Transition Metal-Carbon Bonds. Part 53.[1] The Further Chemistry of Cyclometallated Complexes formed from $Bu^t_2P(CH_2)_5PBu^t_2$ and $PtCl_2$: Crystal Structure of $[PtCl\{Bu^t_2PCH_2CH_2C{=}CHCH_2PBu^t_2\}]$ †

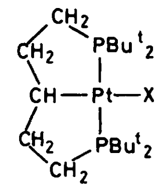
By **John R. Briggs, Anthony G. Constable, Walter S. McDonald,***‡ and **Bernard L. Shaw,*** School of Chemistry, The University of Leeds, Leeds LS2 9JT

The cyclometallated complex $[PtCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$ (1a) reacts with CO, CNMe, or $CNBu^t$ (Y) in the presence of $NaBPh_4$ to give the salts $[PtY\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}][BPh_4]$ (2). The carbonyl complex when treated with NaOMe gives the hydride $[PtH\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$. We have previously reported that $[PtCl_2(NCBu^t)_2]$ reacts with $Bu^t_2P(CH_2)_5PBu^t_2$ to give a number of species, including (1a) inseparably mixed with another complex. We have now separated this complex and identified it as $[PtCl\{Bu^t_2PCH_2CH_2C{=}CHCH_2PBu^t_2\}]$ (3). The compound $Ph_3C^+BF_4^-$ converts (1a) into the olefin complex $[PtCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2PBu^t_2\}][BF_4]$ (5). Attempts to deprotonate (5) and other complexes with various bases, to give (3), were unsuccessful; various products were formed for which some structures are suggested. Crystals of (3) are monoclinic, space group $P2_1/c$, with a = 1.2319(3), b = 1.4370(4), c = 1.4693(3) nm, and β = 104.58(2)°. The structure was determined from 2 457 F_o and refined to R = 0.049. The molecule is disordered.

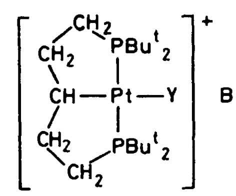
In previous papers from this laboratory we have shown that bulky bis(tertiary-butylphosphino) groups in bis(di-tertiary-butylphosphino)alkane ligands, $Bu^t_2P(CH_2)_n$-PBu^t_2 (n = 5—10 or 12), can promote large chelate-ring formation and cyclometallation reactions.[2-7] This paper describes work extending the chemistry of the pentamethylene diphosphine, $Bu^t_2P(CH_2)_5PBu^t_2$, with platinum. We have previously shown that treatment of either $[PtCl_2(NCBu^t)_2]$ or $[PtCl_2(NCPh)_2]$, in refluxing toluene or 2-methoxyethanol, with this diphosphine, gives a variety of products. In addition to an insoluble large ring complex, $[PtCl_2\{Bu^t_2P(CH_2)_5PBu^t_2\}]_x$ (where x is probably 2), a mixture of two light petroleum-soluble complexes (A) and (B) was obtained.[4] This highly soluble mixture [typically 80% (A) and 20% (B)] could not be separated. On one occasion, however, pure (A) was obtained and shown to be the cyclometallated complex $[PtCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$ (1a). It was then found that the pure complex (1a), uncontaminated by (B), could be prepared by treating the binuclear complex, $[Pt_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, with CF_3CO_2H to give the cyclometallated trifluoroacetate (1b), which was then converted into (1a) with lithium chloride in acetone. The corresponding complexes (1c), (1d), and (1e) with X = Br, I, or H respectively were also prepared.[4] Moreover, the (A), (B) chloride mixture was converted into the corresponding mixture with the anionic ligands: O_2CCF_3, Br, Ir, or H. In each case the same proportions (typically 4 : 1) were preserved and the mixture could not be separated. The ^{31}P-$\{^1H\}$ n.m.r. spectra showed that δ(P) for the (B) type complex was *ca.* 3 p.p.m. to high frequency of that of the corresponding (A) complex, (1a)—(1e), and ^1J(PtP) was 100—200 Hz less.[4] In our previous paper we tentatively formulated these (B) complexes with a π-allylic system *viz.* as $[PtX\{Bu^t_2PCH_2CH \cdots CH \cdots CHCH_2PBu^t_2\}]$.[4] We now show that this is wrong and have determined their true nature.

