Inorganic Chemistry

Article

pubs.acs.org/IC

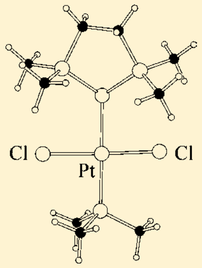
Platinum(II) Complexes of Cyclic Triphosphenium Ions: a ^{31}P NMR Spectroscopic and Computational Study

Philippa K. Coffer (née Monks), Robert M. K. Deng,† Keith B. Dillon,* Mark A. Fox, and Richard J. Olivey

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.

Ⓢ *Supporting Information*

ABSTRACT: The first transition metal complexes of cyclic triphosphenium ions have been unequivocally identified in solution by ^{31}P NMR spectroscopy. The ligands coordinate to platinum(II) via the central phosphorus atom, but only when at least one of the outer phosphorus atoms has non-aromatic substituents. Depending on the system, either trans- (the kinetic reaction product) and/or cis- (the thermodynamic reaction product) complexes are formed. The ^{1}J coupling constants between ^{195}Pt and the central phosphorus atom of the CTI (P_A) are small for both cis- and trans-isomers, between 900 and 1300 Hz, whereas other phosphanes in these complexes derived from the platinum(II) starting material show normal $^{1}J_{PtP}$ values. These results suggest a possible long P−Pt bond between the overall positively charged ligand and the platinum(II) cation. Calculations including predicted ^{31}P NMR shifts for the CTIs and their Pt(II) complexes largely support our experimental findings.



INTRODUCTION

Cyclic triphosphenium ions (CTIs) are positively charged heterocycles with a hydrocarbon backbone and three linked phosphorus atoms, the middle one of these being "bare" and nominally in the +1 oxidation state, Figure 1. The first example of a CTI was prepared and structurally characterized by Schmidpeter and co-workers in 1982.[1] Several other examples have subsequently been synthesized,[2−17] particularly by Macdonald et al.[7−10] and by our research group,[12−17] with ring sizes varying from 4 to 8. They feature in a review by Ellis and Macdonald,[18] and may be readily recognized by ^{31}P NMR solution-state spectroscopy, with a large $^{1}J_{PP}$ and a marked shift difference between P_A and P_B (Figure 1). Where these species have been characterized by single-crystal X-ray diffraction, the P−P distances lie between 2.11 and 2.15 Å, intermediate between normal P−P single and double bonds, providing clear evidence for a delocalized system.[1,7−13,16] The mechanism of their formation, at least for certain substituents, has been established.[19] The ions may be regarded as consisting of a phosphide(I) anion coordinated by two phosphonium(V) cations, Figure 2, which gives rise to the possibility of coordination to a transition metal fragment via a lone pair on the central phosphorus atom. No examples of such complexes have been reported, however. It is reasonable to expect that coordination may be weak to a metal cation because of repulsion between the positive charges. This may have applications in areas such as catalysis, where displacement of a weakly bound ligand may be advantageous.

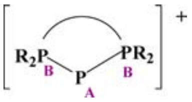


Figure 1. General structure of a CTI.

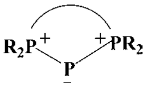


Figure 2. Charge distribution in a CTI.

We now report the unequivocal identification by ^{31}P NMR solution-state spectroscopy of the first platinum(II) complexes of cyclic triphosphenium ions, clearly coordinated to the metal via the central phosphorus atom. The platinum(II) precursors used were dimeric halogen-bridged complexes *trans*-[Pt(PR$_3$)X(μ-X)]$_2$, with R$_3$ = Et$_3$, PhMe$_2$ or Ph$_2$Me and X = Cl or Br.[20−23]

Most of the CTIs prepared by other research groups have aromatic, usually phenyl, substituents on the outer (phosphonium) phosphorus atoms.[1−17] We have found no evidence for coordination by these ligands to our platinum(II) substrates, suggesting that they are not good enough donors (Results and Discussion). Complexation does occur, however, for alkyl or alicyclic substituents, and even for an unsymmetrical CTI with ethyl substituents on one of the outer phosphorus atoms and phenyl groups on the other. Several examples of both trans- (the kinetic product) and cis- (the thermodynamic product) complexes have been identified in solution by ^{31}P NMR spectroscopy, as described below.

Received: June 1, 2012
Published: September 4, 2012

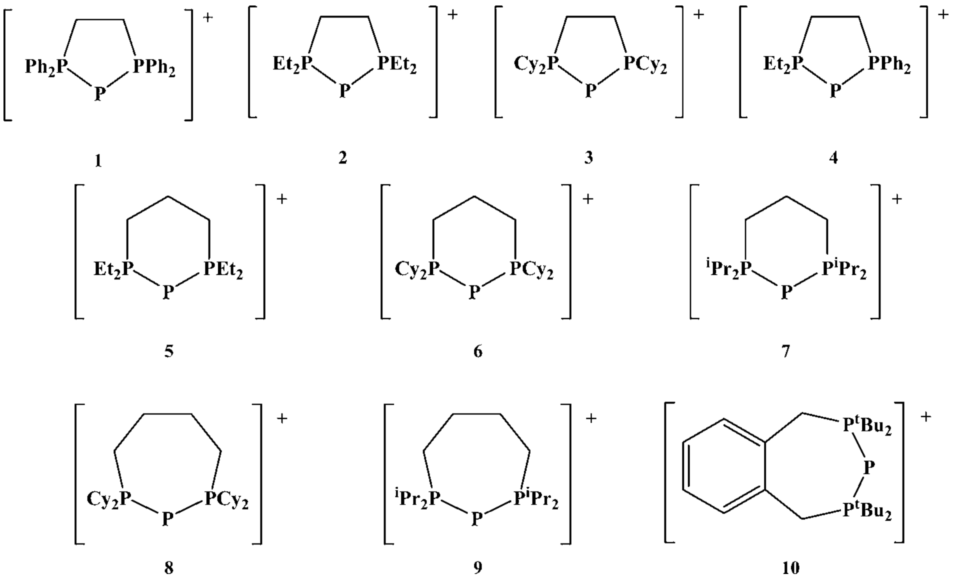


Figure 3. CTIs used in this study.

RESULTS AND DISCUSSION

Synthesis of CTIs. Using literature methods,[13,15,17,19,24] various CTIs (Figure 3) were synthesized and their formation confirmed using ^{31}P NMR spectroscopy (Table 1).

Table 1. ^{31}P NMR Data for CTIs Used in This Study

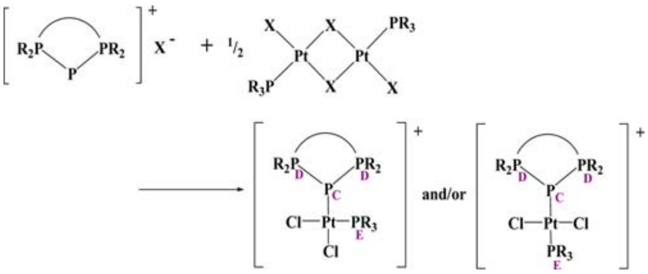
CTI number	SnCl$_2$ present	δP$_{B'}$,[b] ppm	δP$_B$, ppm	δP$_A$, ppm	$^1J_{PA\text{-}PB}$, Hz	$^1J_{PA\text{-}PB'}$, Hz	reference
1	×		65.0	−229.5	450		*a*
2	×		81.5	−269.0	437		13
2	√		80.5	−264.1	444		13
3	×		87.3	−289.3	457		24
3	√		87.2	−289.0	455		17
4	×	78.0	67.1	−251.0	431	460	13
4	√	81.3	69.4	−251.0	434	466	13
5	×		31.1	−253.3	417		15
5	√		30.5	−252.3	419		19
6	×		36.5	−297.4	452		19
6	√		36.6	−292.9	456		*a*
7	×		44.7	−299.6	458		19
7	√		44.8	−299.4	457		17
8	×		48.3	−262.5	472		15
8	√		48.1	−260.8	476		*a*
9	×		55.9	−264.8	474		17
9	√		55.5	−262.5	480		17
10	√		45.5	−237.5	565		*a*

[a] This work. [b] B′ = Ph$_2\underline{P}$ in dedppe.

