Inorganica Chimica Acta, *155* (1989) 217–220

Applications of ^{31}P 2-D Exchange NMR Spectroscopy to Platinum Chemistry

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(Received June 10, 1988)

Abstract

^{31}P 2-D exchange NMR spectroscopy is shown to be useful for detecting multiple exchange processes and determining reaction mechanisms in platinum complexes. For complexes where isotopomers are possible, e.g., $^{195}Pt-^{31}P$, $^{194}Pt-^{31}P$ or $^{117,119}Sn-^{31}P$, $^{118}Sn-Pt-^{31}P$, the 2-D exchange spectrum can differentiate between inter- and intramolecular processes. A five-coordinate $Pt-SnCl_2$ species is suggested to account for the exchange between the non-equivalent ^{31}P spins in $Pt(SnCl_3)(COEt)\{Ph_2P(CH_2)_4PPh_2)\}$.

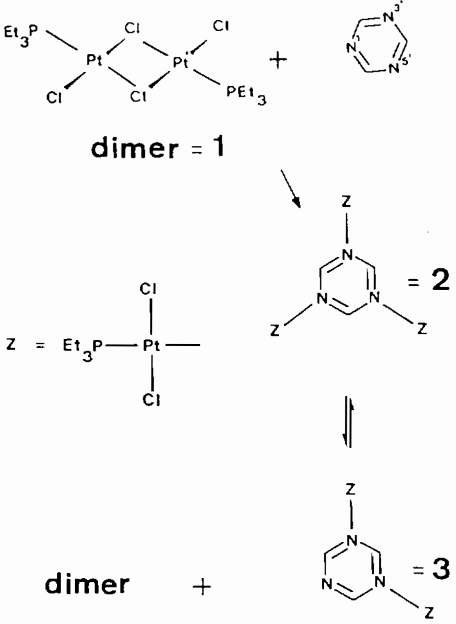
Introduction

Exchange reactions occur frequently in the chemistry of complexes associated with organometallic reactions [1]. Apart from classical methods, NMR spectroscopy offers unique possibilities for monitoring these dynamics, with magnetization transfer processes [2, 3] figuring prominently in this area. To date there are relatively few examples of exchange (NOESY) spectroscopy involving heavier spins [4], which is surprising considering the number of phosphine complexes involved in homogeneously catalysed reactions where dynamics could be monitored by ^{31}P NMR. In contrast to ^{1}H NMR spectroscopy, there is little or no $^{31}P-^{31}P$ NOE [5, 6] and as the ^{31}P spins will not always be spin–spin coupled, complications due to zero-quantum transitions [7], need not interfere. While it is not simple to obtain quantitative rate data from such measurements, the recognition of the exchange can provide useful mechanistic insight and, in some cases, exclude and/or define reaction pathways [8, 9]. We present here three examples from our platinum chemistry of ^{31}P exchange spectroscopy ranging from superficial to subtle and suggest this form of ^{31}P NMR to be very promising.

Results and Discussion

1,3,5-Pyrazine Chemistry

As shown in Scheme 1, 1,3,5-pyrazine reacts with 1.5 equiv. of the dinuclear platinum complex **1**, to afford **2**, whose structure has been determined by diffraction methods [10]. In $CDCl_3$ solution complex **2** reacts to afford one equivalent of '$PtCl_2(PEt_3)$' – which dimerizes to **1** – yielding a mixture of **1**, **2** and dinuclear compound **3**. The similarity of the PEt_3 ^{1}H shifts in **1**–**3** prevents the use of ^{1}H magnetization transfer methods. The pyrazine proton resonances can be employed to study equilibria involving **2** and **3**; however, this excludes a direct observation of the participation of **1**. The 2-D ^{31}P exchange spectrum (Fig. 1) clearly shows cross peaks due to exchange so that all three complexes are participating in the dynamics.



Scheme 1.

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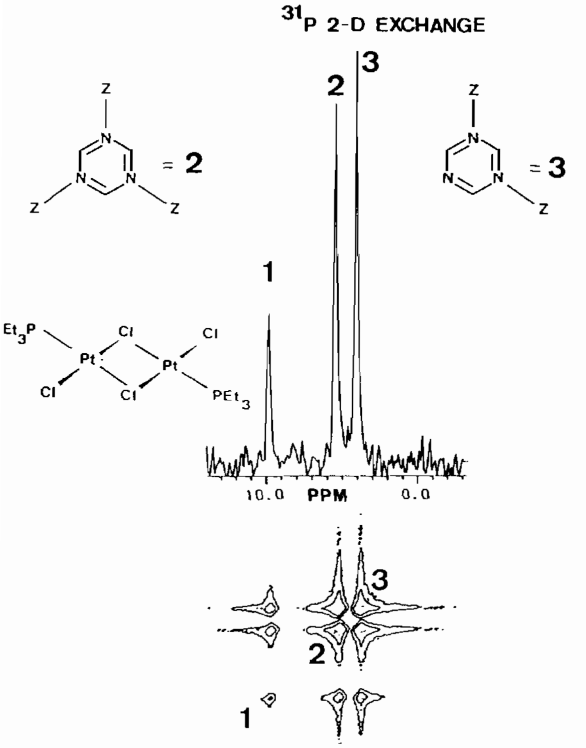
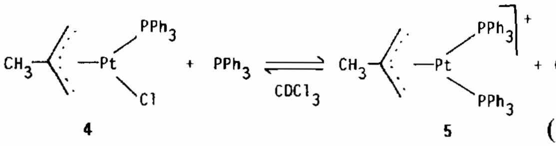


Fig. 1. ^{31}P 2-D exchange spectrum of a mixture of **1**, **2** and **3**. Cross peaks indicating exchange within the main bands are seen for all three complexes. (^{195}Pt satellites not shown.)

