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Preliminary communication

APPLICATION OF DOUBLE QUANTUM FILTERED PHASE SENSITIVE TWO-DIMENSIONAL NMR SPECTROSCOPY: CHEMISTRY OF PENTAMETHYLCYCLOPENTADIENYL- AND INDENYL-PLATINUM COMPLEXES

DERMOT O'HARE

Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR (Great Britain)

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Summary

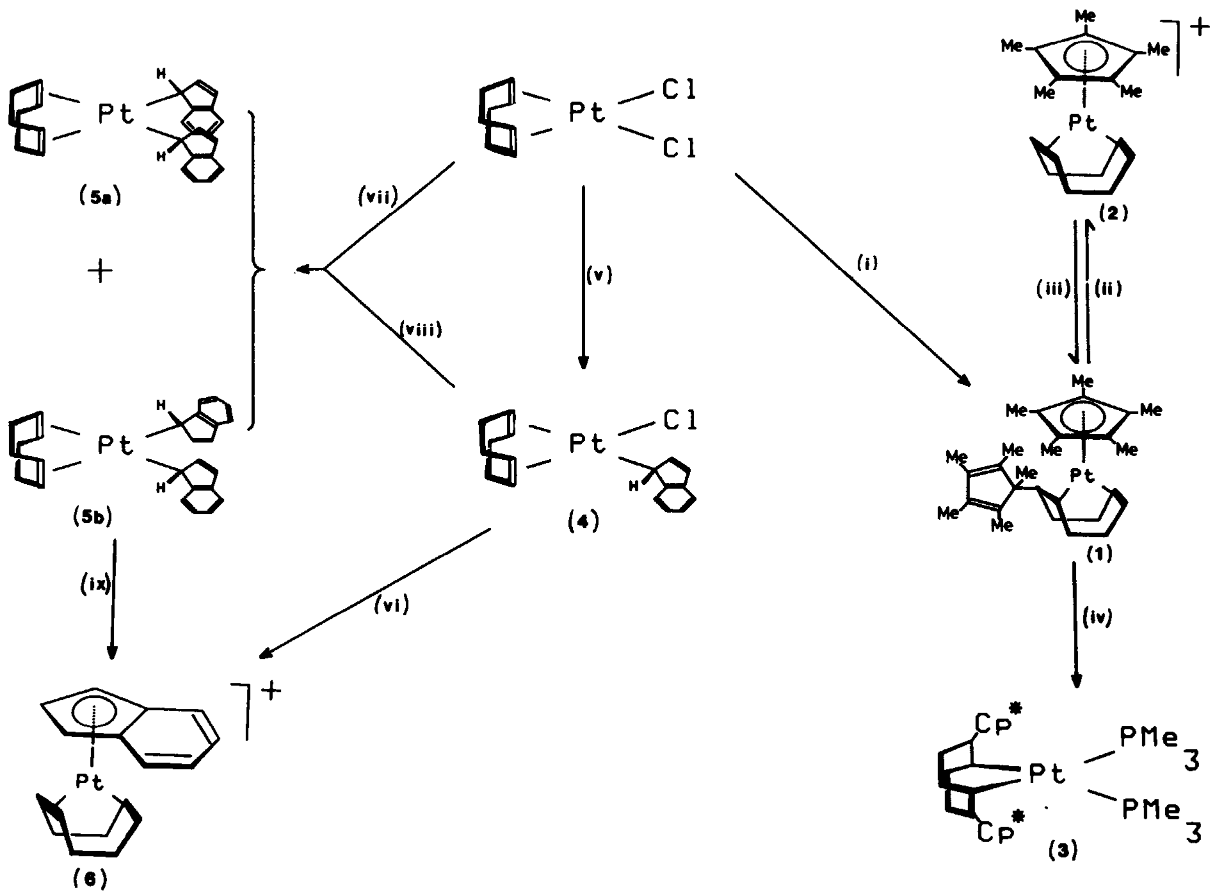
Two-dimensional double quantum filtered phase sensitive (DQPH)COSY NMR spectroscopy has been used to aid characterization of new η-pentamethylcyclopentadienyl- and η-indenyl-platinum complexes. The syntheses of the first mononuclear η-pentamethylcyclopentadienylplatinum complexes are reported.