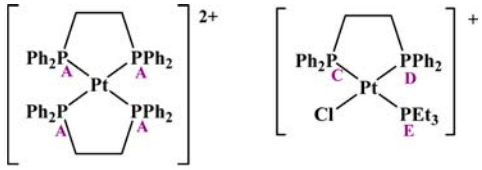
It should be noted that CTIs were sometimes prepared as their simple chloride salt, but in other reactions tin(II) chloride was added (Experimental Section), making $[SnCl_6]^{2-}$ the most probable counterion, although the possibility of $[SnCl_5]^-$ cannot be discounted. If excess SnCl$_2$ is present, this introduces the possibility of $SnCl_3^-$ rather than Cl$^-$ as a ligand on platinum(II),[25−31] which is sometimes reflected in chemical shift and coupling constant differences for the phosphorus-containing ligands, as discussed below. This does not apply to the five-membered ring CTI systems, however, where no such pairs of complexes were investigated. Hence the identity of the two nonphosphorus ligands in monomeric platinum(II) complexes where SnCl$_2$ is present in the reaction mixture cannot be specified, although Cl$^-$ may clearly be assumed when no SnCl$_2$ is present. What is certain in all systems is the identity of the phosphorus ligands attached to platinum(II), and their relative positions, that is, cis or trans, since the NMR evidence on these points is clear. The CTI complexes with Pt(II) described here will also carry an overall charge of +1, for which various counterions may be present in solution.

Solution Studies on Pt(II) Complexes of CTIs. Scheme 1 shows the general reaction (for all ring sizes) between one mole of a dimeric platinum(II) precursor and two moles of a CTI. The kinetic product is the trans-complex, whereas the thermodynamic product is the cis-complex.

Scheme 1. Synthesis of Pt(II) Complexes of CTIs



(i). Attempted Formation of Pt(II) Chloro-Complexes of Five-Membered Ring CTIs. The initial experiment attempted was a 2:1 reaction of the CTI **1** derived from dppe with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$; the ^{31}P NMR spectrum was recorded as soon as possible after addition of the dimer solution. There was no evidence of complexation of the CTI, even though the NMR spectrum indicated that some unreacted CTI was still present (δ ^{31}P$_B$ 65.0(d), δ ^{31}P$_B$ −229.5(t) ppm, $^1J_{PP}$ 450 Hz). The major products of the reaction were identified as $[Pt(dppe)_2]^{2+}$ and $[Pt(dppe)(PEt_3)Cl]^+$, Figure 4. The ^{31}P NMR data for these complexes, along with literature values, are shown in Table 2. This result suggests that ring scission is the preferred reaction with purely aromatic substituents on the outer phosphorus atoms of the CTI.



[Pt (dppe)$_2$]$^{2+}$ [Pt (dppe) (PEt$_3$) Cl]$^+$

Figure 4. Reaction products from CTI **1** and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$.

The reactions with the depe derivative **2** (Figure 3) were usually carried out with SnCl$_2$ present; for R$_3$ = PEt$_3$ or PhMe$_2$ in *trans*-[Pt(PR$_3$)X(μ-X)]$_2$, cis-complexes only were observed, as shown in Table 3. For R$_3$ = Ph$_2$Me, no ring complexation was apparent, just coordination of depe to platinum(II), indicating the break-up of the CTI. Similar results were obtained for this system without SnCl$_2$ present.

For CTI **3** synthesized from dcype (Figure 3), the reactions with R$_3$ = Et$_3$ were performed for the chloride salt, since the hexachlorostannate appeared to be sparingly soluble and no reliable results could be obtained. Both the trans- and cis-complexes were identified in solution (Table 3); the results clearly demonstrate coordination by the central phosphorus atom of the CTI to Pt(II). For reactions of **3** with the Pt(II) precursors where R$_3$ = PhMe$_2$ or Ph$_2$Me, SnCl$_2$ was present. The trans- and cis-complexes were both detected for PPh$_2$Me as coligand, but only the cis-isomer for PPhMe$_2$ (Table 3).

In view of the results above, a particularly interesting system to study was CTI **4**, derived from the unsymmetrical diphosphane dedppe, Et$_2$P(CH$_2$)$_2$PPh$_2$ (Figure 3).[13] The NMR spectra from the CTI itself and its potential platinum(II) complexes are more complicated than usual, because all three phosphorus atoms in the CTI are nonequivalent. The results in Table 4 clearly show that this CTI, too, will coordinate via the central phosphorus atom to form a cis-complex upon reaction with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$. (We did not have enough material to investigate its reactions with the other Pt dimers.)

In each of the new Pt(II) complexes containing a five-membered ring CTI the most notable feature is the comparatively low value for $^1J_{\mathrm{PtP}}$ to the CTI, irrespective of whether the geometry is cis or trans, as shown in Tables 3 and 4. The ^1J values range from 1023 to 1183 Hz, and where both isomers have been identified in solution these are higher for the cis-complex than for the trans-complex, as is usually the case for other phosphorus donors to platinum(II).[34] The phosphanes PR$_3$ introduced with the platinum(II) precursor have completely normal ^1J values for cis- (3385–3625 Hz) or trans- (2783–2972 Hz) Pt(II) complexes. The chemical shift of the central phosphorus atom of the CTI also moves to much higher frequency on complexation, as shown by a comparison of the data in Table 1 with those in Tables 3 and 4. Where isomeric pairs have been identified, this shift is larger for the cis- than for the trans-complex. These observations are discussed further below.

(ii). Formation of Pt(II) Chloro-Complexes of Six-Membered Ring CTIs. CTIs **5**, **6**, and **7** (Figure 3) were synthesized from the diphosphanes depp, dcypp, and dippp, respectively.

Reaction of **5** as its chloride salt with *trans*-[Pt(PEt$_3$)X(μ-X)]$_2$ afforded both cis- and trans-complexes (Table 5). The signals from the trans-isomer were weak, however, and not all of the coupling constants could be recorded. This system was also investigated with SnCl$_2$ present, when only the cis-complex was detected. The differences in the results for the cis-complex with Cl$^-$ only and with SnCl$_2$ also present, particularly δP$_\mathrm{E}$, suggest that a change in one or both coligands from Cl to SnCl$_3$ is quite probable here. The reactions of **5** with *trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$, where R$_3$ = PhMe$_2$ and Ph$_2$Me, were both carried out with SnCl$_2$ present; a cis-complex was formed in each instance.

Reaction of **6** with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ and no SnCl$_2$ initially afforded only the trans-complex (Table 5). Weak signals of the cis-isomer subsequently appeared, although these signals were recorded more readily in the same reaction with SnCl$_2$ present. Analogous reactions of **6** with *trans*-[Pt(PR$_3$)-Cl(μ-Cl)]$_2$, where R$_3$ = PhMe$_2$ and R$_3$ = Ph$_2$Me, were also performed. The reaction for R$_3$ = PhMe$_2$ was carried out only in the presence of SnCl$_2$, yielding a cis-complex. Both trans- and cis-isomers were observed for R$_3$ = Ph$_2$Me in the absence of SnCl$_2$, though again the signals from the trans-complex were weak, and not all coupling constants could be measured.

Experiments with **7** were only performed with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$; in the absence of SnCl$_2$, the cis-complex was detected, but in the presence of SnCl$_2$ both cis- and trans-species were apparent, Figure 5. The signals from the trans-complex were again weak, and it was not possible to assign δP$_{\mathrm{E(trans)}}$ with certainty (Table 5). Comparison of the results for the cis-complex with and without SnCl$_2$ again suggests the strong possibility of a change of coligand, with differences in both chemical shifts and coupling constants being apparent.

