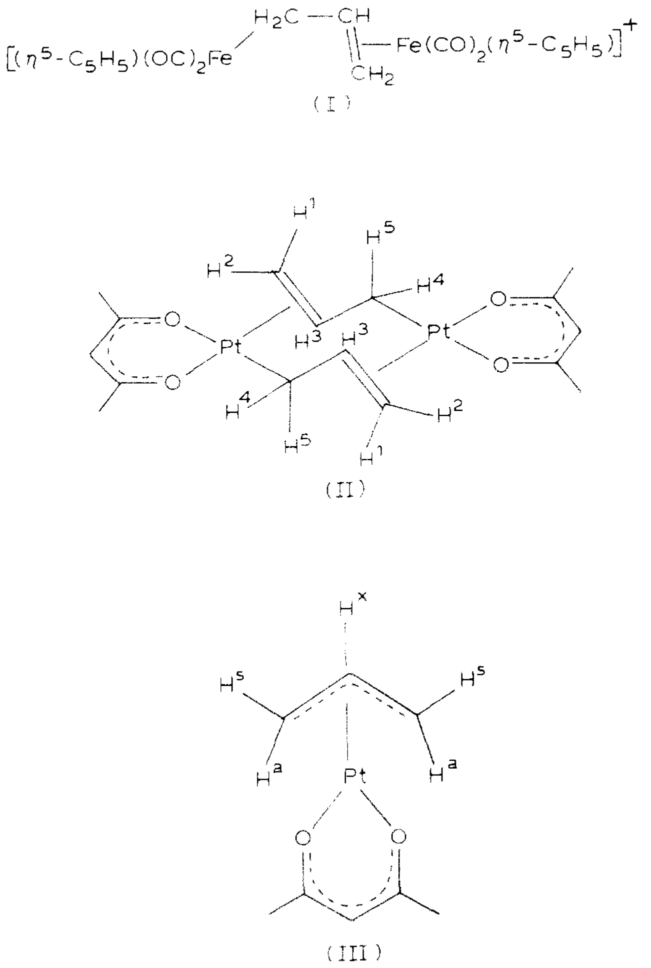

SCHEME 1

performed to show that H^1 and H^5 and H^2 and H^4 exchange pairwise at 21°C with a rate constant of 12 s^{-1}, corresponding to $\Delta G^{\ddagger}$ 15.8 kcal mol^{-1} (see Fig. 1b).

On standing, a second set of signals appear, which are consistent with III (see Fig. 2). The assignments are $\delta(H^a)$ 2.18, $\delta(H^s)$ 3.72, $\delta(H^x)$ 4.53, $\delta\{CH(acac)\}$ 5.55, and $\delta\{CH_3(acac)\}$ 1.95 ppm. These values are in good agreement with those already reported for Pt(2-methylallyl)(acac) [3], and remeasured in CD_2Cl_2. The attainment of the equilibrium between II and III was monitored by ^1H NMR spectroscopy to yield a rate of 5×10^{-5} s^{-1} at 21°C, which corresponds to $\Delta G^{\ddagger}$ 23.0 kcal mol^{-1}. At equilibrium, the ratio of II/III is 2.1/1 which gives $\Delta G°$ 0.43 kcal mol^{-1}.

These observations are in direct contrast with those reported for $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\eta^1,\eta^2\text{-}C_3H_5)]^+$ where exchange of all four methylene protons was observed, rather than pairwise exchange as observed for II. This difference arises from the double bridge, preventing rotation about the Pt–CH_2 bond, and the retention of one bridge during any fluxional process will retain a chiral centre in the