Two-dimensional correlated spectroscopy (COSY) [1] is a much used NMR technique for the elucidation of spin–spin coupling networks in complex systems such as proteins [2]. While the early investigations used absolute value presentations of the data, more recent work has shown that phase sensitive COSY spectroscopy can provide important additional information, particularly with additional double quantum filtration [3] to overcome problems in lineshape [4].

The (DQPH)-COSY experiment allows identification of the active coupling between two connected multiplets, information which is not available from a normal COSY experiment, together with quantitative measurements of the spin–spin coupling constants in the limit at which linewidths are much less than the scalar couplings [5].

The chemistry of the η-cyclopentadienyl derivatives of platinum, in contrast with that of other transition metals, is relatively unexplored. Indeed, only one η-C_5Me_5 complex of platinum has been reported previously, namely the dinuclear complex $[(\eta\text{-}C_5Me_5)Pt(\mu\text{-}Br)_3Pt(\eta\text{-}C_5Me_5)]Br_3$ [6]. We describe here the use of the two-dimensional (DQPH)-COSY NMR procedure to characterize new η-pentamethylcyclopentadienyl- and η-indenyl-platinum complexes.

Treatment of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ with two equivalents of either LiCp* or NaCp* (Cp* = C_5Me_5) in tetrahydrofuran gives good yields of yellow air sensitive crystals of $[Pt(\eta\text{-}C_5Me_5)\{\sigma:\eta^2\text{-}C_8H_{12}(Cp^\star)\}]$ (**1**). When $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ was treated with one equivalent of LiCp* we were only able to isolate **1** and unchanged [Pt(η-



SCHEME 1. Reagents and conditions: (i) NaCp* or LiCp* (2 equiv.) in thf at r.t.; (60%). (ii) HBF_4 in Et_2O (2–3 drops) in pentane at −78 °C.; (70%). (iii) LiCp* in thf r.t.; (80%). (iv) PMe_3 (excess) in thf at r.t. for 12 h; (80%). (v) NaInd (1 equiv.) in thf at r.t. for 12 h; (70%). (vi) $AgBF_4$ (1 equiv.) in thf at r.t.; (90%). (vii) NaInd (excess) in thf at r.t. for 12 h; (70%). (viii) $LiCH_2PMe_2$ in Et_2O at r.t.; (40%). (ix) HBF_4 in Et_2O (2–3 drops), −78 °C (90%).

$C_8H_{12})Cl_2$]. It is probable that the [Pt(η^1-C_5Me_5)(η-C_8H_{12})Cl] is an intermediate in this reaction but is unstable, and rapidly isomerises to [Pt(η^5-C_5Me_5)(η^4-C_8H_{12})][Cl], which further reacts with LiCp* to yield **1**. In fact, [Pt(η^1-C_5H_5)(η^4-C_8H_{12})Cl] is isolable, and rapidly isomerises in CH_3CN solution to [Pt(η^5-C_5H_5)(η^4-C_8H_{12})]-[Cl]. Treatment of **1** with HBF_4 in diethyl ether resulted in elimination of Cp*H to give [Pt(η-C_5Me_5)(η-C_8H_{12})][BF_4] (**2**). Reaction of **2** with LiCp* gave **1** in high yield.

Compound **1** was found to react with trimethylphosphine to give [Pt(PMe_3)$_2$-{σ : σ-C_8H_{12}(Cp*)$_2$}] (**3**). It is noteworthy that the migration of the η-Cp* ligand to the {σ : η^2-C_8H_{12}(Cp*)} ligand took place regiospecifically to give the isomer possessing a C_2 symmetry axis bisecting the P–Pt–P angle as demonstrated by observation of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum and a binomial triplet in the $^{195}Pt\{^1H\}$ NMR spectrum with a characteristic $^1J(^{195}Pt-^{31}P)$ coupling constant of 1550 Hz [7].