As for the five-membered ring CTIs, the six-membered ring analogues show a very significant shift to higher frequency for the central coordinated phosphorus atom, which is larger for cis-complexes than for their trans-isomers. All of the $^1J_{\mathrm{PtP}}$ values for this atom lie between 1100 and 1300 Hz, where they could be recorded.

(iii). Formation of Pt(II) Chloro-Complexes of Seven-Membered Ring CTIs. CTIs **8**, **9**, and **10** (Figure 3) were synthesized from the diphosphanes dcypb, dippb, and dtbpox, respectively. Reaction of **8** as its chloride salt with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, yielded a cis-complex, whereas in the presence of SnCl$_2$ a trans-complex was detected, Table 6. It is probable that there is also a change in coligand from Cl to SnCl$_3$, since $^1J_{\mathrm{PtP}}$ to the central phosphorus atom of the CTI is slightly higher for the trans-complex than for the cis-complex,

Table 2. ^{31}**P NMR Data for Products from the Reaction of CTI 1 and** ***trans*****-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$**

	δP$_\mathrm{A}$, ppm	$^1J_{\mathrm{Pt\text{-}PC}}$, Hz
[Pt(dppe)$_2$]$^{2+}$	48.3	2356
literature data for [Pt(dppe)$_2$]$^{2+32}$	47.0	2360

	δP$_\mathrm{C}$, ppm	δP$_\mathrm{D}$, ppm	δP$_\mathrm{E}$, ppm	$^1J_{\mathrm{Pt\text{-}PC}}$, Hz	$^1J_{\mathrm{Pt\text{-}PD}}$, Hz	$^1J_{\mathrm{Pt\text{-}PE}}$, Hz	$^2J_{\mathrm{PC\text{-}PE}}$, Hz
[Pt(dppe)(PEt$_3$)Cl]$^+$	53.5	43.7	17.2	2260	3542	2282	369
literature data for [Pt(dppe)(PEt$_3$)Cl]$^{+33}$	53.1	43.3	16.6	2263	3527	2282	368

Table 3. ^{31}P NMR Data for 5-Membered Ring Chloro-Complexes of CTIs

complex number	CTI	$SnCl_2$ present	PR_3	cis/trans	δP_D ppm	δP_C, ppm	δP_E, ppm	$^1J_{PC\text{-}PD}$, Hz	$^1J_{Pt\text{-}PC}$, Hz	$^1J_{Pt\text{-}PE}$, Hz	$^2J_{PC\text{-}PE}$, Hz
11	2	√	PEt_3	cis	70.0	−104.3	11.4	363	1059	3407	
12	2	√	$PPhMe_2$	cis	69.3	−113.2	−14.0	359	1120	3534	
13	3	×	PEt_3	cis	69.9	−107.2	8.9	384	1099	3422	
14	3	×	PEt_3	trans	72.6	−148.2	16.3	408	1023	2972	321
15	3	√	$PPhMe_2$	cis	69.9	−111.6	−19.6	381	1179	3492	
16	3	√	PPh_2Me	trans	72.1	−124.7	14.4	380	1032	2783	215
17	3	√	PPh_2Me	cis	72.9	−104.1	0.2	392	1183	3625	

Table 4. ^{31}P NMR Data for 5-Membered Ring Chloro-Complexes of CTI 4

compound number	CTI	$SnCl_2$ present	PR_3	cis/ trans	$\delta P_{D'}$[a], ppm	δP_D, ppm	δP_C, ppm	δP_E, ppm	$^1J_{PC\text{-}PD'}$, Hz	$^1J_{PC\text{-}PD}$, Hz	$^1J_{Pt\text{-}PC}$, Hz	$^1J_{Pt\text{-}PE}$, Hz
18	4	√	PEt_3	cis	72.9	50.8	−89.5	10.7	359	365	1096	3385

[a] D′ = $Ph_2\underline{P}$ in dedppe.

Table 5. ^{31}P NMR Data for Chloro-Complexes of 6-Membered Ring CTIs[a]

compound number	CTI	$SnCl_2$ present	PR_3	cis/trans	δP_D, ppm	δP_C, ppm	δP_E, ppm	$^1J_{PC\text{-}PD}$, Hz	$^1J_{Pt\text{-}PC}$, Hz	$^1J_{Pt\text{-}PE}$, Hz	$^2J_{PC\text{-}PE}$, Hz
19	5	×	PEt_3	cis	19.1	−102.3	3.2	340	1104	3369	
20	5	×	PEt_3	trans	26.1	−136.0	9.3	348	nr	nr	170
21	5	√	PEt_3	cis	18.0	−98.6	9.7	344	1117	3392	
22	5	√	$PPhMe_2$	cis	18.8	−108.3	−14.4	338	1166	3550	
23	5	√	PPh_2Me	cis	18.8	−111.6	−11.0	344	∼1200	3642	
24	6	×	PEt_3	cis	20.3	−102.7	3.4	371	nr	nr	
25	6	×	PEt_3	trans	27.5	−151.9	15.6	369	nr	2815	172
26	6	√	PEt_3	cis	20.5	−102.3	3.6	375	1154	3456	
27	6	√	$PPhMe_2$	cis	20.4	−104.7	−13.6	372	1227	3513	
28	6	×	PPh_2Me	cis	20.0	−97.0	0.1	380	1267	3628	
29	6	×	PPh_2Me	trans	27.6	−148.0	3.9	366	nr	nr	266
30	7	×	PEt_3	cis	27.6	−94.6	0.2	374	1223	3628	
31	7	√	PEt_3	cis	27.7	−99.1	4.7	369	1133	3447	
32	7	√	PEt_3	trans	34.8	−122.4	nr	380	1115	nr	172

[a] nr = not recorded.

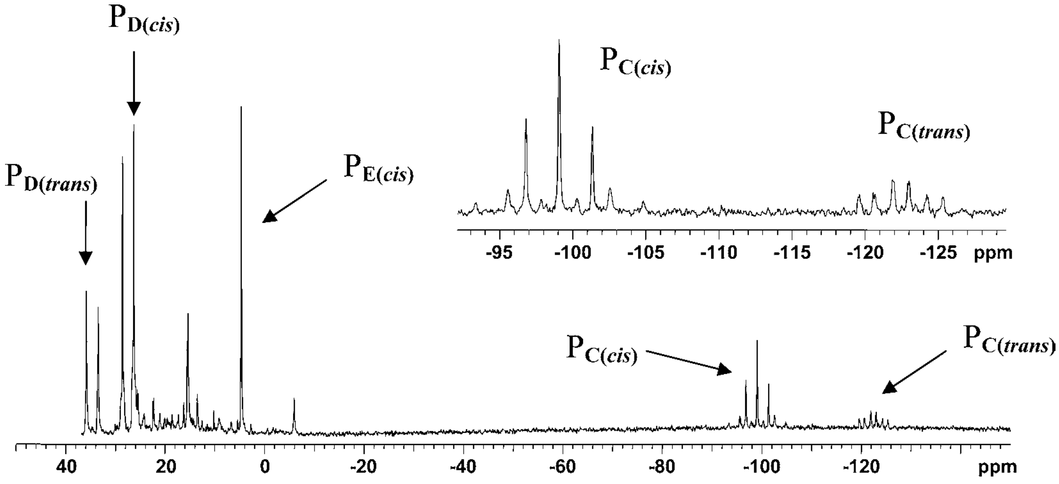


Figure 5. ^{31}P NMR spectrum of the reaction between **7** and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ to give complexes **31** and **32**.

opposite to the normal trend if all other ligands are kept constant.

Reactions of **8** with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ for R_3 = $PhMe_2$ and Ph_2Me were only carried out with $SnCl_2$ present. The initial product was a trans-isomer in each case (Table 6). The ^{31}P NMR spectrum of the trans-complex formed in the reaction of **7** with *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ is depicted in Figure 6. The experiment with $PPhMe_2$ as coligand was repeated, to ascertain whether the trans-complex would convert to its cis-isomer on standing. Very weak signals for a cis-complex were obtained soon after mixing the solutions (Table 6), but because of weak satellite peaks one of the coupling constants could not be measured. After 1 day, these signals had disappeared, and no CTI complexes were observed in solution.

