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^{31}P and ^{195}Pt NMR studies on fluxional η^1-ligated 1,2,4-triphosphacyclopentadienyl palladium(II) and platinum(II) complexes

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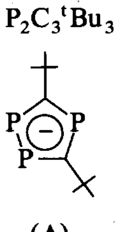
Abstract

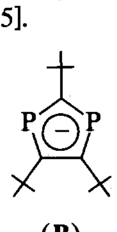
Detailed ^{31}P and ^{195}Pt NMR studies on complexes of the type *trans*-[MCl($P_3C_2{}^tBu_2$)(PR_3)$_2$], *trans*-[M($P_3C_2{}^tBu_2$)$_2$(PR_3)$_2$], (M = Pd, Pt), and *cis*-[Pt($P_3C_2{}^tBu_2$)$_2$(dppe)], including variable temperature measurements, have given information on (i) the structures of the complexes, (ii) the mechanism of the 'fluxional' process involving the $P_3C_2{}^tBu_2$ ring, and (iii) the signs of certain coupling constants.

1. Introduction

Since the development of synthetic routes to the cyclic anions $P_3C_2{}^tBu_2$ (A) and $P_2C_3{}^tBu_3$ (B) from the phosphaalkyne ^{t}Bu CP, [1,2], their utility as ligands in organotransition metal chemistry, paralleling the behaviour of the better known cyclopentadienyl anions C_5R_5, has been established. Both ring systems can form η^5-ligated complexes, *e.g.*, as in [M(η^5-$P_3C_2{}^tBu_2$)] (M = Fe, Cr) [3,4] and [M′(η^5-$P_3C_2{}^tBu_2$)(η^5-$P_2C_3{}^tBu_3$)] (M′ = Fe) [3], but the $P_2C_3{}^tBu_3$ ring can also ligate in an η^3-fashion, as in [Ni(η^5-$P_3C_2{}^tBu_2$)(η^3-$P_2C_3{}^tBu_3$)] [5].



(A)



(B)

Previously [6,7], we showed that the $P_3C_2{}^tBu_2$ ring can interact with transition metals in an η^1-bonded form and presented full X-ray crystallographic structural information on [PtX($P_3C_2{}^tBu_2$)(PR_3)] (R = Et, X = Cl; R = Ph, X = I) and [Pt($P_3C_2{}^tBu_2$)$_2$(PEt_3)$_2$], together with some limited NMR spectroscopic studies. Here we present a fuller account of both the ^{31}P and ^{195}Pt NMR spectra of these types of complexes, including variable temperature NMR studies that provide information regarding the mechanism of a 'fluxional' process involving the $P_3C_2{}^tBu_2$ ring.

2. Results and discussion

2.1. NMR studies on trans-[MCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$] (M = Pd, Pt)

The 32.4 MHz ^{31}P{^{1}H} NMR spectrum of *trans*-[PdCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$], (**1**), measured at temperatures below −70°C, is shown in Fig. 1(c) and exhibits a pattern of lines typical of the [AMNX$_2$] spin system expected for the static structure. The $P_{(A)}$ resonance occurs at a similar shift to that of the [AB$_2$] pattern known for Li($P_3C_2{}^tBu_2$) ($\Delta\delta_{P(A)} = +4$ ppm) [1,2], but $P_{(M)}$ and $P_{(N)}$ are shifted to higher field as a result of the coordination of $P_{(N)}$ to the palladium ($\Delta\delta_{P(M)} = -82$, $\Delta\delta_{P(N)} = -119$ ppm). Both coordinated triethylphosphanes ($P_{(X)}$) are isochronous and their chemical shift is similar to that of [PdCl$_2$(PEt_3)$_2$].

From the low-temperature NMR spectrum it can be readily established that the *trans* relationship observed crystallographically for the complex *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$] is maintained in solution. The presence of a single resonance for the two triethylphosphane

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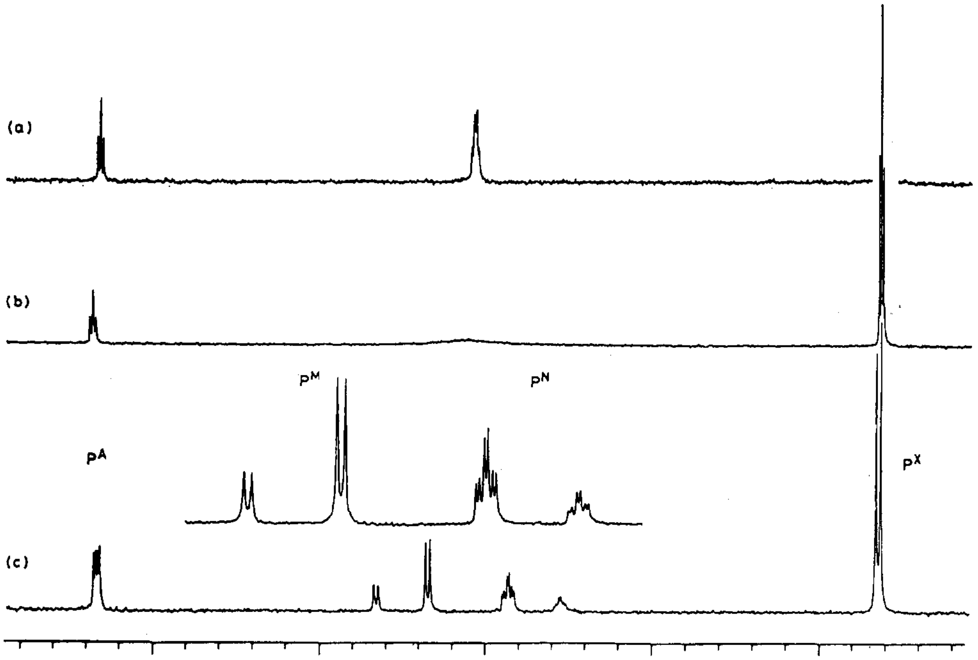
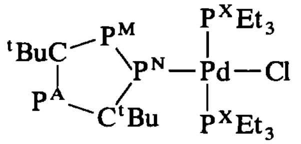