RESULTS AND DISCUSSION

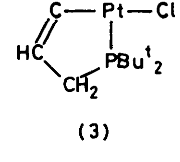
The complexes (A) [*i.e.* (1a)] and (B) have many similar properties, *e.g.* solubility, volatility, and chromatographic behaviour and all attempts to separate them by physical means were unsuccessful. However, we had observed



(1a) X = Cl
(1b) X = O_2CCF_3
(1c) X = Br
(1d) X = I
(1e) X = H



(2a) Y = CO
(2b) Y = CNMe
(2c) Y = $CNBu^t$



(3)

---

† [1,5-Bis(di-t-butylphosphino)pent-2-en-3-yl-C^3PP']chloroplatinum(II).

‡ For correspondence on crystallographic part.

TABLE 1

Analytical (%: calculated values in parentheses), conductivity, and melting point data for the pentamethylene diphosphine derivatives

	Analyses				
Complex	C	H	N	Conductivity [a]	M.p. (θ_c/°C)
(2a)	60.9 (61.25)	7.05 (7.25)		98.7	205—207
(2b)	61.75 (61.7)	7.45 (7.5)	1.6 (1.55)	77.2	245—249
(2c)	62.8 (62.75)	7.55 (7.8)	1.55 (1.5)	87.9	215—217
(5)	37.55 (37.3)	6.55 (6.55)		67.5	225—245 [b]

[a] In Ω^{-1} mol^{-1} cm^2. At 20 °C in acetone. [b] With decomposition.

TABLE 2

Phosphorus-31 and ^{1}H n.m.r. data

Complex	δ(P) [a]	^1J(PtP)/Hz	δ(PBu^t)	$\lvert{}^3J$(PH) + ^5J(PH)$\rvert$/ Hz	δ(RNC) [b]
(2a)	102.9	2 613	1.27	12.2	
			1.30	12.2	
(2b)	92.9	2 766	1.24	13.9	2.21
			1.28	13.9	
(2c)	93.4	2 776	1.26	13.7	1.41
			1.30	14.2	
(5)	72.2 [c]	2 258	1.39	14.2	
	−67.7	1 590	1.40	15.1	
			1.48	14.4	
			1.58	15.9	
(3)	79.8	2 988	1.41	13.7	

In CDCl$_3$. In p.p.m. to high frequency of H$_3$PO$_4$. [b] In p.p.m. relative to SiMe$_4$. [c] ^2J(PP) = 347 Hz.

that for (1a) ν(Pt–Cl) = 270 cm^{-1} and for (B) ν(Pt–Cl) = 280 cm^{-1}. We reasoned therefore that the chlorine in (1a) might be more readily displaced by a neutral ligand, to give a salt than the chlorine from (B). We thus first studied the formation of cations from (1a).

We find that treatment of (1a) with carbon monoxide, methyl isocyanide, or t-butyl isocyanide in refluxing ethanol, in the presence of sodium tetraphenylborate, gives $[PtY\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}][BPh_4]$ [Y = CO (2a); CNMe (2b); CNBu^t (2c)]. Characterizing microanalytical, and conductivity data are in Table 1, and n.m.r. data in Table 2. The complexes are colourless, crystalline solids which are stable in air and in solution. The ^{31}P-{^{1}H} n.m.r. spectra show 1 : 4 : 1 triplets, the values of ^1J(PtP), at 2 600—2 800 Hz, being several hundred Hz lower than that of (1a) (3 164 Hz). The ^{1}H n.m.r. spectra show two triplets for the two sets of inequivalent Bu^t groups, which collapse into singlets in the ^{1}H-{^{31}P} spectrum.