Reactions of **9** with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ were performed both with and without $SnCl_2$. A trans-isomer was

Table 6. ^{31}P NMR Data for 7-Membered Ring Chloro-Complexes of CTIs[a]

Compound number	CTI	$SnCl_2$ present	PR_3	*cis/trans*	δP_D, ppm	δP_C, ppm	δP_E, ppm	$^1J_{PC\text{-}PD}$, Hz	$^1J_{Pt\text{-}PC}$, Hz	$^1J_{Pt\text{-}PE}$, Hz	$^2J_{PC\text{-}PE}$, Hz
33	8	×	PEt_3	cis	38.5	−78.6	3.9	418	1222	3431	
34	8	√	PEt_3	trans	43.3	−127.8	14.6	423	1245	2842	281
35	8	√	$PPhMe_2$	cis	40.0	−78.5	−15.1	421	nr	3630	
36	8	√	$PPhMe_2$	trans	44.0	−124.1	3.4	420	1017	2512	291
37	8	√	PPh_2Me	trans	43.7	−124.1	2.3	421	1030	2586	287
38	9	×	PEt_3	trans	50.9	−133.1	15.7	418	943	2840	275
39	9	√	PEt_3	trans	50.9	−132.5	15.6	420	949	2842	275
40	9	×	PPh_2Me	trans	51.1	−127.7	5.1	417	1013	2873	287
41	10	√	PEt_3	trans	50.8	−136.5	11.4	550	nr	nr	375

[a] nr = not recorded.

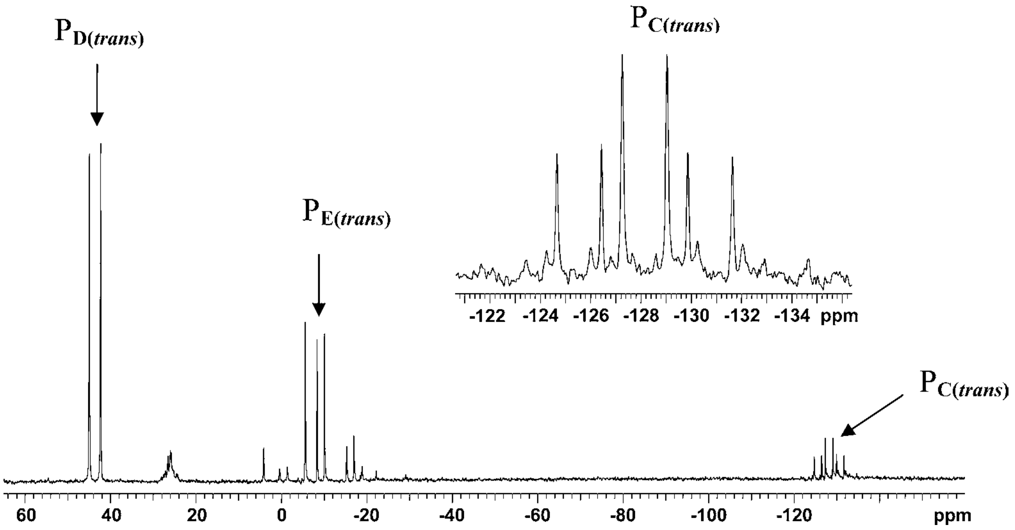


Figure 6. ^{31}P NMR spectrum of the reaction between **8** and *trans*-[Pt($PPhMe_2$)Cl(μ-Cl)]$_2$ to give complex **36**.

Table 7. ^{31}P NMR Data for 5-Membered Ring Bromo-Complexes of CTI 2

compound number	CTI	PR_3	cis/trans	δP_D, ppm	δP_C, ppm	δP_E, ppm	$^1J_{PC\text{-}PD}$, Hz	$^1J_{Pt\text{-}PC}$, Hz	$^1J_{Pt\text{-}PE}$, Hz
42	2	PEt_3	cis	71.0	−103.9	3.6	369	1032	3584

formed in each case. The NMR data (Table 6) are so similar here that the coligands may be reasonably assumed to be chlorides in both reactions. A trans-complex was also produced from reaction of **9** with *trans*-[Pt(Ph_2Me)Cl(μ-Cl)]$_2$ with no $SnCl_2$ added (Table 6).

A new CTI, **10**, was prepared from dtbpox by reaction with PCl_3 in the presence of $SnCl_2$. Formation of the CTI was confirmed by a doublet, δ ^{31}P 45.5 ppm, and a triplet, δ ^{31}P −237.5 ppm, for P_B and P_A respectively, $^1J_{PP}$ 565 Hz, in the ^{31}P NMR solution spectrum. Only the reaction of **10** with *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ was carried out, because of only a small amount of the diphosphane being available. Weak signals from a trans-complex were apparent in the ^{31}P NMR spectra (Table 6), but reliable values could not be obtained for either $^1J_{PtP}$, because of the very low intensities of the satellite signals.

The same overall trends are again apparent in Table 6 that were noted for the smaller ring CTIs. Where they could be measured, the $^1J_{PtP}$ values to the central phosphorus atom of the CTI are again low, between 940 and 1250 Hz, whereas the phosphane coligands show normal $^1J_{PtP}$ values for cis- or trans-complexes. There is a large shift to higher frequency for the central phosphorus atom of the CTI on complexation, which is greater for cis-complexes than for their trans-isomers. The outer phosphorus atoms of the CTI are very little affected by complexation, as is reasonable for coordination via the central P atom.

The P−P coupling constant within the CTI decreases somewhat on complexation to platinum(II) in all cases, irrespective of ring size, although the change is less marked than that which occurs on either protonation[3,15,24,35] or alkylation[3,14,36−38] of the central phosphorus atom. The latter reactions result in a change of formal oxidation state of P_A from +1 to +3, and the P−P bonds become normal single bonds, with distances between 2.191(1) and 2.233(1) Å in all the structures that have been determined by single-crystal X-ray diffraction.[37,38] Complexation to a transition metal such as platinum(II) changes the geometry at the central phosphorus atom of the CTI, but not its formal oxidation state. A reduction in $^1J_{PP}$ is expected on complexation because of the transfer of electron density away from phosphorus to the metal, but it seems entirely reasonable that this reduction should be smaller than that caused by protonation or alkylation. The consequence may well be a slight lengthening of the P−P bonds in the CTI complexes relative to those in the free ligand, but they will probably still be shorter than usually found for P−P single bonds.

(iv). Attempted Formation of Pt(II) Bromo-Complexes of Five-Membered Ring CTIs. In an attempt to obtain a

crystallizable complex, reactions were carried out between **2** as its bromide salt and the platinum(II) bromo-dimers *trans*-$[Pt(PR_3)Br(\mu\text{-}Br)]_2$ (where R_3 = Et_3, $PhMe_2$ or Ph_2Me).[21,23]

Formation of a platinum(II) complex was only observed for the reaction between **2** and *trans*-$[Pt(PEt_3)Br(\mu\text{-}Br)]_2$; the ^{31}P NMR parameters for this cis-species are given in Table 7. The data are entirely in keeping with those for the analogous chloro-complex in Table 3. In the chloro-systems a cis-complex was also formed for R_3 = $PhMe_2$, though not for R_3 = Ph_2Me, possibly suggesting that a better donor phosphane as coligand is necessary in the bromo-complexes. The same feature of a normal $^1J_{PP}$ for a *cis*-PEt_3 group but a comparatively low $^1J_{PP}$ for the coordinated CTI is apparent as in the chloro-complexes.