Fig. 1. 32.4 MHz $^{31}P\text{-}\{^1H\}$ NMR spectrum of 1 recorded at (a) +30°C, (b) −30°C, and (c) −75°C (toluene-d_8).

ligands is in agreement with an $[NX_2]$ spin system for the atoms forming the coordination sphere ($P_{(N)}$ and $P_{(X)}$). The splitting patterns observed are also as expected for the proposed static structure, with a large one-bond coupling between the now non-equivalent phosphorus atoms $P_{(M)}$ and $P_{(N)}$, and several smaller two- and three-bond couplings. The resonance due to P(A) consists of four lines resulting from two doublet splittings, $^2J_{P(A)P(M)}$ (43 Hz) and $^2J_{P(A)P(N)}$ (20 Hz). The latter is smaller than might be expected for a bond order greater than one, but it should be noted that the observed coupling constants will consist of contributions from both two-bond and three-bond couplings, and these may be of opposite sign.

The resonances due to $P_{(M)}$ ($\delta_P = +19.1$ ppm) and $P_{(N)}$ ($\delta_P = -18.0$ ppm) show splittings due to a mutual coupling and also coupling to $P_{(A)}$. The former is large (507 Hz) and is comparable with the values observed for phosphorus–phosphorus double bonds, for example 500–600 Hz in diphosphene compounds. In addition to couplings due to $P_{(M)}$ and $P_{(A)}$, $P_{(N)}$ also shows a further interaction with the two PEt_3 ($P_{(X)}$) phosphorus atoms (44 Hz) *. A slight distortion of the $P_{(M)}$ and $P_{(N)}$ resonances occurs at 32.4 MHz and they appear as the familiar '[AB] quartet', owing to the large value of $^1J_{P(M)P(N)}$ (507 Hz), and the comparatively small value of $\Delta\delta$ (37.1 ppm = 1202 Hz).

The low temperature 32.4 MHz $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[PdCl(P_3C_2{}^tBu_2)(PEt_3)_2]$ (−75°C in toluene-*d*) showed that the five phosphorus atoms occupy four distinct phosphorus environments described by an $[AMNX_2]$ spin system in accord with the η^1-structure shown:



(1)

On raising the temperature, the resonances due to the two directly bonded phosphorus atoms $P_{(M)}$ and $P_{(N)}$ broaden, coalescence occurring at *ca.* 248 K. At +30°C a new doublet of triplets was observed, whose chemical shift is at the mean of the original $P_{(M)}$ and $P_{(N)}$ resonances, thus establishing that these previously distinct phosphorus environments have now become equivalent. The patterns due to $P_{(A)}$ and $P_{(X)}$ also simplify accordingly, and at +30°C these signals appear as triplets. The fast exchange spectrum is therefore typical of an $[AM_2X_2]$ spin system, and the $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[PdCl(P_3C_2{}^tBu_2)(PEt_3)_2]$, measured at +30, −30, and −75°C, is shown in Fig. 1(a)–1(c).

More information about the static structure and dynamic behaviour of these η^1-ligated $P_3C_2{}^tBu_2$ complexes can be obtained from the Pt^{II} analogues. Complexes with platinum as the central atom show spectra of essentially the same type, the major difference arising from the presence of satellite subspectra due to

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* See Table 1 for chemical shift and coupling constant data for complexes of the type $[PtX(P_3C_2R_2)(PEt_3)]$ (X = Cl, I; R = ^{t}Bu, Ad).

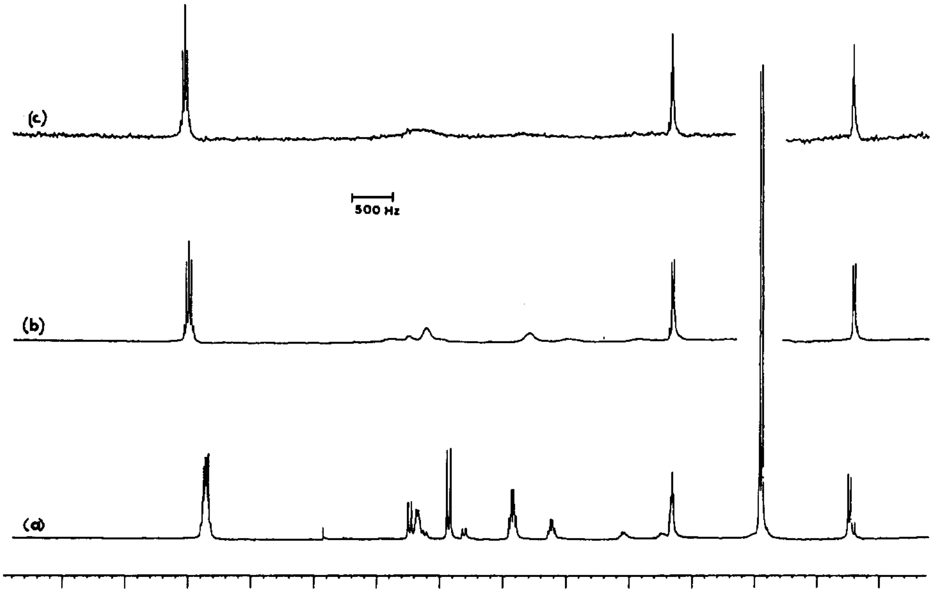


Fig. 2. ^{31}P-{^{1}H} NMR spectrum of *trans*-[PtCl($P_3C_2Ad_2$)(PEt_3)$_2$] at (a) −65°C, (b) +37°C, and (c) +60°C (toluene-d_8).

^{195}Pt (I = 1/2, 33.8%), which are also temperature dependent. Figure 2 shows the ^{31}P{^{1}H} NMR spectrum for *trans*-[PtCl($P_3C_2Ad_2$)(PEt_3)$_2$] measured at −65, +37, and +60°C, (see also Table 1).