We then treated the (A),(B) mixture with carbon monoxide in refluxing ethanol–NaBPh$_4$ for 1 h and were gratified to find, by ^{31}P-{^{1}H} n.m.r. spectroscopy, that (A) [*i.e.* (1a)] was completely converted to the salt (2a) under these conditions, but that (B) was largely untouched. There were, additionally, resonances due to a small amount of a new complex, which was possibly a carbon monoxide salt generated from (B) [δ(P) = 105.7 p.p.m., ^1J(PtP) = 2 463 Hz]. The separation of neutral (B) from the salt (2a) *etc.*, was readily achieved and it formed needles from hexane. The mass spectrum of (B) shows a molecular ion cluster, *m/e* 584—592, corresponding to $C_{21}H_{43}ClP_2Pt$, with the most intense peak at *m/e* = 588, *i.e.* two hydrogens less than (1a) which shows a molecular ion cluster, 586—594, with the most intense peak at *m/e* = 590. The ^{31}P-{^{1}H} n.m.r. spectrum at 40 MHz showed a sharp central peak with sharp satellites due to platinum-195 coupling. This led us to think that the phosphorus atoms are chemically and magnetically equivalent. However, a ^{31}P-{^{1}H} n.m.r. spectrum at 160 MHz just resolved the central peak and one of the satellites into 1 : 1 doublets (see Figure 1). We interpret this spectrum as showing that the two phosphorus atoms have slightly different chemical shifts but that the outer peaks of the resultant AB patterns are so weak as not to be observed. In the proton spectrum at 400 MHz the t-butyl resonances occur as two equally intense triplets, $|{}^3J(PH) + {}^5J(PH)|$ = 13.5 Hz. The methylene resonances were not resolved but there was a resonance corresponding to one hydrogen at δ = 5.69, with a very complex central pattern with satellites due to platinum-195 coupling, J(PtH) ~ 110 Hz (see Figure 2). We assign this to an alkenyl hydrogen and formulate the complex (B) as in (3), $[PtCl\{Bu^t_2PCH_2CH_2C{=}CHCH_2PBu^t_2\}]$ with two phosphorus donor atoms which have almost the same chemical shift. The value of J(PtH) (110 Hz) is typical of a three bond coupling.[8,9] We have attempted to determine the crystal structure of the complex by X-ray diffraction.

Crystal Structure.—The structure of the complex is shown in Figure 3 and some bond lengths and angles are given in Table 3. The structure shows quite clearly that C(2) and C(4) are not bonded to platinum; in fact C(2), C(3), C(4), and Pt are in a plane [the bond angles at C(3) are 120.1(12), 119.5(13), and 120.4(16)°]. However, the bond lengths C(2)–C(3) [1.414(23) Å] and C(3)–C(4) [1.430(23) Å] are approximately intermediate between those of double and single bonds and there are large

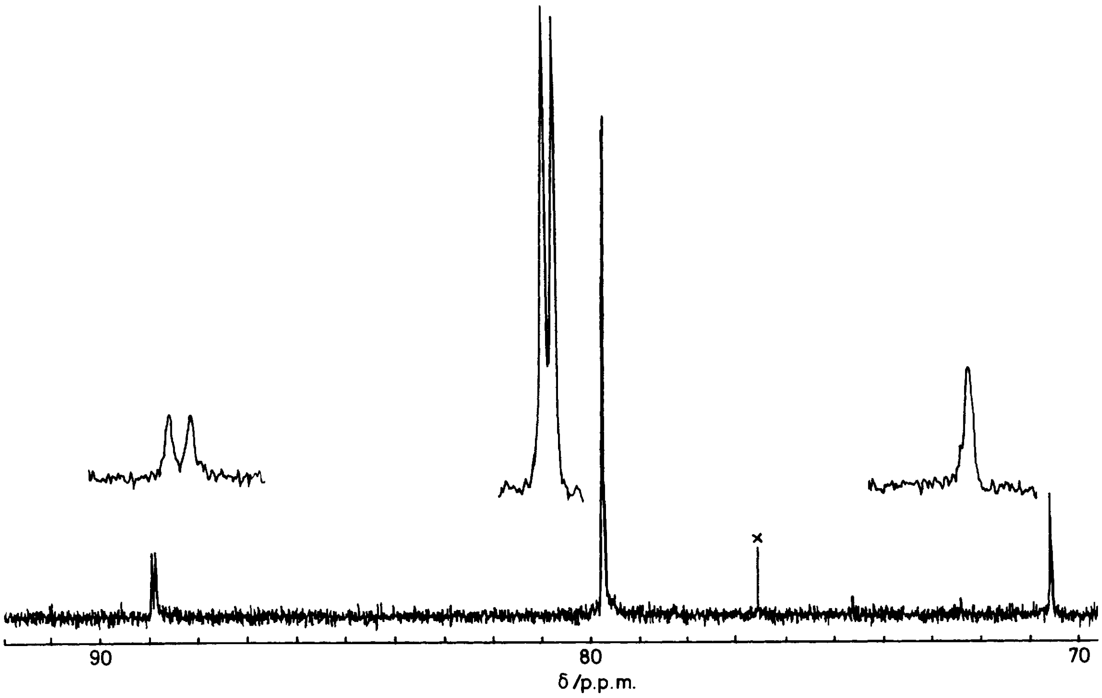


FIGURE 1 $^{31}P-\{^1H\}$ n.m.r. spectrum of (3), recorded at 160 MHz and −10 °C, in $CDCl_3$. The expansions are ×6.4. X = Impurity