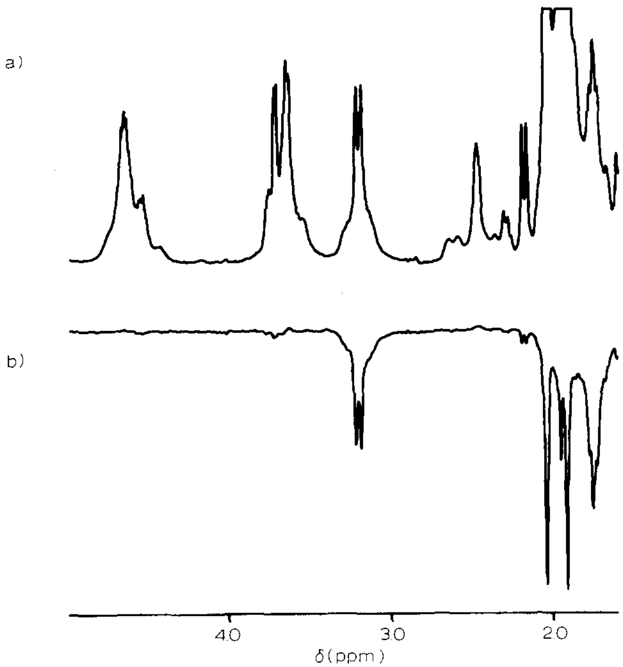

Fig. 1. (a) The ^{1}H NMR spectrum of a freshly prepared solution of $Pt_2(\eta^1,\eta^2\text{-}C_3H_5)_2(acac)_2$ in CD_2Cl_2 at 21°C, (b) the magnetization transfer between H^5 and H^1 after 0.1 s.

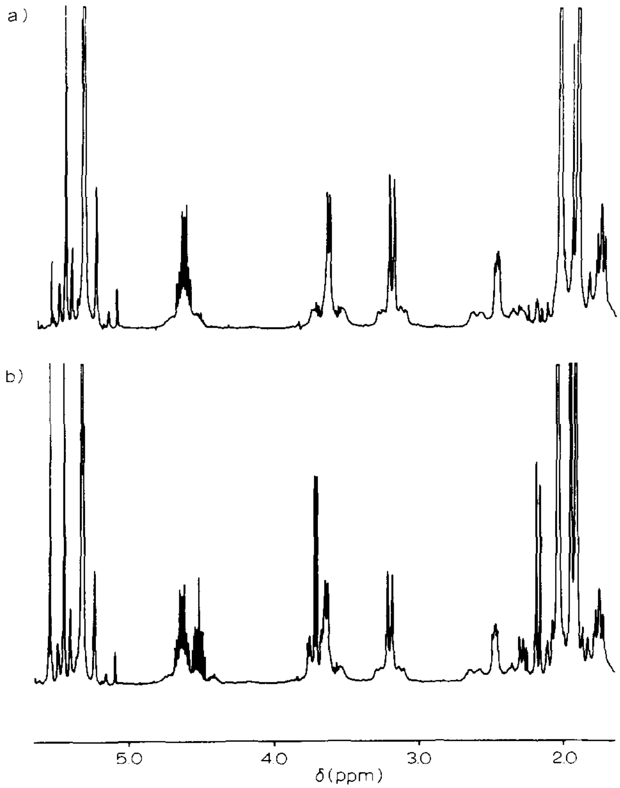

Fig. 2. The ^{1}H NMR spectrum of $Pt_2(\eta^1,\eta^2\text{-}C_3H_5)_2(acac)_2$ and $Pt(\eta^3\text{-}C_3H_5)(acac)$ in CD_2Cl_2 at 21°C; (a) freshly prepared solution, (b) equilibrium mixture.

bridging η^1,η^2-allyl ligand. This chiral centre could direct a terminal allyl to reform the bridge in the mode that it broke. It is therefore unlikely that the fluxional mechanism goes via a π-allyl intermediate. Consistent with this interpretation is that dissociation to III, is far slower than intramolecular exchange. Examination of the X-ray structure shows that this exchange only requires a movement of the allyl units by considerably less than 1 Å. Despite both allyl units having to move, the activation energy is similar to that reported for I. This implies that for a single allyl exchange on platinum, the activation energy would be considerably lower. Attempts to detect a similar dimer in a solution containing Pt(η^3-2-MeC$_3$H$_4$)(acac) have failed.

Although the activation energy for exchange in this platinum complex is high, many metals give far more kinetically labile compounds. The equilibrium between II and III can then provide a mechanism for intermolecular exchange for allyl groups, with a structure equivalent to II acting as the intermediate or transition state.

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