2.2. ^{31}P–^{195}Pt satellite subspectra in trans-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$]

For the complex *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$], the 32.4 MHz ^{31}P{^{1}H} NMR spectrum, measured at temperatures below −60°C (Fig. 3), exhibits interesting additional features in its satellite subspectra. The spectrum arising from molecules containing ^{194}Pt and ^{196}Pt isotopomers ($I = 0$) has the same basic pattern as that observed for the palladium analogue, *i.e.*, that of an [$AMNX_2$] spin system showing a large one-bond $P_{(M)}$–$P_{(N)}$ coupling (497 Hz), a similar slight distortion of the $P_{(M)}$ and $P_{(N)}$ signals ($\Delta\delta$ = 36.9 ppm), and several small splittings in the range 20–45 Hz.

The spectrum arising from molecules containing the ^{195}Pt isomer does not appear as the simple 'satellite' pattern normally observed. Although the $P_{(A)}$ resonance does not allow the examination of individual subspectra, owing to the small value of $^3J_{PtP(A)}$, those for $P_{(M)}$, $P_{(N)}$, and $P_{(X)}$ are clearly visible. In each case, the ^{195}Pt satellite which is situated at high field of the main resonance shows the expected pattern, but satellites at low field show major differences on account of the very small value of $\Delta\delta_{P(N)P(M)}$ at this field strength, and the very large value of $^1J_{P(M)P(N)}$.

TABLE 1. ^{31}P{^{1}H} NMR chemical shift and coupling constant data for η^1-$P_3C_2R_2$ (R = ^{t}Bu, Ad) complexes of Pd^{II} and Pt^{II} (δ in ppm, J in Hz)

	$\delta_{P(A)}$	$\delta_{P(M)}$	$\delta_{P(N)}$	$\delta_{P(X)}$	$J_{PtP(N)}$	$J_{PtP(X)}$	$J_{PtP(M)}$	$J_{PtP(A)}$	$J_{P(M)P(N)}$	$J_{(P(A)P(M)}$	$J_{P(A)P(N)}$	$J_{P(N)P(X)}$
[PtCl(^{t}Bu$_2$C$_2$P$_3$)(PEt$_3$)$_2$]	+102.2	+1.8	−35.1	−127.6	2833	2283	396	59	497	43	22	33
[PtBr(^{t}Bu$_2$C$_2$P$_3$)(PEt$_3$)$_2$]	+101.3	+4.6	−30.4	−130.6	2795	2258	391	73	500	43	24	31
[PtI(^{t}Bu$_2$C$_2$P$_3$)(PEt$_3$)$_2$]	+95.7	−1.7	−33.2	−140.5	2699	2232	381	60	483	44	22	36
[PtCl(Ad$_2$C$_2$P$_3$)(PEt$_3$)$_2$]	+92.2	+2.7	−35.1	−127.3	2920	2298	333	61	498	41	24	34
[PtI(^{t}Bu$_2$C$_2$P$_3$)(PPh$_3$)$_2$]	+86.2	−6.8	−8.5	−126.2	2679	2512	276	83	500	35	23	36
[PdCl(^{t}Bu$_2$C$_2$P$_3$)(PEt$_3$)$_2$]	+112.0	+19.1	−18.0	−122.5	–	–	–	–	507	43	20	44
[Pt(^{t}Bu$_2$C$_2$P$_3$)$_2$(PEt$_3$)$_2$]	+123.6	+34.5	−20.3	−133.4	1860	2225	–	–	465	–	–	–
[Pd(^{t}Bu$_2$C$_2$P$_3$)$_2$(PEt$_3$)$_2$]	+124.0	+35.2	−14.2	−132.0	–	–	–	–	480	–	–	–
[Pt(^{t}Bu$_2$C$_2$P$_3$)$_2$(dppe)]	+116.8	+40.4	−32.6	−96.3	1875	2506	259	44	492	46	24	145 [a]

[a] *trans*-$^2J_{P(N)P(X)}$ − *cis*-$^2J_{P(N)P(X)}$ ≃ *trans*-$^3J_{P(M)P(X)}$ ≃ 15 Hz.

The phosphorus atom labels ($P_{(A)}$ *etc.*) refer to a structure of the general type:

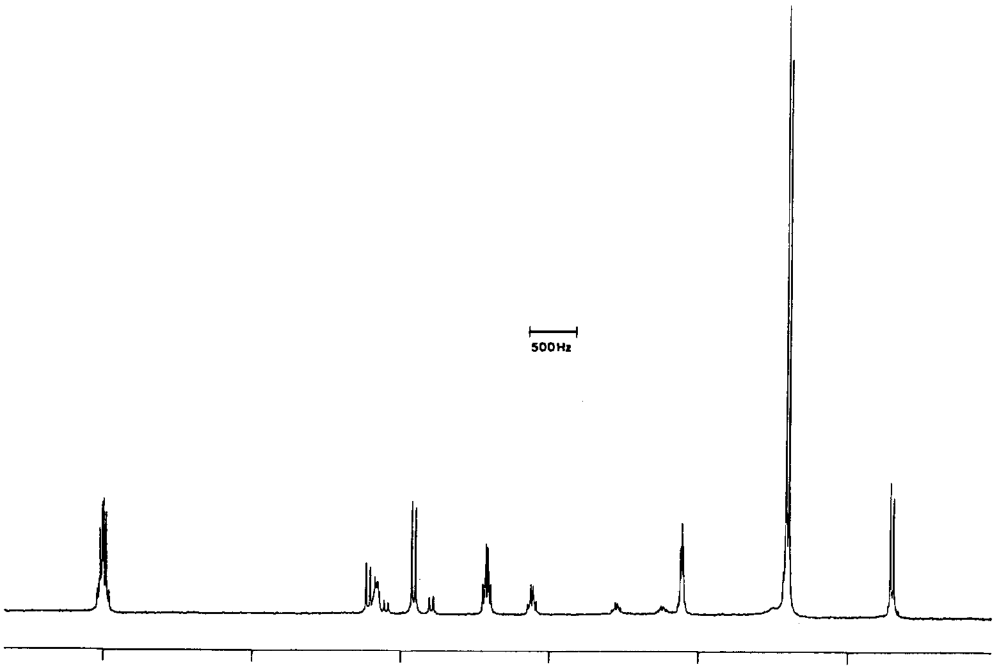


Fig. 3. ^{31}P-{^{1}H} NMR spectrum *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$] at −65°C (toluene-d_8).