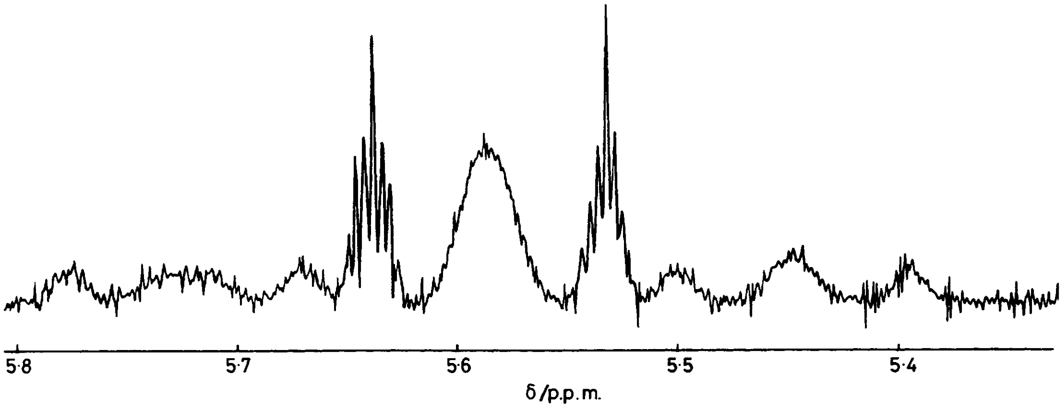


FIGURE 2 ^1H n.m.r. spectrum of (3) from δ 5.4 to 5.9 p.p.m., recorded at 400 MHz and *ca.* 20 °C, in $CDCl_3$. The resonance corresponds to one proton *i.e.* the single alkenyl proton in (3)

thermal vibrations for C(2) and C(4) at right angles to the co-ordination plane. We interpret these results in terms of a disordered structure with the carbon–carbon double bond disordered between C(2)–C(3) and C(3)–C(4). The effect of disorder in giving rise to unexpectedly short bonds between atoms and apparently high thermal vibrations is a recognised effect (see for example ref. 10).

If the structure is not disordered then it would indicate the presence of the highly improbable moiety (4), and one other hydrogen must be accommodated. There is no evidence for the presence of Pt–H from i.r. and n.m.r. spectroscopy, or crystallography, *e.g.* C(3), Pt, Cl, and the two P's are very nearly coplanar. Thus we feel that the only way we can reconcile the mass spectral and n.m.r. evidence with the crystal structure is with disorder of the C=C bond in the solid state.

Attempts to Dehydrogenate the Cyclometallated Complex (1a).—Since the alkenyl complex (3) is in effect a dehydrogenation product of (1a) we have attempted to convert (1a) into (3). On strong heating or sublimation (1a) shows no evidence of loss of dihydrogen to give (3). We have thus attempted to effect the conversion by successive loss of H^+ and H^-; or of H^- followed by H^+.

We first tried to deprotonate the cyclometallated complex (1a) or one of its salts, (2a)—(2c), by treatment with a base. In an early experiment we treated a (1a)–(3) mixture in $CDCl_3$ solution with an excess of sodium propan-2-oxide at 20 °C but observed no interchange or alteration in the proportions of the two complexes by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. However, treatment of (1a) with a large (*ca.* 20 fold) excess of sodium propan-2-oxide in refluxing propan-2-ol for 5 h gave a *ca.* 5%

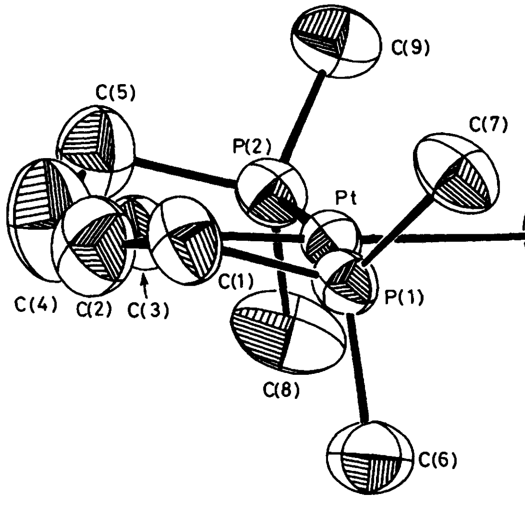


FIGURE 3 ORTEP drawing of the molecular structure of (3) showing atom numbering. For clarity, the methyls have been omitted; 50% probability thermal ellipsoids are shown