The π-Allyl Chemistry

The π-allyl complex **4** reacts with PPh_3 to yield **5**. If the chemistry is carried out using *ca.* 0.5 equiv.



(1)

of PPh_3 the result is a mixture of roughly equal amounts of both complexes. This problem represents a simple two site exchange situation (**4** and **5**), with an interesting additional component: since only *ca.* 1/3 of the platinum has $I = 1/2$, there are isotopomers for both complexes, *i.e.* some complexes of the type ^{195}Pt–P and some with ^{194}Pt–P composition. Consequently, when intermolecular exchange of PPh_3 occurs, this can be recognized via cross peaks between complexes as well as cross peaks between isotopomers. This latter point is useful for detecting intermolecular exchange which transfers PPh_3, but does not lead to new product.

Figure 2 shows the ^{31}P 2-D exchange spectrum for this chemistry. The most prominent feature involves the cross peaks arising from the equilibrium of eqn. (1); however, closer inspection shows cross peaks between the main-band and ^{195}Pt satellites for **5** (see Fig. 2). Consequently, it is obvious from the 2-D spectrum that intermolecular exchange takes place.

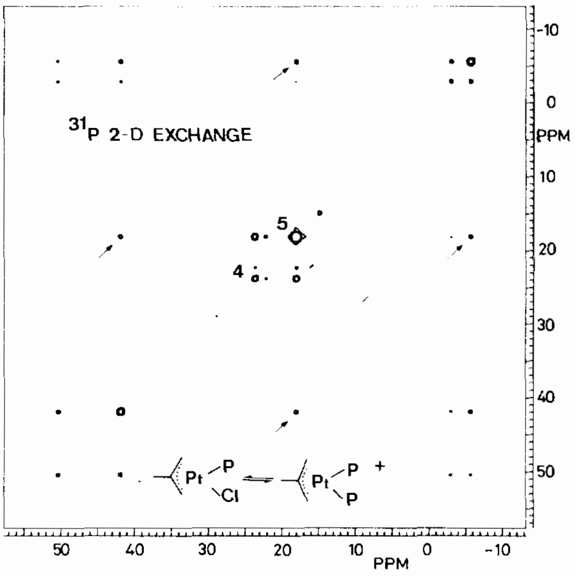
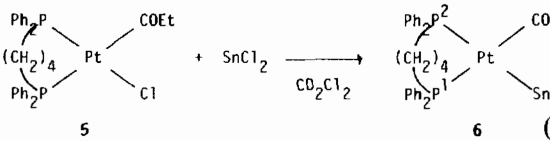


Fig. 2. ^{31}P 2-D exchange spectrum for the equilibrium involving **4** and **5**. Apart from the obvious cross peaks due to exchange between these species, there are cross peaks arising from exchange between isotopomers (arrows).

Trichlorostannate Chemistry

Examples **1** and **2** were chose as a prelude to the more complicated chemistry of eqn. (2). Here, we



(2)

generate the acyl trichlorostannate complex **6**, from the chloro-analog **5**, and, using the principles demonstrated above, consider the dynamics of **6** with the following questions in mind: (a) is there exchange between P^1 and P^2 and (b) how might this exchange occur? Is **5** involved?

The 2-D Exchange ^{31}P spectrum of **6** does indeed show exchange between P^1 and P^2. Moreover, there is no $^{195}\mathrm{Pt{-}P} \rightleftharpoons {}^{194}\mathrm{Pt{-}P}$ exchange, thereby eliminating phosphine dissociation. Since ^{117}Sn and ^{119}Sn are NMR active isotopes of Sn (see Fig. 3 for high resolution 1-D spectrum, Fig. 4 for 2-D) we can consider $^{31}\mathrm{P{-}Pt{-}}^{117,119}\mathrm{Sn} \rightleftharpoons {}^{31}\mathrm{P{-}Pt{-}}^{118}\mathrm{Sn}$[*] processes, in analogy with the ^{195}Pt example and, indeed,

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[*] ^{118}Sn is intended to represent all non NMR active isotopes of tin. We neglect ^{115}Sn, $I = 1/2$, since it is only present in *ca.* 0.35%.

