Reactions of R₂P–P(SiMe₃)Li with $[(R'_3P)_2PtCl_2]$. A general and efficient entry to phosphanylphosphinidene complexes of platinum. Syntheses and structures of $[(\eta^2-P=P^iPr_2)Pt(p-Tol_3P)_2]$, $[(\eta^2-P=P^tBu_2)Pt(p-Tol_3P)_2]$, $[\{\eta^2-P=P(N^iPr_2)_2\}Pt(p-Tol_3P)_2]$ and $[\{(Et_2PhP)_2Pt\}_2P_2]^{\dagger}$

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The reactions of lithium derivatives of diphosphanes $R_2P-P(SiMe_3)Li$ ($R = {}^{1}Bu$, ${}^{1}Pr$, Et_2N and ${}^{1}Pr_2N$) with $[(R'_3P)_2PtCl_2]$ ($R'_3P = Et_3P$, Et_2PhP , $EtPh_2P$ and p-Tol₃P) proceed in a facile manner to afford side-on bonded phosphanylphosphinidene complexes of platinum $[(\eta^2-P=PR_2)Pt(PR'_3)_2]$. The related reactions of $Ph_2P-P(SiMe_3)Li$ with $[(R'_3P)_2PtCl_2]$ did not yield $[(\eta^2-P=PPh_2)Pt(PR'_3)_2]$ and resulted mainly in the formation of $[\{(R'_3P)_2Pt_2P_2], Ph_2P-PLi-PPh_2, (Me_3Si)_2PLi$ and $(Me_3Si)_3P$. Crystallographic data are reported for the compounds $[(\eta^2-P=PR_2)Pt(p-Tol_3P)_2]$ ($R = {}^{1}Bu$, ${}^{1}Pr$, $({}^{1}Pr_2N)_2P$) and for $[\{(Et_2PhP)_2Pt_2P_2]$.

1. Introduction

The chemistry of di-*tert*-butylphosphanylphosphinidene as a ligand in transition metal complexes was initiated with ${}^{t}Bu_{2}P-P=P{}^{t}Bu_{2}Me$ as a source of this species.^{1,2} We have shown that ${}^{t}Bu_{2}P-P(SiMe_{3})Li$ can also act as precursor for the ${}^{t}Bu_{2}P-P$ ligand. We obtained $[\mu-(1,2:2-\eta-{}^{t}Bu_{2}P=P){Zr(Cl)Cp_{2}}_{2}]$ and $[(\eta^{1}-{}^{t}Bu_{2}P-P){Zr(PPhMe_{2})Cp_{2}}]$ - the first complexes of early transition metals with the ${}^{t}Bu_{2}P-P$ group.³ Another entry to complexes of diorganophosphanylphosphinidenes *via* phosphides of niobium⁴ and *via* phosphides of tungsten⁵ was presented by Cummins *et al.*

The reactivity of $[(Et_3P)_2PtCl_2]$ towards $LiP(SiMe_3)_2$ and towards ${}^{1}Bu(Me_3Si)P-P(SiMe_3)_2$ was studied and it was established that under elimination of LiCl or Me_3SiCl a variety of complexes of platinum incorporating ligands with multiple P-P bonds were formed.⁶ Similarly, reactions of PhPLi-PPhLi with $[MCl_2L_2]$ (M = Pd or Pt, L = 1/2 dppe $[(Ph_2PCH_2)_2]$ or Ph_3P) yielded smoothly the side-on bonded diphosphene complexes $[L_2M(\eta^2-PhP=PPh)]$.⁷

Recently we have found that 1,1-disilyldiphosphanes $R_2P-P(SiMe_3)_2$ ($R = {}^{t}Bu$, ${}^{i}Pr$, Et_2N and ${}^{i}Pr_2N$) react with $[(R'_3P)_2PtCl_2]$ ($R'_3P = Et_3P$, Et_2PhP , $EtPh_2P$ and p-Tol_3P) in a complex manner and, to our surprise, mainly diphosphorus complexes $[\{(R'_3P)_2Pt\}_2P_2]$ were formed. The formation of small amounts of $[(\eta^2-P=PR_2)Pt(PR'_3)]$ was observed only for bulky R groups ($R = {}^{t}Bu$, ${}^{i}Pr_2N$).⁸

Subsequently, we have studied reactions of ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2$ with [(Et₃P)₂MCl₂] (M = Ni, Pd, Pt) and established the formation of [(1,2-\eta-{}^{t}Bu_2P=P-P{}^{t}Bu_2)M(PEt_3)Cl] (M = Ni, Pd),⁹ where the {}^{t}Bu_2P-P-P{}^{t}Bu_2 ligand can be regarded as a side-on bonded phosphanylphosphenium cation.¹⁰