conversion to two new complexes. The ^{31}P n.m.r. parameters for these two complexes were $\delta P = 77.3$, $^1J(PtP) = 3\,213$ and $\delta P = 80.2$ p.p.m., $^1J(PtP) = 3\,237$ Hz, but none of complex (3). We did not pursue this line further and did not identify the complexes. Treatment of the carbonyl cationic complex (2a) with the sterically hindered base $LiNPr^i_2$ led to decomposition, and treatment with sodium methoxide in methanol gave a low (5%) isolated yield of the known hydride, $[\overline{PtH\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}}]$,[4] identified by its i.r. and n.m.r. parameters. This hydride was probably formed by attack of OH^- (from moisture in the sodium methoxide) on the co-ordinated carbonyl group followed by loss of CO_2 (as carbonate). Treatment of the methyl isocyanide complex, (2b), with either methyl- or n-butyl-lithium in refluxing hexane gave a very air-sensitive orange solution, from which we were unable to isolate a pure complex. The corresponding t-butyl isocyanide complex, (2c) did not react with either methyl- or t-butyl-lithium and we therefore suggest that the orange product was formed by removal of a proton from the isocyanide methyl group.

TABLE 3

Selected bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

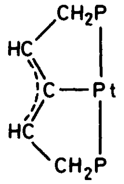
Pt–Cl	2.404(4)	Cl–Pt–P(1)	96.4(1)
Pt–P(1)	2.288(4)	Cl–Pt–P(2)	95.6(1)
Pt–P(2)	2.298(4)	C(3)–Pt–P(1)	83.7(5)
Pt–C(3)	2.033(15)	C(3)–Pt–P(2)	84.3(5)
P(1)–C(1)	1.833(15)	Cl–Pt–C(3)	176.9(5)
P(1)–C(6)	1.886(16)	Pt–P(1)–C(1)	103.1(5)
P(1)–C(7)	1.889(16)	P(1)–C(1)–C(2)	107.8(11)
P(2)–C(5)	1.884(17)	C(1)–C(2)–C(3)	120.3(15)
P(2)–C(8)	1.886(18)	C(2)–C(3)–Pt	120.1(12)
P(2)–C(9)	1.883(16)	C(4)–C(3)–Pt	119.5(13)
C(1)–C(2)	1.506(23)	C(2)–C(3)–C(4)	120.4(16)
C(2)–C(3)	1.414(23)	C(3)–C(4)–C(5)	118.5(17)
C(3)–C(4)	1.430(23)	C(4)–C(5)–P(2)	106.4(12)
C(4)–C(5)	1.506(26)	Pt–P(2)–C(5)	102.3(6)
		P(1)–Pt–P(2)	167.9(1)

Our failure to convert (1a) or the salts (2a)—(2c) to (3), or its derivative, by initial deprotonation caused us to try hydride abstraction. The hydride abstracting reagent $[CPh_3][BF_4]$ has been widely used to remove H^- from polyolefin ligands in transition metal complexes [11,12] and we hoped that it might abstract a hydride ion from (1a). Treatment of a solution of (1a) in refluxing dichloromethane with $[CPh_3][BF_4]$ for 18 h gave a moderate isolated yield (42%) of the olefin complex $[\overline{PtCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2PBu^t_2\}}][BF_4]$ (5). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this complex shows the