If we consider *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$] containing only $^{194/196}$Pt isotopes, and ignoring P–P couplings, single line resonances for $P_{(M)}$ and $P_{(N)}$ would result at $\delta_{P(M)} = +1.8$ ppm, and $\delta_{P(N)} = -35.1$ ppm. The introduction of the ^{195}Pt isotope would create three subspectra for each signal, giving rise to splittings due to $^1J_{PtP(N)}$ and $^2J_{PtP(M)}$. Different values for $\Delta\delta_{P(M)P(N)}$ in each subspectrum would result, *e.g.*, increasing to 74.5 ppm in the high field subspectrum and decreasing to 0.7 ppm in the low field subspectrum. The two ^{31}P–^{195}Pt subspectra now have different spin systems, [AB] and [AX], and will be affected to a different degree by the introduction of a further large coupling, such as $^1J_{P(M)P(N)}$. Hence, for the low field subspectrum the [AB] quartet would show a large distortion ($\Delta\delta \ll J$) (in the extreme case the outer lines would be lost) and the resulting doublet would be further complicated by splittings due to $P_{(A)}$ and $P_{(X)}$. A distortion of the low field subspectrum of the $P_{(X)}$ resonance is also observed resulting from this effect, and it appears as a broadened triplet. This analysis is shown schematically in Fig. 4 and the results have been simulated for [PtCl($P_3C_2R_2$)(PEt_3)$_2$] (R = ^{t}Bu, Ad), as shown in Fig. 5.

2.3. ^{195}*Platinum NMR studies of trans-[PtCl(*$P_3C_2{}^tBu_2$*)(*PEt_3*)*$_2$*]*

For the complex *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$], the ^{195}Pt{^{1}H} NMR spectrum is structurally diagnostic, but yields no additional information to that available from the ^{31}P{^{1}H} NMR spectrum. Since the molecule is fluxional at room temperature, it is necessary to record the spectrum at lower temperatures, although generally not as low as those required for the ^{31}P spectrum.

The 77.2 MHz ^{195}Pt{^{1}H} NMR spectrum, measured at −15°C in toluene-d_8, Fig. 6(b), consists of a symmetrical twenty-four line multiplet centred at $\delta_{Pt} = +172$ ppm, which falls in the range observed for [PtCl$_2$(PR$'_3$)$_2$] (−100 → +800 ppm), representing a doublet of doublets of triplets, arising from coupling to

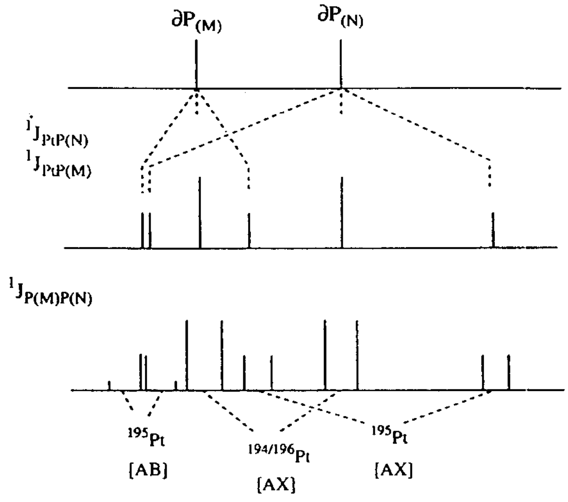


Fig. 4. Analysis of the distortions in the satellite subspectra of *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$].

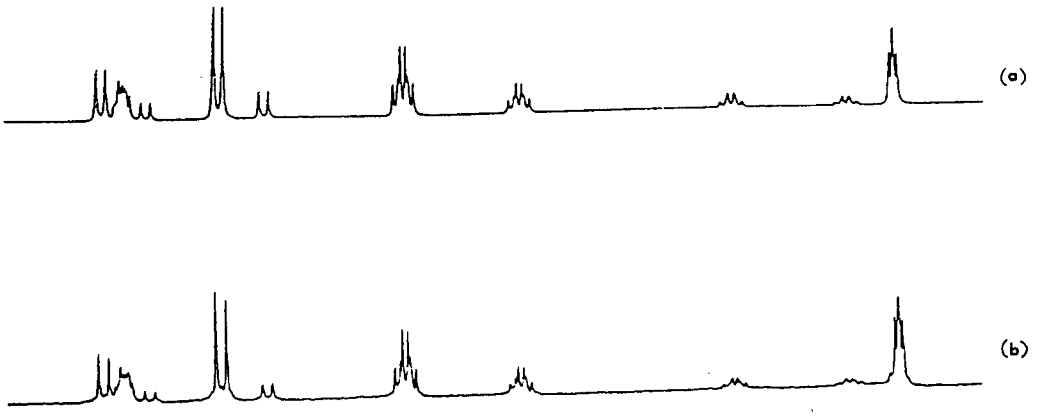


Fig. 5. Calculated (a) and observed (b) $^{31}P\text{-}\{^1H\}$ NMR spectra of *trans*-$[PtCl(P_3C_2{}^tBu_2)(PEt_3)_2]$ between +50 ppm and −110 ppm.

the five phosphorus atoms in their four chemically distinct environments. As with the $^{31}P\{^1H\}$ spectrum, the $^{195}Pt\{^1H\}$ NMR spectrum can be fully rationalised in terms of the crystallographically established structure for *trans*-$[PtCl(P_3C_2{}^tBu_2)(PEt_3)_2]$ containing an η^1-ligated $P_3C_2{}^tBu_2$ ring [6,7]. The construction of the multiplet from its constituent couplings can be illustrated as shown in Fig. 6(c).