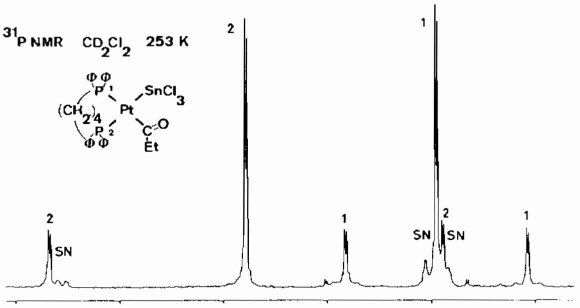


Fig. 3. Conventional ^{31}P spectrum for complex **6**. There are two very different values of $^2J(Sn, P)$.

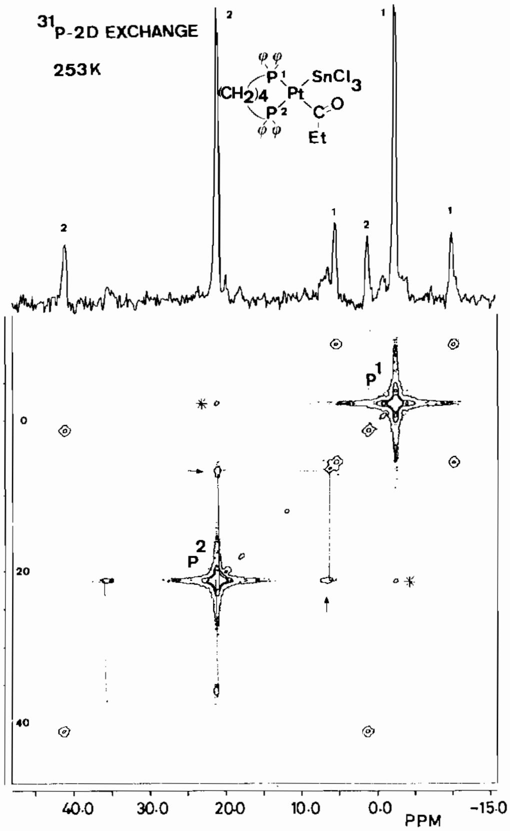
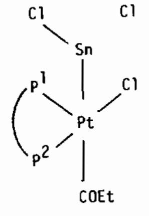


Fig. 4. ^{31}P 2-D exchange spectrum for **6**. Note the exchange arising from the different tin isotopomers (arrows), as well as the exchange between the two different phosphorus environments, P^1 and P^2 (stars).

this type of exchange can be observed (noted in the Figure). Consequently, the exchange of P^1 and P^2 occurs via Sn ligand (or fragment) transfer and intramolecular rearrangement via a five-coordinate species, e.g. **7**, can be excluded.

Further, we can discount reaction mechanisms involving only four-coordinate platinum such as **8**, since this does not exchange P^1 and P^2 although it does exchange tin isotopomers. However, intermolecular $SnCl_2$ combined with a five-coordinate transition state (or non-observed intermediate) – as shown in Scheme 2 – satisfies all the boundary conditions, assuming that the five-coordinate complex undergoes the usual 'Berry' or 'turnstile' rearrangement. This mechanism implies that **5** is involved in the exchange. We cannot exclude a three-coordinate species such as **9**, based on our data, although this seems unlikely to form at low temperature in a non-polar solvent such as CD_2Cl_2.



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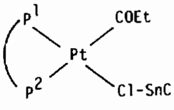

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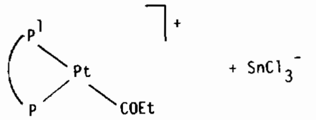

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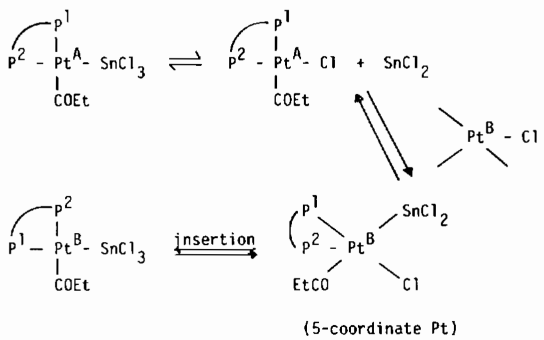

Scheme 2.

In view of the qualitative nature of these experiments, exact rate constants are not readily obtained*. However, it is clear that this methodology, when combined with more classical kinetic work, offers a valuable complement to those involved in determining reaction mechanisms.

Experimental

^{31}P 2-D Measurements were performed using Bruker WM-250 and AC-200 NMR spectrometers using a conventional [9, 12] pulse sequence. Mixing

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*Rate data can be obtained, see refs. 4b and 11.

times were 0.3, 0.3 and 0.4 s, respectively, for the three experiments.

The pyrazine [9] and π-allyl [13] complexes were prepared as described in the literature. The chloro complex **5** was prepared by one of us earlier [14]; the $SnCl_3$ analog was obtained by reacting **5** with one equiv. or $SnCl_2$ in CH_2Cl_2 solution under a CO atmosphere at −10 °C.

Acknowledgements

We thank the Swiss National Science Foundation for support, the Johnson-Matthey research centre for the loan of platinum salts, and Prof. L. M. Venanzi for complex **2**.

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