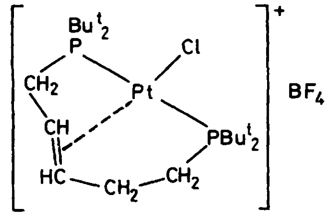
TABLE 4

Atomic co-ordinates with estimated standard deviations in parentheses

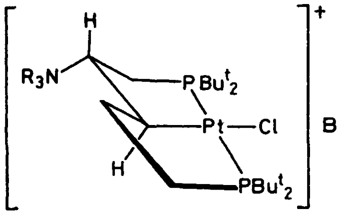
Atom	*x*	*y*	*z*
Pt	0.274 40(4)	0.033 80(4)	0.282 36(4)
Cl	0.302 5(2)	0.176 1(2)	0.205 3(2)
P(1)	0.410 0(2)	−0.050 2(2)	0.237 5(2)
P(2)	0.135 2(2)	0.090 8(2)	0.345 7(2)
C(1)	0.432 7(12)	−0.149 4(11)	0.318 5(12)
C(2)	0.329 1(17)	−0.160 6(12)	0.354 2(13)
C(3)	0.256 8(13)	−0.084 1(11)	0.353 9(11)
C(4)	0.167 9(19)	−0.090 4(13)	0.400 0(17)
C(5)	0.124 4(17)	−0.002 2(12)	0.433 4(13)
C(6)	0.361 9(13)	−0.099 6(12)	0.115 0(12)
C(7)	0.552 6(12)	0.006 7(11)	0.260 9(12)
C(8)	−0.005 2(12)	0.103 2(16)	0.258 2(16)
C(9)	0.169 5(13)	0.196 5(12)	0.423 5(12)
C(61)	0.455 6(14)	−0.155 8(13)	0.084 3(13)
C(62)	0.264 3(16)	−0.167 0(14)	0.117 7(16)
C(63)	0.319 0(18)	−0.017 8(13)	0.046 6(12)
C(71)	0.650 8(12)	−0.067 4(12)	0.270 6(13)
C(72)	0.569 4(13)	0.055 5(12)	0.355 7(13)
C(73)	0.555 9(13)	0.075 0(12)	0.182 1(13)
C(81)	−0.097 4(14)	0.135 1(14)	0.307 0(17)
C(82)	0.004 6(16)	0.168 2(17)	0.178 7(13)
C(83)	−0.037 3(18)	0.000 7(16)	0.223 9(18)
C(91)	0.104 0(18)	0.202 2(16)	0.497 9(14)
C(92)	0.296 9(14)	0.186 6(14)	0.473 1(12)
C(93)	0.155 0(18)	0.286 1(12)	0.366 4(16)



(4)



(5)



(6a) R = Me
(6b) R = Et

expected pattern; the chemical shifts of the two phosphorus nuclei being widely different (72.2 and −67.7 p.p.m.). The large negative chemical shift is characteristic of phosphorus in a four-membered ring.[6,13] The ^{1}H n.m.r. spectrum is complex but the ^{1}H-{^{31}P} n.m.r. spectrum shows four Bu^{t} resonances (δ 1.39—1.58 p.p.m.). We could not identify the alkenyl hydrogen resonances, however. Since additions to, or eliminations from, olefins prefer an antiperiplanar arrangement of the adding (eliminating) groups or atoms it is anticipated that the hydride ion lost is antiperiplanar to the platinum, *i.e.* that it is a pseudo-equatorial hydrogen and that the resultant double bond is *trans* or *E*, as shown in (5). The ion was sufficiently volatile for its tetrafluoroborate salt to give a mass spectrum around $m/e = 587$, corresponding to $[\mathrm{PtCl\{Bu^t_2PCH_2CH{=}CH(CH_2)_2PBu^t_2\}}]^+$. We hoped that treatment of this ion with a base might remove an alkenyl proton from the central carbon atom and give (3). We treated a dichloromethane solution of the salt (5) with various bases in n.m.r. tubes and followed reactions by ^{31}P-{^{1}H} n.m.r. spectroscopy. Treatment with either n-butyl-lithium or lithium di-isopropylamide gave a *ca.* 1 : 1 mixture of two products in each case. In all four complexes the ^{31}P-{^{1}H} spectra show that none of these contains strained rings, *i.e.* the δ(P) values all lie in the range +60 to +70 p.p.m., but that none of (3) was formed. We did not identify these products. We also treated a $\mathrm{CDCl_3}$ solution of the fluoroborate salt (5) with the strong base 1,8-bis(dimethylamino)naphthalene, *i.e.* ' proton sponge.' This converted it over a period of a few minutes into two very similar species, (X) and (Y), characterized by their ^{31}P n.m.r. parameters [(X) : $\delta(\mathrm{P^1}) = 74.8$, $\delta(\mathrm{P^2}) = 30.1$ p.p.m., $^{1}J(\mathrm{PtP^1}) = 3\,111$, $^{1}J(\mathrm{PtP^2}) = 2\,790$, $^{2}J(\mathrm{P^1P^2}) = 369$ Hz and (Y) : $\delta(\mathrm{P^1}) = 74.3$, $\delta(\mathrm{P^2}) = 30.0$ p.p.m., $^{1}J(\mathrm{PtP^1}) = 3\,097$, $^{1}J(\mathrm{PtP^2}) = 2\,783$, $^{2}J(\mathrm{P^1P^2}) = 371$ Hz] but no resonance due to (3) could be detected. The relatively high and positive δ(P) values suggested that none of the phosphorus donors was in a strained, *i.e.* four-membered ring and suggested that the products were formed by nucleophilic (*i.e.* nitrogen) attack on the co-ordinated olefinic double bond. Supporting evidence for this was obtained by treating a deuteriochloroform solution of (5) with $\mathrm{NMe_3}$ or $\mathrm{NEt_3}$. The ^{31}P-{^{1}H} n.m.r. spectra showed that in each case a single product was formed with very similar n.m.r. parameters to those formed by proton sponge, *viz.* for $\mathrm{NMe_3}$: $\delta(\mathrm{P^1}) = 74.1$, $\delta(\mathrm{P^2}) = 40.8$ p.p.m., $^{1}J(\mathrm{PtP^1}) = 3\,055$, $^{1}J(\mathrm{PtP^2}) = 2\,820$, $^{2}J(\mathrm{P^1P^2}) = 371$ Hz and for $\mathrm{NEt_3}$: $\delta(\mathrm{P^1}) = 75.9$, $\delta(\mathrm{P^2}) = 31.1$ p.p.m., $^{1}J(\mathrm{PtP^1}) = 3\,110$, $^{1}J(\mathrm{PtP^2}) = 2\,802$, $^{2}J(\mathrm{P^1P^2}) = 371$ Hz, as before no complex (3) was formed. We tentatively formulate these products of $\mathrm{NMe_3}$ or $\mathrm{NEt_3}$ attack as zwitterionic salts (6a) or (6b) respectively, with the amine in the pseudo-equatorial position, rather than the pseudo-axial position, which is much more sterically hindered. The 1,8-bis(dimethylamino)naphthalene products could be similar with restricted rotation around the $\mathrm{CH{-}NMe_2}$ bond giving two rotamers, *i.e.* in one case the unco-ordinated $\mathrm{NMe_2}$ group would be above the co-ordination plane ' and, in the other, below it. Tertiary amines have been shown to readily attack olefin–platinum(II)–tertiary phosphine complexes, to give zwitterions.[9,14-16] We did not attempt to characterize these products of treating (5) with tertiary amines because our principal objective was a synthesis of (3) and we had so little of (5) available (its synthesis is multi-stage and difficult). Thus, although we have not derived a good synthesis of (3) our work on hydride and proton abstraction reactions and on nucleophilic attack on these cyclometallated complexes suggest that several such reactions are possible and might yield interesting products.