While these species are the first transition metal derivatives of CTIs, complexes of phosphenium ions with heavier transition metals, including rhodium(I),[39] platinum(0),[40,41] and palladium(0)[41,42] have been described. In these, the phosphenium ion is usually stabilized by two adjacent nitrogen atoms in a heterocyclic system. The platinum derivatives were formed by reaction with $Pt(PPh_3)_4$. They have very short Pt—P bond distances to the phosphenium ion in structurally characterized compounds, regarded as double bonds, between 2.1073(9) and 2.116(3) Å, with correspondingly very high $^1J_{PtP}$ values, ranging from 6446 to 7354 Hz (not in the same sequence).[40,41] The platinum(II) complexes in the present work are much more similar in their NMR behavior to terminal phosphido complexes with PR_1R_2 ligands, which have long Pt—P distances in structurally characterized compounds, from 2.351(2) to 2.4117(10) Å, and low $^1J_{PtP}$ values, from 643 to 1239 Hz.[43] The small coupling constants and long Pt—P distances in these complexes have been attributed to the bonding phosphorus atom remaining pyramidal,[43a,e] and to a low degree of s character in the Pt—P bond.[43e] The conclusion that phosphido complexes form a better model for CTI complexes than the phosphenium complexes mentioned above is supported by theoretical calculations described below.

DFT Calculations. *(i). CTIs and Their Protonated Derivatives.* As we have not yet succeeded in obtaining suitable crystals of the platinum(II) complexes of CTIs **2**−**10** for X-ray structural determinations, density functional theory (DFT) calculations were carried out on model systems to give insight into their geometries. As far as we are aware, there are no reported X-ray data on monocationic CTIs with alkyl substituents on the P_B atom. There are also no X-ray structures of any protonated forms of CTIs with P_A-H bonds.

To estimate the accuracy of the optimized geometries, the experimental and computed geometries of $[(Ph_3P)_2P]^+$ and $[(Ph_3P)_2PH]^{2+}$ were compared, as crystal structures of both compounds have been published.[35,44,45] The calculated P—P bond lengths of $[(Ph_3P)_2P]^+$ and $[(Ph_3P)_2PH]^{2+}$ are 2.186 and 2.273 Å, respectively, whereas the corresponding observed values are 2.131 and 2.215 Å. While the calculated P—P bonds are 0.055−0.058 Å longer than observed, the differences in the bond lengths between the two cations in both calculated and observed values are virtually the same.

One way to confirm good agreement between computed and experimental geometries is by comparison of the observed and calculated ^{31}P NMR shifts. Experimentally, these are 30 and −174 ppm for $[(Ph_3P)_2P]^+$ and 23 and −120 ppm for $[(Ph_3P)_2PH]^{2+}$, whereas computationally they are 37.5 and −103 ppm for $[(Ph_3P)_2P]^+$ and 32.3 and −44.1 ppm for $[(Ph_3P)_2PH]^{2+}$, respectively.[35,44] While the actual shift values are different, the correlation between observed and computed values is acceptable, with a line fitting error value of R = 0.982. This is in spite of the probable free rotations of the PPh_3 groups in solution. This computed NMR procedure was applied to the CTIs **1**−**10** here. Figure 7 shows the excellent agreement between observed and computed ^{31}P NMR shifts. The line fitting error values of R = 0.999 were found for the 5- and 6-membered ring CTIs whereas a slightly less accurate fit of R = 0.998 was estimated for the 7-membered ring CTIs. The optimized geometries of **1**−**10** are therefore appropriate and likely to be found experimentally.

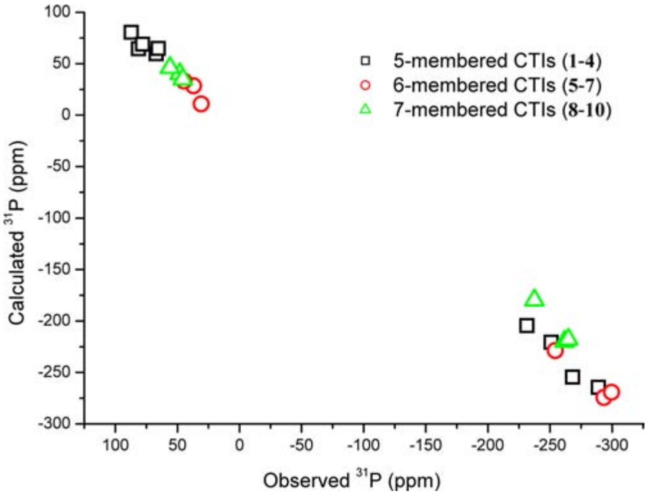
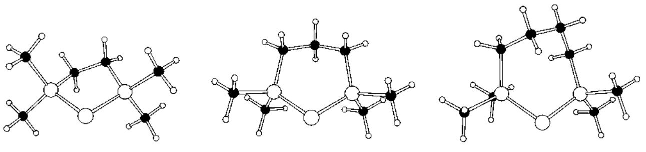


Figure 7. Comparison between computed and observed values for CTIs **1**−**10**.

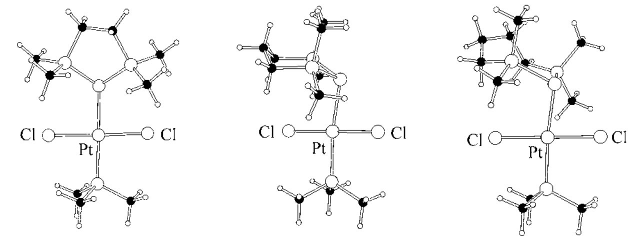
Figure 8 shows three optimized model geometries of **43**, **44**, and **45** to represent the 5- (**2**−**4**), 6- (**5**−**7**), and 7- (**8**−**10**) membered CTIs, respectively. It is shown here that the P—P—P angles and P—P—P—C torsion angles widen as the ring size increases, yet the averaged P—P bond lengths are similar. The seven-membered ring CTI has two nonequivalent P—P bonds and P—P—P—C torsion angles; thus, it is likely that the two mirror image conformers are fluxional in solution, which may explain the slightly lower R = 0.998 value for the 7-membered ring CTIs. The methyl groups point toward the area of the P_A phosphorus atom as the ring size increases. Hence steric effects increase, especially with more bulky groups than methyl, when coordination to the P_A atom is considered.



	43	**44**	**45**
P-P	2.164 Å	2.161 Å	2.156/2.171 Å
P-P-P	90.3°	96.1°	99.5°
P-P-P-C	10.4°	38.7°	16.8/54.8°

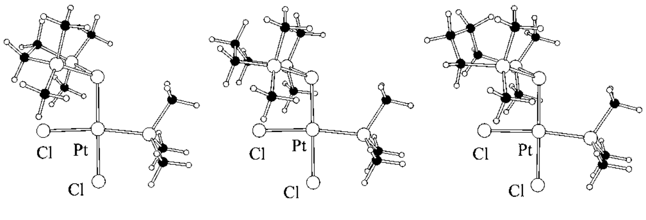
Figure 8. Calculated geometries of model CTIs **43** (n = 2), **44** (n = 3), and **45** (n = 4) derived from $Me_2P(CH_2)_nPMe_2$.

(ii). Pt(II) Complexes of CTIs. The geometries of the platinum complexes were optimized with the model CTIs **43**, **44** and **45** as the CTI ligand and trimethylphosphine, PMe_3, was used to model the phosphine ligand, PEt_3, PMe_2Ph or $PMePh_2$. Figures 9 and 10 depict the most stable geometries



trans-Pt complex with CTI **43** *trans*-Pt complex with CTI **44** *trans*-Pt complex with CTI **45**

Figure 9. Optimized geometries of *trans*-Pt(PMe_3)(CTI)Cl_2 complexes.



cis-Pt complex with CTI **43** *cis*-Pt complex with CTI **44** *cis*-Pt complex with CTI **45**

Figure 10. Computed geometries of *cis*-Pt(PMe_3)(CTI)Cl_2 complexes.

located for the trans- and cis-platinum complexes. The three trans-complexes show different CTI orientations, reflecting the steric influences of the different CTI ring sizes. These orientations affect the P−P bond lengths from 2.206 for the 5-membered, 2.218 for the 6-membered, and 2.224 Å for the 7-membered CTI ligand. The Pt−P bonds are, however, consistent across the series with ranges of 2.338−2.342 Å determined for Pt−P(phosphine, PMe_3) bonds and 2.391−2.431 Å for the Pt−P(CTI) bonds. The short Pt-phosphine and long Pt−P(CTI) bonds are in accord with the large ^1J(Pt−P) values observed for the P(phosphine) peaks and small ^1J(Pt−P) coupling constants for the P(CTI) peaks.