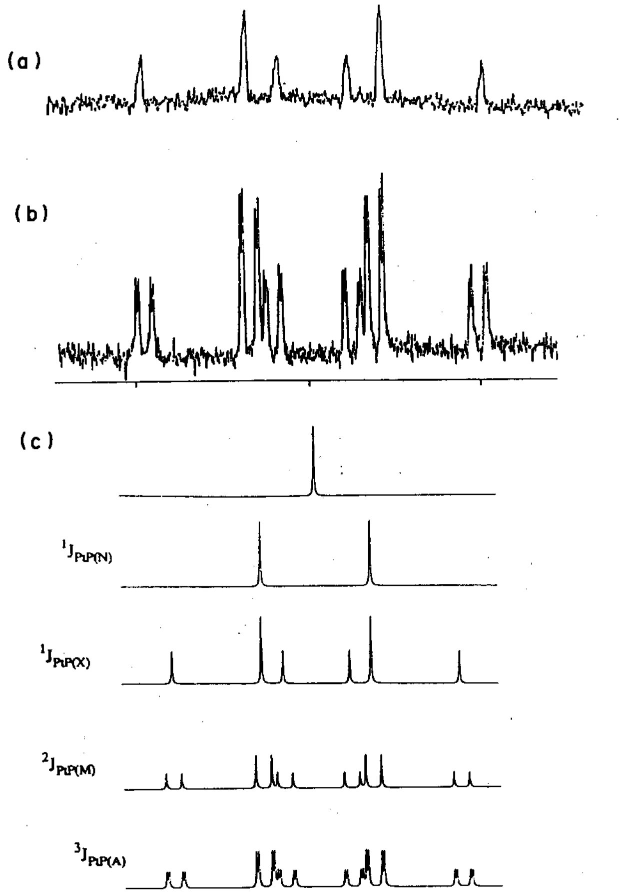


Fig. 6. $^{195}Pt\text{-}\{^1H\}$ NMR spectrum of *trans*-$[PtCl(P_3C_2{}^tBu_2)(PEt_3)_2]$ at (a) +60°C (toluene-d_8), and (b) −15°C; (c) construction of the 24-line ^{195}Pt resonance for *trans*-$[PtCl(P_3C_2{}^tBu_2)(PEt_3)_2]$ from its constituent couplings.

2.4. Variable temperature ^{195}Pt NMR studies

For the complex *trans*-$[PtCl(P_3C_2{}^tBu_2)(PEt_3)_2]$, a variable temperature $^{195}Pt\{^1H\}$ NMR study was undertaken and is reported in Fig. 6. The results led to similar conclusions to those drawn from the variable temperature ^{31}P NMR study. At low temperatures (−15°C), the spectrum consists of a 24-line multiplet resulting from couplings to all five of the phosphorus atoms. On raising the temperature the spectrum simplified, and at ambient temperature an incomplete collapse of the two-bond splitting was observed, while at +60°C the spectrum consisted of a doublet of triplets. It was not possible to observe the complete equivalence of $P_{(M)}$ and $P_{(N)}$ (to give a triplet of triplets), due to the high temperatures required.

2.5. $^{31}P\{^1H\}$ NMR spectra of $[M(P_3C_2R_2)_2(PR'_3)_2]$

The disubstituted complexes show similar properties to their monosubstituted counterparts. They are also fluxional in solution, and their low temperature spectra indicate that the metal–ring bond is of the η^1-type. In the low temperature spectra of the previously discussed complexes *trans*-$[MX(P_3C_2{}^tBu_2)(PEt_3)_2]$, four phosphorus environments described five phosphorus atoms, whereas in the disubstituted complexes four similar environments describe eight phosphorus atoms, related by an $[AMNX]_2$ spin system. Small changes in chemical shifts occur on coordination of the second ring, notably downfield shifts for $P_{(A)}$, $P_{(M)}$, and $P_{(N)}$, but the value for the large one-bond P–P coupling constant remains in the range 450–550 Hz.

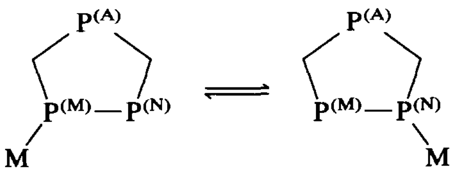
In the monosubstituted complexes, the presence of a single resonance for the PR_3 ligands was indicative of an $[NX_2]$ spin system, and hence a *trans* geometry. For the disubstituted complexes, both *cis* and *trans* isomers would give a single resonance, due to symmetry induced chemical equivalence. It is possible to distinguish between the two, as only the *trans* isomer will also feature magnetic equivalence. This can be illustrated by considering the spin systems present for the components of the coordination sphere, $(P_3C_2R_2)$ $(P_{(N)})$ and PR_3 $(P_{(X)})$. The resultant spin systems would be $[NX]_2$ for the *trans* isomer, and [NN'XX'] for the *cis* isomer.

Consequently, in the latter case, large *trans* ^{2}PMP couplings of the order of 250–550 Hz would be expected. Although it was not possible to resolve the small couplings in the low temperature spectra of $[M(P_3C_2{}^tBu_2)_2(PEt_3)_2]$ (M = Pd, Pt), sufficient information was available from the splitting patterns of the PEt_3 resonance at ambient temperature. As the spectra observed are averaged, the splittings reflect an average coupling consisting of both a relatively small *cis* $^2J_{PP}$ and a relatively large *trans* $^2J_{PP}$. In both isomers, *cis* $^2J_{PP}$ would contribute, but the larger *trans* $^2J_{PP}$ would only contribute in the *cis* isomer due to magnetic non-equivalence.