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.[1] The ^{1}H, ^{1}H-{^{31}P}, and ^{31}P-{^{1}H} n.m.r. spectra were recorded with a JEOL FX 100Q n.m.r. spectrometer using an internal deuterium lock or, when indicated, on a Bruker 400 MHz spectrometer using the Science and Engineering Research Council high field n.m.r. service.

$[\mathrm{Pt(CNMe)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}][\mathrm{BPh_4}]$ (2b).—Methyl isocyanide (0.038 g, 0.93 mmol) was added to a mixture of $[\mathrm{PtCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}]$ (0.57 g, 0.85 mmol) and $\mathrm{NaBPh_4}$ (0.36 g, 1.05 mmol) in ethanol (15 cm^{3}). This mixture was refluxed for 24 h. After removal of the solvent, the residue was dissolved in dichloromethane and filtered to remove the excess of $\mathrm{NaBPh_4}$. The required product was obtained by the addition of light petroleum (b.p. 60—80 °C) as white microprisms (0.70 g, 83%). Compound $[\mathrm{Pt(CNBu^t)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}][\mathrm{BPh_4}]$ (2c) (65%) was prepared similarly.

$[\mathrm{Pt(CO)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}][\mathrm{BPh_4}]$ (2a).—Compounds $[\mathrm{Pt(O_2CCF_3)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}]$ (0.75 g, 1.12 mmol) and $\mathrm{NaBPh_4}$ (0.5 g, 1.46 mmol) were refluxed together in ethanol (15 cm^{3}) for 1 h. During this time carbon monoxide was bubbled slowly through the solution. The solvent was then removed under reduced pressure, the residue washed with water, and recrystallized from acetone as white prisms (0.73 g, 72%). This complex was also prepared from $[\mathrm{PtCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}]$.