For the cis-complexes with model CTIs **43**, **44**, and **45**, the orientation of the CTI ligand is inevitably identical across the series, because of unfavorable steric interactions with the neighboring phosphine, PMe_3. The Pt-phosphine bond lengths are 2.306−2.309 Å, which are some 0.03 Å shorter that those found for the trans-complexes. This is reflected in the larger Pt−P coupling constants seen for the phosphine peaks in the cis-isomers compared to those couplings observed for the phosphine peaks in the trans-complexes. However, the geometries for the cis-complexes show comparatively short Pt−P(CTI) bonds of 2.328−2.332 Å which, while still longer than the Pt−P phosphine bonds, do not support the small ^1J(Pt−P) coupling constants observed for the P(CTI) peaks, assuming that these coupling constants are directly related to Pt−P distances. The experimental results are entirely self-consistent, however, suggesting that there may be other factors involved which we are unable to model satisfactorily. The long calculated P−P distances of 2.244 to 2.258 Å suggest that they are single bonds.

Figure 11 shows the comparison between observed and computed ^{31}P NMR shifts for the trans- and cis-complexes of the CTIs **2**−**10** with the phosphine, PMe_3, used to model the PR_3 ligand in all cases. It is clear that while the shifts of the phosphines (P_E) and the P_D atoms of the CTI ligands are in broad agreement, the shifts for the P_C atoms vary considerably. The optimized geometries for the trans-complexes with 5- and 6- membered ring CTIs (*R* = 0.998 and 0.992 respectively) are considered as appropriate models, whereas the optimized geometries for the trans- and cis-complexes with 7-membered CTIs are likely to have the environment of the P_C atom incorrectly modeled (with *R* values between 0.572 and 0.965).

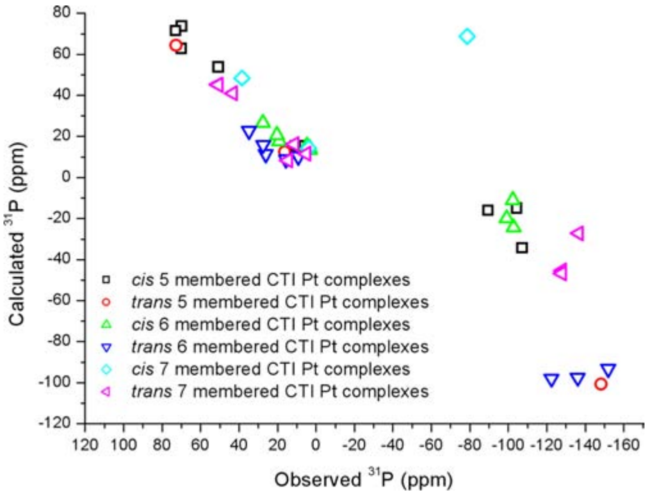


Figure 11. Comparison between computed and observed values for platinum complexes of CTIs **2**−**10** with the PMe_3 ligand in the optimized geometries and the PEt_3 ligand in experimental complexes.

Despite the poor agreement for the P_E and P_C atoms in some complexes, computed NMR shifts for all complexes show that the predicted ^{31}P shift for P_C is always at a higher frequency than for P_E within each complex. This is in accord with experimental ^{31}P data where both isomers of the complex could be observed.

The cis-isomer is considered as the thermodynamic product whereas the trans-isomer is the kinetic product according to NMR observations. Here, relative energies computed using the solvation model (with a dielectric constant, *ε*, of 35.7) support this deduction (Table 8).[46] For complexes from the CTIs **1**−**9**, the energies required for cis to trans isomerization are between 4.1 and 10.0 kcalmol^{-1}. The calculated isomerization energy at 0.0 kcal mol^{-1} for the complexes from the 7-membered CTI **10**, suggests that the steric effects of the 7-membered CTI **10** are considerable compared to other CTIs in the cis-complexes here.

The question of why the CTI **1** derived from dppe does not form a Pt complex has been explored here by looking at the relative energies of the CTI Pt complexes and $[(Me_3P)PtCl_2]_2$ with different CTIs (Table 8). The reaction of $[(Me_3P)PtCl_2]_2$ with CTI **1** to form the cis-complex is endothermic (5.6 kcalmol^{-1}) whereas the reaction of $[(Me_3P)PtCl_2]_2$ with CTI **2** to form the cis-complex is exothermic (−5.5 kcalmol^{-1}). The Pt complex with CTI **10** is endothermic at 13.8 kcalmol^{-1} because of the considerable steric effects of the *tert*-butyl groups in the cis-complex. The cis-complex from CTI **10** was not observed experimentally. Examination of the optimized geometry of the Pt complex with CTI **1** did not show any obvious steric effects. It is likely that formation of the Pt complex would not be favorable because of electronic effects, where the phenyl groups reduce the electron density on the P_A atom, making it a poor donor, so that it does not coordinate to the platinum experimentally.

The relationship between the CTI, the heterocyclic N−P−N phosphenium cation, and the Ph_2P phosphide anion was explored using models **43**, **46**, and **47** for these respective

Table 8. Energies[a] for the cis to trans Isomerizations of the Model Pt Complexes and for Formations of the Model Pt Complexes

CTI	cis to trans isomerization of the Pt complex	formation of the cis-complex 0.5 $[(Me_3P)PtCl_2]_2$ and CTI **1** to $(Me_3P)Pt(CTI)Cl_2$
1	4.4	5.6
2	5.5	−5.5
3	7.2	0.9
4	6.9	−2.7
5	7.3	−12.5
6	9.2	−0.3
7	5.2	−4.5
8	10.0	1.3
9	4.1	−2.8
10	0.0	13.8

[a] In kcal mol^{-1}.

ligands (Figure 12). Calculated natural charges for these models show that the CTI ligand has the charge distribution shown in Figure 2, and the charge on the P_A atom is more like that on the P atom in the phosphide **47** than in the phosphenium ion **46**.

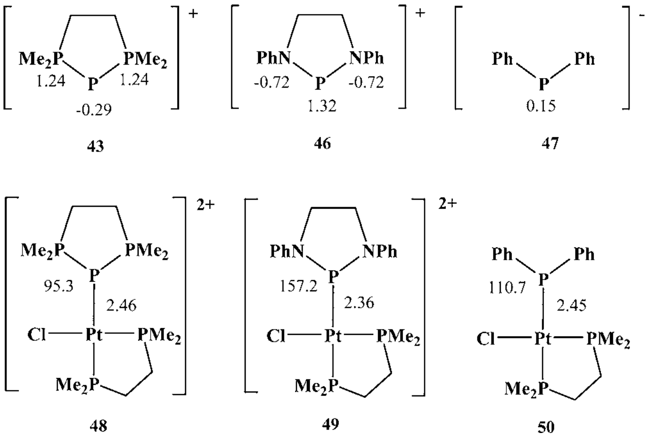


Figure 12. Comparison of (above) natural charges at P and N atoms for model ligands **43**, **46**, and **47** and (below) of P−Pt bond lengths and pyramidal angles at P for model complexes **48**, **49**, and **50**.