For $[M(P_3C_2{}^tBu_2)_2(PEt_3)_2]$ (M = Pd, Pt), the PEt_3 resonance is observed as a quintet pattern with an averaged coupling of 15 Hz (M = Pt), and 21 Hz (M = Pd). It follows therefore that the ligands in these complexes have a *trans* geometry, as the small nature of these values are not consistent with a contribution from *trans* couplings. This has subsequently been confirmed in the case of the Pt complex by a single crystal X-ray diffraction study [7]. Conversely, in the ambient $^{31}P\{^1H\}$ NMR spectrum of $[Pt(P_3C_2{}^tBu_2)_2(dppe)]$, where the chelating dppe ligand ensures a *cis*-complex, the dppe resonance, as expected, exhibits a splitting of *ca.* 160 Hz, indicative of an averaged splitting from both *cis* and *trans* contributions, (see also Table 1). Very recently we have obtained confirmation of the *cis*-structure via a single crystal X-ray structural analysis [8].

2.6. Suggested fluxional mechanism

The fluxional process, resulting in the observed changes in both the variable temperature $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR studies, is best visualised as a non-dissociative 1,2-shift of the metal atom between the two phosphorus atoms $P_{(M)}$ and $P_{(N)}$.



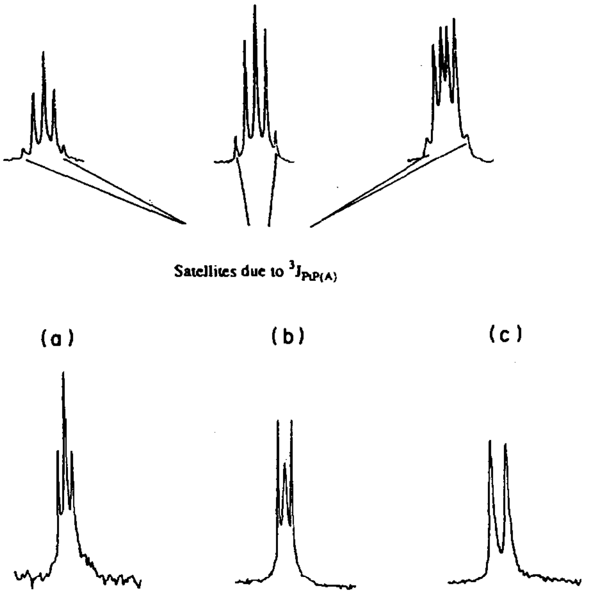


Fig. 7. 32.4 MHz $^{31}P\text{-}\{^1H\}$ NMR spectrum ($P_{(A)}$ resonance top, $P_{(X)}$ resonance bottom) measured at (a) +60°C, (b) +37°C, and (c) −65°C.

Although a number of similar examples of 'shuttling' processes have been identified for systems involving the donor atoms nitrogen, selenium, and sulphur, there appear to be no previous literature reports involving phosphorus as the donor atoms [9,10].

η^1-Cyclopentadienyl complexes also show fluxional behaviour in solution, but in contrast to the η^1-$P_3C_2{}^tBu_2$ ring systems studied here, several different processes are possible. Both 1,2- and 1,3-shifts are common and usually render all ring positions equivalent, whilst $\eta^1\text{-}\leftrightarrow\eta^5$-interconversions have also been identified. For the complexes studied here, there is considerable evidence against contributions from either a dissociative mechanism or the involvement of $P_{(A)}$.

Examination of the $^{31}P\{^1H\}$ triethylphosphane resonance in Fig. 2 reveals that the satellites due to $^1J_{PtP(X)}$ are present throughout the temperature range and remain well resolved, suggesting that any dissociation of the PEt_3 ligands is slow on the NMR timescale. Satellites due to $^3J_{PtP(A)}$ are also present throughout the temperature range, remaining sharp (see Fig. 7), suggesting that the same is true for the ring. It is noteworthy that the resonance due to $P_{(X)}$ ($^{194/196}$Pt and ^{195}Pt) retains its coupling to the ring via $^2J_{P(N)P(X)}$ throughout the temperature range.

Conclusive evidence is available from the individual resonances at intermediate temperatures. For these complexes, all of the phosphorus nuclei show couplings to $P_{(M)}$ and $P_{(N)}$, as does the ^{195}Pt. For each of these

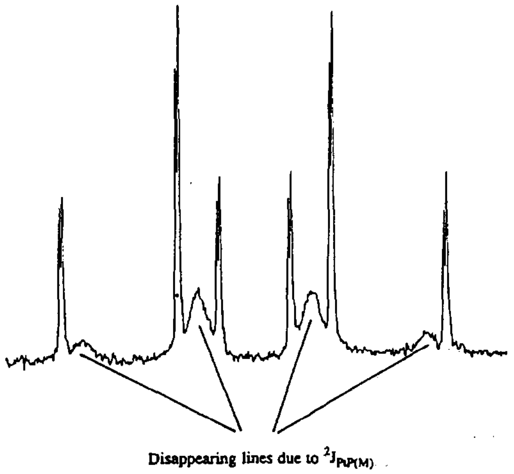


Fig. 8. 77.2 MHz ^{195}Pt-{^{1}H} NMR spectrum of *trans*-[PtCl-($P_3C_2{}^tBu_2$)(PEt_3)$_2$] measured at +28°C.

resonances, the equivalence of $P_{(M)}$ and $P_{(N)}$ results in a simplification of the observed splitting pattern involving the presence of invariant lines. This can be clearly seen for the $P_{(X)}$ resonance in the ^{31}P{^{1}H} NMR spectrum (Fig. 7, bottom), and also for the ^{195}Pt resonance (Fig. 8). The presence of invariant lines results from the relationship between the spin states of the nucleus observed and those of the exchanging nuclei, and is indicative of a non-dissociative averaging process.

The proposed mechanism excludes the involvement of $P_{(A)}$ in the fluxional process, which could theoretically be included via two possible alternative mechanisms: (i) 1,3-shifts of the metal involving all three phosphorus atoms; or (ii) η^1-↔ η^5-inverconversions.