In this paper we will focus on the reactivity of lithiated diphosphanes $R_2P-P(SiMe_3)Li$ toward $[(R'_3P)_2PtCl_2]$ in order to study whether these compounds are able to yield phosphanylphosphinidene complexes of platinum. Moreover, we want to elucidate the influence of the R and R' groups on the reactions of $R_2P-P(SiMe_3)Li$ with $[(R'_3P)_2PtCl_2]$ and on the properties of the related complexes $[(\eta^2-P=PR_2)Pt(PR'_3)_2]$. The scope of this work has been presented in preliminary form.¹¹

2. Results

2.1. Reactivity of $R_2P-P(SiMe_3)Li$ towards $[(R'_3P)_2PtCl_2]$

Generally R_2P -P(SiMe₃)Li reacts with $[(R'_3P)_2PtCl_2]$ in molar ratio of 2:1 according to eqn (1). This reaction offers an efficient access to phosphanylphosphinidene complexes of platinum (R = 'Bu, 'Pr, Et₂N and 'Pr₂N, PR'₃ = tertiary phosphanes, but not 1/2 dppe):

The reaction mixtures were studied (usually within 3 days) using ${}^{31}P{}^{1}H$ NMR and indicate that the general reaction (eqn (1)) is accompanied by side reactions. They yield some amounts of compounds which are connected with reactions involving R₂P–P(SiMe₃)Li or R₂P–P(SiMe₃)₂: R₂PH, R₂P–PH(SiMe₃), R₂PSiMe₃, R₂P–PR₂, R₂P–P(SiMe₃)–PR₂, R₂P–PH–PR₂ and some compounds which are connected with reactions involving metal centers: [{(R'₃P)₂Pt}₂P₂] and [2,3-\eta-(R₂P–P=P–PR₂)Pt(PR'₃)₂] and unidentified Pt complexes. Almost all of these

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²J P3P4 1.0 2.0 9.1 3.7 2.8

4.1

4.5

140.	R	R' ₃	δ P1	¹ J PtP1	δ Ρ2	¹ J PtP2	δ Ρ3	¹ J PtP3	δ Ρ4	¹ J PtP4	¹ J P1P2	² J P1P3	² J P1P4	² J P2P3	² J P2P4
1	ⁱ Pr	Et ₃	62.4	1807	-108.2	124.6	15.0	3338	16.6	3210	621	201.6	34.3	7.1	18.1
2	ⁱ Pr	Et ₂ Ph	61.5	1831	-105.0	113.7	12.8	3339	15.1	3187	621	207.2	35.0	8.6	19.5
3	ⁱ Pr	EtPh ₂	59.5	1870	-97.2	113.1	24.1	3378	20.4	3281	623	201.3	22.4	2.7	16.8
4	ⁱ Pr	pTol ₃	65.1	1834	-87.2	97.4	31.5	3406	24.8	3358	632	197.1	34.2		17.5
5	^t Bu	Êt ₃	81.8	1831	-66.2	96.0	14.9	3371	16.8	3223	609	212.1	36.1	6.1	18.7
6	^t Bu	pTol ₃	77.5	1906	-38.8	52.1	30.5	3452	22.5	3397	615	205.5	33.5	1.7	21.0
6A	^t Bu	a	53.1	1941	-82.5	Ь	70.6.	3373	22.2	3226	615	204.2	34.4	16.0	6.9
7	Et_2N	E_3	110.7	2322	-145.3	117.7	8.9	2774	16.2	3228	667	270.3	40.9	18.8	9.8
8	Et_2N	Et ₂ Ph	109.0	2341	-145.0	109.0	6.7	2779	14.7	3213	665	269.1	39.2	21.8	10.9
9	Et_2N	EtPh ₂	103.0	2380	-139.2	95.9	17.3	2795	21.2	3313	671	259.4	41.5	17.4	8.7
10	Et_2N	pTol ₃	103.1	2378	-139.0	96.0	17.1	2794	21.1	3310	671	259.1	41.1	18.9	8.1
11	i P r_{2} N	Et ₃	86.4	2512	-79.8	83.0	8.6	2801	13.8	3231	651	292.1	41.4	16.8	13.1
12	$^{i}Pr_{2}N$	Et ₂ Ph	84.9	2540	-83.5	88.1	5.2	2799	13.6	3216	651	291.1	39.8	21.5	14.7
13	$^{i}Pr_{2}N$	pTol ₃	76.9	2553	-63.1	54.1	25.5	2846	24.7	3416	662	269.2	39.8	11.2	12.3

Table 1 ${}^{31}P{}^{1}H$ NMR data of $[(\eta^2 - P = PR_2)Pt(R'_3P)_2]$

compounds can be regarded as products of reactions of $R_2P-P(SiMe_3)_2$ with $[(R'_3P)_2PtCl_2]$ (for detailed discussion see ref. 8).