Optimized geometries for model platinum complexes $[Pt(dpme)Cl(L)]^{n+}$ **48**, **49**, and **50** with L as **43**, **46**, and **47** respectively (Figure 12) reveal long Pt−P bonds of 2.45−2.46 Å and pyramidal coordination at P for the ligands L in **48** and **50**. By contrast, the Pt−P bond is shorter at 2.36 Å and a more planar conformation is found at the P atom in the phosphenium ligand. Thus the CTI as a ligand behaves similarly to the Ph_2P monoanion (terminal phosphide) in complex **50** rather than to the phosphenium cation in complex **49**.

■ CONCLUSIONS

We have shown conclusively that CTIs of various ring sizes are capable of coordinating to a platinum(II) moiety via the central phosphorus atom, P_A, provided that the substituents on the outer phosphorus atoms (P_B and/or $P_{B'}$) are not all aromatic groups. Even the CTI derived from dedppe formed complexes in this way. Both trans- (the kinetic reaction product) and/or cis- (the thermodynamic reaction product) complexes have been identified in solution by ^{31}P NMR spectroscopy; over 30 complexes have been thus produced. Unfortunately, despite our best efforts to obtain one of the complexes in crystalline form, any crystals isolated have been from either the platinum(II) dimer starting material or the decomposition products. Nevertheless, the geometries of the complexes are supported by DFT calculations. Complete removal of solvent was not attempted, since it was clear from the NMR spectra (see Figures 5 and 6 for typical examples) that although the CTI complexes were the predominant species in solution, there were minor amounts of impurities present. Hence the likelihood of obtaining pure material for further characterization was remote. Since these complexes are necessarily ionic, with very large cations, it seems probable that they will have very low lattice energies, and will be soluble in nonpolar as well as polar solvents, similar to salts of large tetra-alkyl ammonium cations. This may explain why techniques such as layering the reaction mixture with a nonpolar solvent such as hexane did not lead to the formation of crystals of the CTI complexes.

Irrespective of CTI ring size or geometry of the complex, the most remarkable feature of the solution-state NMR results is a comparatively small $^1J_{PtP}$ to the central phosphorus atom (P_C) of the CTI, between 943 and 1267 Hz, whereas the phosphane coligand which is an artifact of the preparative procedure has a normal $^1J_{PtP}$ value (2200−3000 Hz for trans, 3200−4000 Hz for cis), consistent with the geometry. In this respect the CTI complexes behave similarly to terminal phosphido-complexes.[43] The data strongly suggest that the CTIs coordinate comparatively weakly and that the bond from platinum to P_C is a long one, possibly because of repulsion between two species with overall positive charges, although the geometry at phosphorus may also play an important role.

■ EXPERIMENTAL SECTION

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo, using standard Schlenk line or glovebox techniques. Chemicals of the best available commercial grade were used, in general without further purification. The ^{31}P NMR spectra of diposphanes were recorded, to verify that no major impurities were present. ^{31}P NMR spectra were recorded on a Varian Mercury 300 or Varian VXR 400 Fourier-transform spectrometer at 121.4 and 161.9 MHz, respectively. Chemical shifts were measured relative to external H_3PO_4 (^{31}P), with the higher frequency direction taken as positive.

Example Reaction. Reaction of the CTI (2) with *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$. depe (0.0300 g, 0.14 mmol) and $SnCl_2$ (0.0265 g, 0.14 mmol) were dissolved in 1.0 mL of $CDCl_3$. PCl_3 (0.014 mL, 0.14 mmol) was then added, and a $^{31}P\{^1H\}$ NMR spectrum recorded soon after mixing to confirm the formation of the cyclic triphosphenium ion. When necessary, residual PCl_3 was removed in vacuo. *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ dimer (0.0560 g, 0.07 mmol) was then added to the solution.

Quantities of reagents used in all reactions are shown in Table 9.

Table 9. Quantities of Reagents Used

compound number	quantity of diphosphane		quantity of PCl_3		quantity of $SnCl_2$		quantity of Pt dimer	
	g	mmol	mL	mmol	g	mmol	g	mmol
11	0.0530	0.26	0.020	0.23	0.0474	0.25	0.0960	0.13
12	0.0300	0.14	0.014	0.16	0.0265	0.14	0.0560	0.07
13/14	0.2061	0.49	0.030	0.34			0.1409	0.18
15	0.0193	0.05	0.004	0.05	0.0095	0.05	0.0202	0.03
16/17	0.0310	0.07	0.010	0.11	0.0139	0.07	0.0342	0.04
18	0.4228	1.40	0.14	1.60	0.2654	1.40	*a*	*a*
19/20	0.0642	0.19	0.015	0.17			0.0456	0.05
21	0.0230	0.10	0.010	0.11	0.0197	0.10	0.0398	0.05
22	0.0140	0.06	0.005	0.06	0.0114	0.06	0.0242	0.03
23	0.0210	0.10	0.010	0.11	0.0190	0.10	0.0242	0.03
24/25	0.0808	0.18	0.010	0.11			0.0547	0.07
26	0.0239	0.05	0.005	0.06	0.0157	0.08	0.0192	0.03
27	0.0260	0.06	0.005	0.06	0.0114	0.06	0.0242	0.03
28/29	0.0446	0.10	0.010	0.11			0.0466	0.05
30	0.0397	0.14	0.010	0.11			0.0513	0.06
31/32	0.0136	0.05	0.004	0.05	0.0100	0.05	0.0191	0.03
33	0.1411	0.31	0.020	0.23			0.1071	0.14
34	0.0900	0.20	0.018	0.20	0.0400	0.20	0.1532	0.20
35/36	0.0733	0.16	0.014	0.16	0.0303	0.16	0.0647	0.08
37	0.0569	0.13	0.010	0.11			0.0498	0.05
38	0.0305	0.11	0.010	0.11			0.0466	0.05
39	0.0280	0.10	0.010	0.11	0.0291	0.15	0.0583	0.08
40	0.0235	0.08	0.007	0.08	0.0151	0.08	0.0323	0.04
41	0.1550	0.40	0.040	0.44	0.0810	0.43	*a*	*a*
42	0.0386	0.18	0.016	0.18			0.0850	0.09

[a] Dimer was not added quantitatively.

COMPUTATIONAL SECTION

All computations were carried out with the Gaussian 09 package.[47] Geometry optimizations for all compounds discussed here were carried out with the DFT-hybrid functional B3LYP[48] using the 6-31G* basis set[49] for all atoms except for Pt where the pseudopotential LANL2DZ[50] was used. No symmetry constraints were used in all cases. Calculated ^{31}P NMR chemical shifts at the GIAO[51]-B3LYP/6-31G* level were obtained from the optimized geometries using the $\delta(^{31}\mathrm{P}) = 350.0 - \sigma(^{31}\mathrm{P})$ scale.

ASSOCIATED CONTENT

Supporting Information

Cartestian coordinates of optimized geometries of CTIs **1−10** and their $(\mathrm{Me_3P})\mathrm{Pt(CTI)Cl_2}$ complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: k.b.dillon@durham.ac.uk.

Present Address

[†] Dr. John Garang Memorial University of Science and Technology, Bor-Jongfei State, Republic of South Sudan.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank A. M. Kenwright, I. H. McKeag, and C. F. Heffernan for their invaluable assistance in recording some of the NMR spectra; the Maria da Graça Memorial Fund/Department of Chemistry, University of Durham for financial support (to P.K.C.); Professor Todd B. Marder of the Department of Chemistry, University of Durham, for a gift of depdppe; and Johnson Matthey for the loan of Pt(II) salts.

ABBREVIATIONS

CTI, cyclic triphosphenium ion; dcypb, 1,4-bis(dicyclohexylphosphino)butane; dcype, 1,2-bis(dicyclohexylphosphino)ethane; dcypp, 1,3-bis(dicyclohexylphosphino)propane; dedppe, (1-diethylphosphino-2-diphenylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; depp, 1,3-bis(diethylphosphino)propane; dippb, 1,4-bis(di-iisopropylphosphino)butane; dippp, 1,3-bis(di-isopropylphosphino)propane; dppe, 1,2-bis(diphenylphosphino)ethane; dtbpox, bis(α,α-di-t-butylphosphino)-o-xylene

REFERENCES

(1) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 63−64.