$[\mathrm{PtCl\{Bu^t_2PCH_2CH{=}C(CH_2)_2PBu^t_2\}}]$ (3).—This complex was separated from a mixture with compound (1a), $[\mathrm{PtCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}}]$ which consisted of *ca.* 60% (1a) and 40% (3), as evidenced from the ^{31}P-{^{1}H} n.m.r. spectrum. A solution of the mixture (108 mg) and $\mathrm{NaBPh_4}$ (330 mg), in ethanol (10 cm^{3}), was refluxed for 1 h, during which carbon monoxide was bubbled through the solution. The solvent was evaporated under reduced pressure and the residue extracted into boiling n-hexane. The required complex separated as colourless needles which sublimed above 210 °C and melted at 255—258 °C. Yield 32 mg, *i.e.* approximately 75% recovery.

$[\mathrm{PtCl\{Bu^t_2PCH_2CH{=}CH(CH_2)_2PBu^t_2\}}][\mathrm{BF_4}]$ (5).—Compounds $[\mathrm{CPh_3}][\mathrm{BF_4}]$ (0.48 g, 1.45 mmol) and (1a) (0.20 g, 0.34 mmol) were mixed and refluxed in dichloromethane (10 cm^3) for 18 h under dry nitrogen. The solvent was then removed under reduced pressure and the residue recrystallized from acetone–diethyl ether at −30 °C. This gave the required product (0.078 g, 42%).

Crystal Data.—$C_{21}H_{43}ClP_2Pt$, $M = 588.07$, Monoclinic, $a = 1.231\,9(3)$, $b = 1.437\,0(4)$, $c = 1.469\,3(3)$ nm, $\beta = 104.58(2)°$, $U = 2.517\,2(10)$ nm^3, $Z = 4$, $D_c = 1.552$ Mg m^{-3}, $F(000) = 1\,176$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 71.069$ pm, μ(Mo-K_α) = 5 868 m^{-1}.

Structure Determination.—Measurements were made on a Syntex $P2_1$ diffractometer using graphite monochromated Mo-K_α radiation. Cell dimensions and their standard deviations were determined by least-squares treatment of the setting angles of 15 reflections with $35 < 2\theta < 40°$. Intensities of all independent reflections (except the 100) with $2\theta < 45°$ were measured in the ω—2θ scan mode, and the 2 457 having $I > 3\sigma(I)$ were used in the structure determination. Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic vibration parameters for all non-hydrogen atoms. Hydrogen atoms were not included, and the weighting function $w^{-1} = \sigma^2(F) + 0.0004(F)^2$ was used, with $\sigma^2(F)$ derived from counting statistics. The final R was 0.049 with $R' = 0.060$. The atomic co-ordinates and their standard deviations are given in Table 4. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23291 (16 pp.).*

We thank the S.E.R.C. for support and Johnson Matthey Ltd. for the generous loan of platinum salts.

[1/1958 *Received, 18th December, 1981*]

REFERENCES

[1] Part 52, C. Crocker, H. D. Empsall, R. J. Errington, E. M. Hyde, W. S. McDonald, R. Markham, M. C. Norton, B. L. Shaw, and B. Weeks, preceding paper.

[2] A. J. Pryde, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 1973, 947.

[3] A. J. Pryde, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1976, 322.

[4] N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1979, 1972.

[5] H. D. Empsall, E. M. Hyde, R. Markham, W. S. McDonald, M. C. Norton, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 1979, 589.

[6] J. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell, and B. L. Shaw, *J. Am. Chem. Soc.*, 1980, **102**, 4373.

[7] B. L. Shaw, *J. Organomet. Chem.*, 1980, **200**, 307.

[8] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Commun.*, 1970, 1333.

[9] J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 575.

[10] M. R. Truter, ' Molecular Structure by Diffraction Methods,' *Annu. Rep. Chem. Soc.*, 1979, **76**, C161.

[11] H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, 1958, **80**, 5570.

[12] E. O. Fischer and G. Burger, *Z. Naturforsch.*, 1961, **166**, 77.

[13] S. Hietkamp, D. J. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, 1979, **169**, 107.

[14] I. M. Al-Najjar and M. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1651.

[15] R. Palumbo, A. de Renzi, A. Panunzi, and G. Paiaro, *J. Am. Chem. Soc.*, 1969, **91**, 3874.

[16] A. de Renzi, B. di Blasio, A. Panunzi, C. Pedone, and A. Vitagliano, *J. Chem. Soc., Dalton Trans.*, 1978, 1392.

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.