In contrast, the mono-η^1-indenyl derivative [Pt(η-C_8H_{12})(η-C_9H_7)Cl] (**4**) can be isolated following reaction of [Pt(η-C_8H_{12})Cl_2] with one equivalent of NaInd (Ind = C_9H_7), further treatment with NaInd gives the thermally unstable di-η^1-indenyl complex [Pt(η-C_8H_{12})(η^1-C_9H_7)$_2$] (**5**). The NMR data for **5** can be interpreted in terms of 1/1 mixture of geometric isomers, as shown in Scheme 1. Abstraction of Cl^- from **4** by $AgBF_4$ results in rearrangement to the η^5-indenyl complex [Pt(η-C_9H_7)(η-C_8H_{12})]BF_4 (**6**). **6** can also be obtained by protonation of **5** with HBF_4.

Compounds **1**–**6** exhibit complex ^1H and ^{13}C NMR spectra. For example, for **1** 18 unique ^1H and 20 unique ^{13}C signals can be seen. However, it is possible to assign the NMR spectra in terms of the structure shown in Scheme 1 by use of the (DQPH)-COSY procedure described previously, together with two-dimensional heteronuclear ($^{13}C-^1H$) correlation experiments [8]. For **1** the analysis of the connectivity started at C_c which exhibited a characteristic $^1J(^{195}Pt-^{13}C)$ coupling constant of 798 Hz. Although the spectroscopic data do not allow us to assign **1** unambiguously as the *endo* or *exo* isomer, the *exo* isomer is to be preferred on steric grounds.

An expansion of the (DQPH)-COSY spectrum of **3** is shown in Fig. 1. The improved resolution and lineshape provided by this procedure compared to those obtained by the normal COSY method at the same digital resolution, enabled cross peaks close to the diagonal to be clearly identified. The reversal in phase exhibited in the off-diagonal elements permit identification of the coupling constants linking any of the connected multiplets. In cases in which the couplings are quite large, quantitative measurements of the active coupling constants can be made. It also proved possible in this example to distinguish the homonuclear $^1H-^1H$ coupling from the heteronuclear $^{31}P-^1H$ coupling, as shown in Fig. 1.

Selected spectroscopic data

Compound **1**: mass spectrum, $m/e = 574$ [P^+]; partial ^1H NMR data (500 MHz in benzene-d_6 at r.t.): 3.28 ppm (2H, m (7 lines), $J(Pt-H^{a/b})$ 88 Hz, $H^a + H^b$), 2.18 ppm (1H, dd, $J(Pt-H^a)$ 124, $J(H^c-H^{k/l})$ 5 Hz, H^c), 1.83 ppm (15H, d, J(Pt–H) 13 Hz, η^5-C_5Me_5): partial ^{13}C NMR data (125.75 MHz in benzene-d_6 at r.t.): 61.2 ppm (dd, $J(Pt-C^{a/b})$ 291 Hz, J(C–H) 151 Hz, C^a or C^b), 49.9 ppm (dd, $J(Pt-C^{b/a})$ 319 Hz, J(C–H) 151 Hz, C^b or C^a), 25.8 ppm (dt, $J(Pt-C^c)$ 798 Hz, J(C–H) 125 Hz, C^c), 9.4 ppm (q, Me(η^5-C_5Me_5): $^{195}Pt\{^1H\}$ NMR data −5515(s) ppm.