(2) Schmidpeter, A.; Lochschmidt, S.; Burget, G.; Sheldrick, W. S. *Phosphorus Sulfur* **1983**, *18*, 23−26.

(3) Schmidpeter, A.; Lochschmidt, S. *Z. Naturforsch. B* **1985**, *40*, 765−773.

(4) Schmidpeter, A.; Lochschmidt, S. *Phosphorus Sulfur* **1986**, *29*, 73−109.

(5) Schmidpeter, A.; Lochschmidt, S. *Inorg. Synth.* **1990**, *27*, 255−256.

(6) Gamper, S. F.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 601−604.

(7) Ellis, B. D.; Carlesimo, M.; Macdonald, C. L. B. *Chem. Commun.* **2003**, 1946−1947.

(8) Ellis, B. D.; Macdonald, C. L. B. *Inorg. Chem.* **2006**, *45*, 6864−6874.

(9) Norton, E. L.; Szekely, K. L. S.; Dube, J. W.; Bomben, P. G.; Macdonald, C. L. B. *Inorg. Chem.* **2008**, *47*, 1196−1203.

(10) Ellis, B. D.; Macdonald, C. L. B. *Acta Crystallogr., Sect. E* **2006**, *62*, m1235−m1236.

(11) Kilian, P.; Slavin, A. M. Z.; Woollins, D. J. *Dalton Trans.* **2006**, 2175−2183.

(12) Boon, J. A.; Byers, H. L.; Dillon, K. B.; Goeta, A. E.; Longbottom, D A. *Heteroat. Chem.* **2000**, *11*, 226−231.

(13) Barnham, R. J.; Deng, R. M. K.; Dillon, K. B.; Goeta, A. E.; Howard, J. A. K.; Puschmann, H. *Heteroat. Chem.* **2001**, *12*, 501−510.

(14) Dillon, K. B.; Monks, P. K.; Olivey, R. J.; Karsch, H. H. *Heteroat. Chem.* **2004**, *15*, 464−467.

(15) Burton, J. D.; Deng, R. M. K.; Dillon, K. B.; Monks, P. K.; Olivey, R. J. *Heteroat. Chem.* **2005**, *16*, 447−452.

(16) Deng, R. M. K.; Dillon, K. B.; Goeta, A. E.; Thompson, A. L. *Acta Crystallogr., Sect. E* **2005**, *61*, m296−m298.

(17) Bashforth, R.; Boyall, A. J.; Dillon, K. B.; Monks, P. K.; Potts, J. C. *Inorg. Chim. Acta* **2011**, *376*, 325−331.

(18) Ellis, B. D.; Macdonald, C. L. B. *Coord. Chem. Rev.* **2007**, *251*, 936−973.

(19) Dillon, K. B.; Monks, P. K. *Dalton Trans.* **2007**, 1420−1424.

(20) Blake, A. J.; Gould, R. O.; Marr, A. M.; Rankin, D. W. H.; Schröder, M. *Acta Crystallogr., Sect. C* **1989**, *45*, 1218−1219.

(21) Cornet, S. M. M.; Dillon, K. B.; Goeta, A. E.; Thompson, A. L. *Acta Crystallogr., Sect. C* **2005**, *61*, m74−m75.

(22) Dillon, K. B.; Goeta, A. E.; Monks, P. K.; Shepherd, H. J. *Polyhedron* **2010**, *29*, 606−612.

(23) Coffer, P. K.; Dillon, K. B.; Howard, J. A. K.; Probert, M. R.; Shepherd, H. J. in preparation.

(24) Boyall, A. J.; Dillon, K. B.; Monks, P. K.; Potts, J. C. *Heteroat. Chem.* **2007**, *18*, 609−612.

(25) Albinati, A.; Pregosin, P. S.; Ruegger, H. *Inorg. Chem.* **1984**, *23*, 3223−3229.

(26) Clark, H. C.; Ferguson, G.; Hampden-Smith, M. J.; Ruegger, H.; Ruhl, B. L. *Can. J. Chem.* **1988**, *66*, 3120−3127.

(27) Gómez, M.; Muller, G.; Sainz, D.; Sales, J.; Solans, X. *Organometallics* **1991**, *10*, 4036−4045.

(28) Cavinato, G.; De Munno, G.; Lami, M.; Marchionna, M.; Toniolo, L.; Viterbo, D. *J. Organomet. Chem.* **1994**, *466*, 277−282.

(29) Farkas, E.; Kollár, L.; Moret, M.; Sironi, A. *Organometallics* **1996**, *15*, 1345−1350.

(30) Dahlenburg, L.; Mertel, S. *J. Organomet. Chem.* **2001**, *630*, 221−243.

(31) Casey, C. P.; Martins, S. C.; Fagan, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 5585−5592.

(32) Anderson, G. K.; Davies, J. A.; Shoeck, D. J. *Inorg. Chim. Acta* **1983**, *76*, L251−L252.

(33) Anderson, G. K.; Lumetta, G. J. *Inorg. Chem.* **1987**, *26*, 1518−1524.

(34) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

(35) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff, K.; Sheldrick, W. S. *J. Chem. Soc., Chem. Commun.* **1985**, 1447−1448.

(36) Dillon, K. B.; Olivey, R. J. *Heteroat. Chem.* **2004**, *15*, 150−154.

(37) Dillon, K. B.; Goeta, A. E.; Howard., J. A. K.; Monks, P. K.; Shepherd, H. J.; Thompson, A. L. *Dalton Trans.* **2008**, 1144−1149.

(38) Bashforth, R.; Boyall, A. J.; Coffer, P. K.; Dillon, K. B.; Goeta, A. E.; Howard, J. A. K.; Kenwright, A. M.; Probert, M. R.; Shepherd, H. J.; Thompson, A. L. *Dalton Trans.* **2012**, *41*, 1165−1172.

(39) Abrams, M. B.; Scott, B. L.; Baker, R. T. *Organometallics* **2000**, *19*, 4944−4956.

(40) Hardman, N. J.; Abrams, M. B.; Pribisko, M. A.; Gilbert, T. M.; Martin, R. L.; Kubas, G. J.; Baker, R. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 1955−1958.

(41) Caputo, C. A.; Jennings, M. C.; Tuononen, H. M.; Jones, N. D. *Organometallics* **2009**, *28*, 990−1000.

(42) Caputo, C. A.; Brazeau, A. L.; Hynes, Z.; Price, J. T.; Tuononen, H. M.; Jones, N. D. *Organometallics* **2009**, *28*, 5261−5265.

(43) (a) Handler, A.; Peringer, P.; Műller, E. P. *J. Chem. Soc., Dalton Trans.* **1990**, 3725−3727. (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *Inorg. Chim. Acta* **1991**, *189*, 105−110. (c) Maassarani, F.; Davidson, M. F.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, M. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1995**, *235*, 327−338. (d) Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125−127. (e) Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Haar, C. M.; Nolan, S. P. *Organometallics* **1998**, *17*, 652−660. (f) Wicht, D. K.; Glueck, D. S.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5130−5140. (g) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141−5151. (h) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381−5394. (i) Kovacik, I.; Wicht, D. K.; Grewal, N. S.; Glueck, D. S.; Incarvito, C. D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2000**, *19*, 950−953. (j) Zhuravel, M. A.; Glueck, D. S.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 3208−3214. (k) Scriban, C.; Glueck, D. S.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2006**, *25*, 5435−5448.

(44) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226−227.

(45) Ellis, B. D.; Macdonald, C. L. B. *Acta Crystallogr., Sect. E* **2006**, *62*, m1869−m1870.

(46) Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278−279.

(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(48) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(49) (a) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081−6090. (b) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193−2218.

(50) (a) Dunning, T. H. Jr.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(51) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807. (b) Rohling, C. M.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9−15. (c) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.