Contributions from these two mechanisms can be discounted on the following grounds: both 1,3-shifts and η^1-↔ η^5-interconversions would involve the coordination of $P_{(A)}$ to the metal during the averaging process and this would result in significant changes in the appearance of the spectrum. The coordination of $P_{(A)}$ to the metal centre by either mechanism would affect its chemical shift in the upper limit spectrum relative to that of the starting material Li($P_3C_2{}^tBu_2$). For $P_{(A)}$, $\Delta\delta_{(coord)}$ is generally less than 25 ppm, whereas for $P_{(M)}$, it lies in the range 100–120 ppm.

In addition, a marked dependence of $\Delta\delta_{P(A)}$ on temperature would be observed, as the contribution from any $P_{(A)}$-coordinated species changed. Variations have been observed of $\delta_{P(A)}$ for both the mono and disubstituted complexes, of between 0.03 and 0.09 ppm/K over a relatively large temperature range, measured at 32.4 MHz in toluene-*d*. Whilst these variations are large compared with tertiary phosphane complexes, they are not dissimilar from those noted for a variety of related low-coordinate organosphosphorus(III) compounds.

Coordination of the platinum to $P_{(A)}$ by means of a σ interaction (*i.e.*, resulting from a 1,3-shift) would be likely to cause a more complicated $P_{(A)}$ resonance, due to contributions from $^1J_{PtP(A)}$ and $^2J_{P(A)P(X)}$. These are not observed, suggesting either that coordination does not occur, or that coupling is lost through a dissociative mechanism. Since it has already been shown that the process cannot be dissociative, this further supports is the non-involvement of $P_{(A)}$ during the fluxional process.

From the variable temperature NMR studies, approximate values for the energies $\Delta G^\ddagger$ of the dynamic process can be obtained, as shown in Table 2.

2.7. *Information on the signs of the platinum–phosphorus coupling constants*

2.7.1. *From the ^{31}P–^{195}Pt satellite subspectra*

Considerable information can be extracted from the observation of second order patterns in the ^{31}P–^{195}Pt satellite subspectra. Of particular importance, the relative signs of the coupling constants $^1J_{PtP(N)}$, $^2J_{PtP(M)}$ and $^1J_{PtP(X)}$ can be deduced, and since the absolute sign of one of these is known, we can therefore assign the other two.

The fact that an interaction between resonances $P_{(M)}$ and $P_{(N)}$ was observed requires that they belong to the same subspectrum, *i.e.*, either Pt^α or Pt^β. Furthermore, other resonances in the same subspectrum that show a coupling to one or both of the interacting nuclei will show a similar distortion. Whilst there is not sufficient separation of the three subspectra of the $P_{(A)}$

TABLE 2. Coalescence Temperatures T_c and $\Delta G^\ddagger$ for some *trans*-[MCl(PEt_3)$_2$($P_3C_2R_2$)] complexes (M = Pd, Pt; R = ^{t}Bu, Ad)

Complex	Coalescence	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol^{-1}) [a]
trans-[PtCl($C_2Ad_2P_3$)(PEt_3)$_2$]	^2J(P(N)P(X))	34	291	60.7
trans-[PtCl($C_2Ad_2P_3$)(PEt_3)$_2$]	$P_{(M)}/P_{(N)}$	1226	336	60.5
trans-[PtCl($C_2{}^tBu_2P_3$)(PEt_3)$_2$]	^2J(PtP(M))	396	322	60.9
trans-[PtCl($C_2{}^tBu_2P_3$)(PEt_3)$_2$]	$P_{(M)}/P_{(N)}$	1197	333	60.0
trans-[PdCl($C_2{}^tBu_2P_3$)(PEt_3)$_2$]	$P_{(M)}/P_{(N)}$	1203	248	44.1

[a] ± 5%.

resonance, this effect is clearly demonstated in the subspectrum to low field of the $I = 0$ case for $P_{(X)}$.

An analysis of the observed distortions has already been presented and it was seen in Fig. (4) that all of the distortions occur in the low field subspectra. This implies that the signs of the three couplings to platinum, ${}^1J_{PtP(X)}$ ${}^1J_{PtP(N)}$, and ${}^2J_{PtP(M)}$, are the same, and this was confirmed by computer simulation (Fig. (5)).

Making the assumption that ${}^1J_{PtP(X)}$ is positive for a trialkylphosphane–Pt^{II} interaction, then the subspectra can be labelled (low field = α, high field = β). It follows that the subspectrum in which the distortions occur here is the α subspectrum, and therefore the signs of ${}^1J_{PtP(N)}$ and ${}^2J_{PtP(M)}$ are positive.

2.7.2. From ${}^{195}Pt\{{}^1H\}$ variable temperature studies

In the variable temperature ^{195}Pt{^{1}H} spectra of *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$], it was noted that invariant lines were observed during the collapse of the low temperature multiplet to the simpler pattern observed at higher temperatures. This arises from the collapse of the lines corresponding to the two bond coupling, ${}^2J_{PtP(M)}$, and it can also be seen that it is the inner lines of the ${}^2J_{PtP(M)}$ 'doublet' that collapse (see Fig. (8)), which is indicative of a positive coupling constant, in agreement with the analysis of the satellite subspectra in the ^{31}P{^{1}H} NMR spectrum.

3. Experimental details

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk tube, syringe and vacuum line techniques. NMR spectra were recorded using a Bruker WP80SY or WM360 instrument at the following operating frequencies (WP80SY ^{31}P 32.4 MHz, ^{195}Pt 17.2 MHz, WM360 ^{31}P 145.8 MHz, ^{195}Pt 77.2 MHz). [Li(dme)$_3$][$P_3C_2{}^tBu_2$] was prepared by the method cited in Ref. 1, and the adamantyl analogue was prepared similarly for the synthesis of [PtCl($P_3C_2Ad_2$)(PEt_3)$_2$], (see below). The preparation of complexes *trans*-[MCl($P_3C_2{}^tBu_2$)0 (PEt_3)$_2$] (M = Pd, Pt) and *trans*-[M($P_3C_2{}^tBu_2$)$_2$-(PEt_3)$_2$] (M = Pd, Pt) have earlier been described in Ref. 7. ^{195}Pt NMR data not previously reported are for *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$], δ_{Pt} + 172 ppm; and for *trans*-[Pt($P_3C_2{}^tBu_2$)$_2$(PEt_3)$_2$], δ_{Pt} −234 ppm.