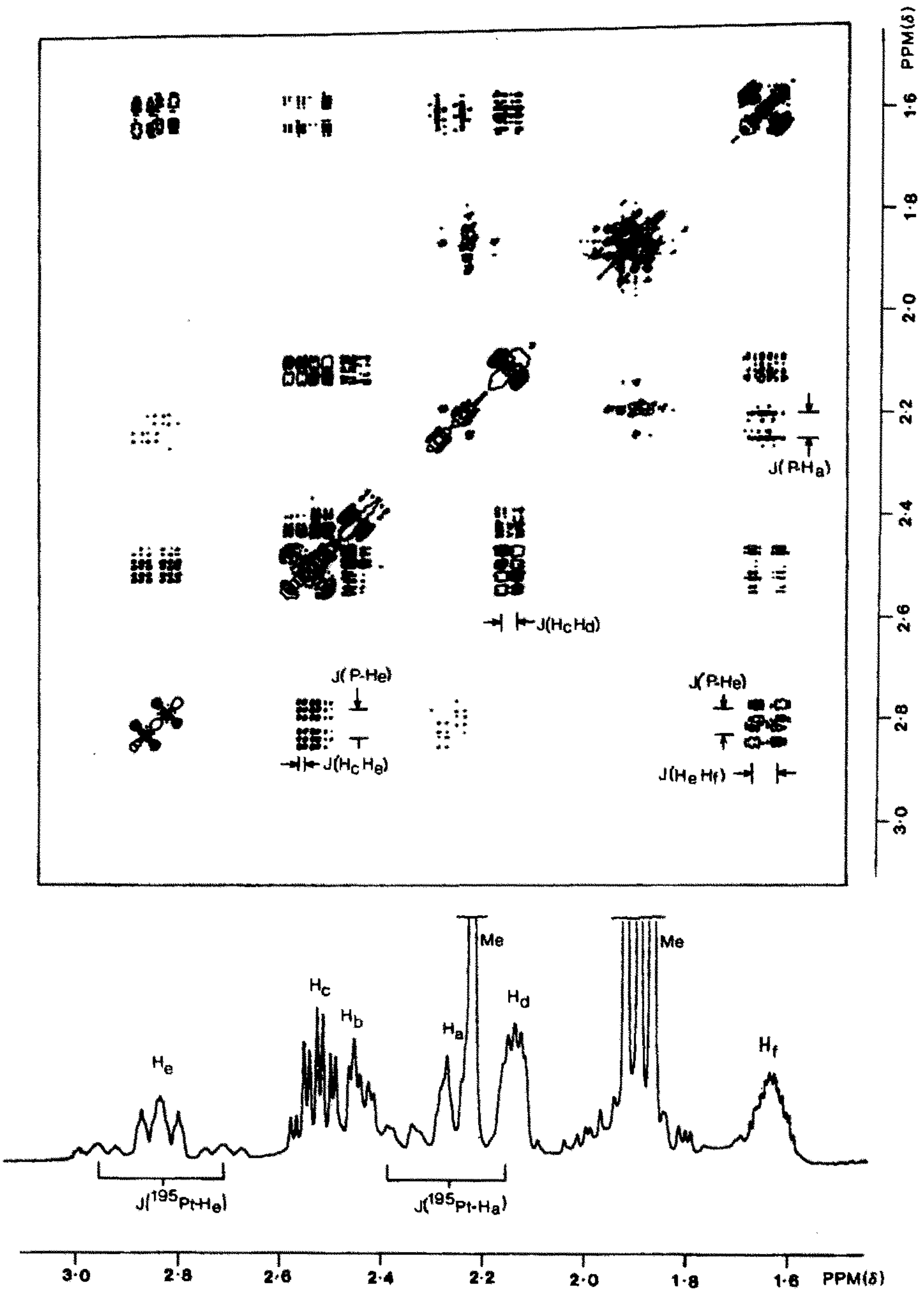


Fig. 1. Expanded region of the 500 MHz two-dimensional (^1H–^1H) DQPH-COSY NMR spectrum of 3 (counter plot), run on a Bruker AM 500. (Negative peaks are given as filled in contours).

Compound 2: partial ^1H NMR data (500 MHz in tetrahydrofuran-d_8 at r.t.): 4.81 ppm (4H, s br, J(Pt–H) 78 Hz, CH(η-C_8H_{12})), 2.58 ppm (8H, br, CH_2(η-C_8H_{12})), 2.18 ppm (15H, d, J(Pt–H) 15 Hz, (η-C_5Me_5)).

Compound **3**: $^{31}P\{^1H\}$ NMR data, -34.2 ppm (2P, s, J(Pt–P) 1550 Hz, PMe_3); $^{195}Pt\{^1H\}$ NMR data, -4684(s) ppm.

In conclusion, it is clear that the two-dimensional (DQPH)-COSY method should prove valuable in the future for characterization of organometallic transition metal compounds with complex hydrocarbon ligand systems. The procedure is straightforward, and the additional processing and display software required is available on most modern high field spectrometers.

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