3.1. Preparation of trans-[Pt($P_3C_2Ad_2$)$_2$(PEt_3)$_2$]

This was prepared by the method of Ref. 7, but using [PtCl$_2$(PEt_3)$_2$] (125 mg, 0.25 mmol) and Li($C_2Ad_2P_3$) (0.25 mmol). After chromatography the yellow product was identified as *trans*-chloro(η^1-3,5-di(adamantyl)-1,2,4-triphosphacyclopentadienyl)bis(triethylphosphane)platinum(II), (62 mg, 29%), on the basis of a variable temperature ^{31}P NMR study (see text).

3.2. Preparation of trans-[PtBr($P_3C_2{}^tBu_2$)(PEt_3)$_2$]

A solution of *trans*-[PtCl($P_3C_2{}^tBu_2$)(PEt_3)$_2$] (140 mg, 0.2 mmol) in thf (2 ml) was added to 1 ml of a thf solution of LiBr (18 mg, 0.2 mmol) and the mixture stirred for 12 h at ambient temperature. The volatile components were removed *in vacuo*, the orange residue extracted into toluene, and the resulting suspension filtered through a short column (Kieselgel/toluene). The solvent was removed to give an orange-yellow solid, which was identified as *trans*-bromo(η^1-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)bis(triethylphosphane)platinum(II), (131 mg, 90%), on the basis of ^{31}P, ^{1}H, and ^{195}Pt NMR spectroscopy and elemental analysis. Found: C 34.9, H 6.0; $C_{22}H_{48}BrP_5Pt$. Requires: C 35.6, H 6.5%. ^{1}H NMR data (360.1 MHz; toluene-d_8): δ_H = 1.71 (s, 18H, ^{t}Bu); δ_H = 1.52 (broad m, 12H, CH_2); δ_H = 0.80 (d × t, 18H, CH_3). ^{195}Pt-{^{1}H} NMR data (77.3 MHz; toluene-d_8; −10°C): δ_{Pt} −73 ppm.

3.3. Preparation of trans-[PtI($P_3C_2{}^tBu_2$)(PEt_3)$_2$]

A solution of NaI (15 mg, 0.1 mmol) in thf (1 ml) was added to a thf solution of *trans*-[PtCl($P_3C_2{}^tBu_2$)-(PEt_3)$_2$] (69 mg, 0.1 mmol, total volume 3 ml), the resulting mixture was stirred for 12 h, and the volatile components removed *in vacuo*. The residue was extracted into toluene and the resulting suspension filtered through a short column (Kieselgel/toluene). Removal of the solvent *in vacuo* gave an orange-yellow solid which was identified as *trans*-iodo(η^1-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)bis(triethylphosphane)platinum(II), (72 mg, 91%), on the basis of ^{31}P-{^{1}H}, ^{195}Pt-{^{1}H}, and ^{1}H NMR spectroscopy and elemental analysis. Found: C 33.0, H 5.8; $C_{22}H_{48}IP_5Pt$. Requires: C 33.5, H 6.1%. ^{1}H NMR data (360.1 MHz; toluene-d_8): δ_H = 1.55 (s, 18H, ^{t}Bu); δ_H = 1.46 (broad m, 12H, CH_2); δ_H = 0.77 (d × t, 18H, CH_3). ^{195}Pt-{^{1}H} NMR data (77.3 MHz; toluene-d_8; −10°C): −436 ppm.

3.4. Preparation of trans-[PtI($P_3C_2{}^tBu_2$)(PPh_3)$_2$]

A solution of Li($P_3C_2{}^tBu_2$) (0.5 mmol) in dme (1 ml) was added to a suspension of [PtI$_2$(PPh_3)$_2$] (145 mg, 0.5 mmol) in dme (2 ml). The mixture was stirred for 12 h and the volatile components removed *in vacuo*. The residue was chromatographed (Kieselgel/toluene) to give an orange-red solid which was recrystallised from toluene and identified as *trans*-iodo(η^1-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)bis(triphenylphosphane)platinum(II), (241 mg, 45%), on the basis of ^{31}P and ^{1}H spectroscopy, elemental analysis, and a single crystal X-ray diffraction study [6]. Found: C 47.7, H 4.6; $C_{46}H_{48}IP_5Pt. C_7H_8$. Requires: C 48.3, H 4.8%. ^1H NMR data (80.1 MHz; $CDCl_3$): δ_H 1.4 (s, 18H, ^tBu); δ_H 7.3–7.6 (broad m, 30H, Ph).

3.5. *Preparation of cis-[Pt($P_3C_2{}^tBu_2$)(dppe)]*

A solution of Li($P_3C_2{}^tBu_2$) (0.5 mmol) in dme (1 ml) was added to a dme suspension of [$PtCl_2$(dppe)] (330 mg, 0.5 mmol, total volume *ca.* 5 ml), and the resulting mixture stirred for 12 h, during which time a yellow solid separated. This was collected, extracted into toluene, and the suspension filtered through a short column (Kieselgel/toluene). The volatile components were removed *in vacuo* and the yellow residue washed with cold dme (2 × 5 ml) and hexane (2 × 5 ml), dried *in vacuo*, and identified as *cis*-bis(η^1-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl{bisdiphenylphosphinoethane}platinum(II), (190 mg, 39%), on the basis of ^{31}P and ^1H NMR spectroscopy and elemental analysis. Recrystallisation from dme gave orange-red cuboids and their identity was confirmed by a single crystal X-ray diffraction study [8]. Found: C 51.9, H 5.9; $C_{50}H_{70}P_8Pt$. Requires: C 52.4, H 6.1%. ^1H NMR data (360.1 MHz; toluene-d_8): δ_H 1.4 (s, 36H, ^tBu); δ_H 2.2–2.3 (broad, 4H, CH_2); δ_H 7.3–7.5 (broad m, 20H, Ph).

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