 ${}^{t}Bu_{2}P-P(SiMe_{3})Li$ reacts smoothly with $[(Et_{3}P)_{2}PtCl_{2}]$ or with $[(p-Tol_{3}P)_{2}PtCl_{2}]$ according to eqn (1). In a reaction of ${}^{t}Bu_{2}P-P(SiMe_{3})Li$ with $[(p-Tol_{3}P)_{2}PtCl_{2}]$ we have observed a ligand exchange reaction involving the side product ${}^{t}Bu_{2}PH$ to yield $[(\eta^{2}-P=P^{t}Bu_{2})Pt(p-Tol_{3}P)({}^{t}Bu_{2}PH)]$ (6A) (see ref. 14 for comparison). Crystals of $[(\eta^{2}-P=P^{t}Bu_{2})Pt(p-Tol_{3}P)_{2}\cdottoluene]$ (6·toluene) are stable for 4 days when exposed to air.

The reactions of ${}^{i}Pr_{2}P-P(SiMe_{3})Li$ with $[(R'_{3}P)_{2}PtCl_{2}]$ afforded $[(\eta^{2}-P=P^{i}Pr_{2})Pt(PR'_{3})_{2}]$ which are relatively unstable both in solution and in the solid state. Solid $[(\eta^{2}-P=P^{i}Pr_{2})Pt(p-Tol_{3}P)_{2}$ ·toluene] (4·toluene) is decomposed in 5 h when exposed to air. 4 decomposes quickly after dissolving in $C_{6}D_{6}$.

 $({}^{i}Pr_{2}N)_{2}P-P(SiMe_{3})Li$ reacts with $[(R'_{3}P)_{2}PtCl_{2}]$ according to eqn (1). The reaction of $({}^{i}Pr_{2}N)_{2}P-P(SiMe_{3})Li$ with $[(p-Tol_{3}P)_{2}PtCl_{2}]$ yields $[\{\eta^{2}-P=P(N^{i}Pr_{2})_{2}\}Pt(p-Tol_{3}P)_{2}\cdot$ toluene] (13·toluene) in an acceptable yield. The ³¹P NMR examination of crystals of $[\{\eta^{2}-P=P(N^{i}Pr_{2})_{2}\}Pt(p-Tol_{3}P)_{2}\cdot$ toluene] (13·toluene) has indicated small signals of an AA'XX' pattern. Crystals of the 13·toluene are stable for two days when exposed to air.

In reactions involving (${}^{i}Pr_{2}N$)₂P–P(SiMe₃)Li an additional side reaction yielding (${}^{i}Pr_{2}N$)₂P–P(N ${}^{i}Pr_{2}$)₂ and [{(R'₃P)₂Pt)₂}P₂] is an important one. In reactions of (${}^{i}Pr_{2}N$)₂P–P(SiMe₃)Li with [(*p*-Tol₃P)₂PtCl₂], in some runs using pentane for crystallisation, we have isolated small amounts of crystals of [{(*p*-Tol₃P)₂Pt}₂P₂]. In the reaction of [(PhEt₂P)₂PtCl₂] with (${}^{i}Pr_{2}N$)₂P–P(SiMe₃)Li crystals of [{(PhEt₂P)₂Pt}₂P₂] (14) were isolated, however, [{ η^{2} -P=P(NⁱPr_{2})_{2}Pt(PhEt₂P)₂] (12) was formed, too. The reaction of (${}^{i}Pr_{2}N$)₂P–P(SiMe₃)Li with [(EtPh₂P)₂PtCl₂] does not afford the expected [{ η^{2} -P=P(NⁱPr_{2})_{2}Pt(PEtPh₂)₂], instead [{(EtPh₂P)₂Pt}₂P₂], (${}^{i}Pr_{2}N$)₂P–P(NⁱPr₂)₂ and (${}^{i}Pr_{2}N$)₂P–P(SiMe₃)–P(NⁱPr₂)₂ were formed.

 $\begin{array}{l} (Et_2N)_2P-P(SiMe_3)Li \ reacts \ with \ [(R'_3P)_2PtCl_2] \ yielding \ [\{\eta^2-P=P(NEt_2)_2\}Pt(PR'_3)_2]. \end{array} \\ The \ reaction \ of \ (Et_2N)_2P-P(SiMe_3)Li \ with \ [(p-Tol_3P)_2PtCl_2] \ yields \ [\{\eta^2-P=P(NEt_2)_2\}Pt(p-Tol_3P)_2] \ as thin \ orange \ needles. An \ attempt \ to \ recrystallize \ these \ needles \ led \ to \ decomposition \ of \ this \ compound. \end{array}$

of $Ph_2P-PLi-PPh_2 \cdot THF$ were isolated from the reaction mixture of $Ph_2P-P(SiMe_3)Li$ with $[(Et_3P)_2PtCl_2]$.^{12,13}

2.2. ³¹P NMR spectra of phosphanylphosphinidene complexes $[(\eta^2-P=PR_2)Pt(PR'_3)_2]$

The ³¹P NMR data for several di-*tert*-butylphosphanylphosphinidene complexes of platinum(0) were reported previously.¹⁴ ³¹P{¹H} NMR data for compounds 1–13 are summarized in Table 1. Scheme 1 shows the labelling pattern of the P atoms. The NMR studies upon 4, 6, 13 and 14 in solution are fully consistent with the X-ray structural data.



Scheme 1

The absolute values of the coupling constants ¹J(Pt,P1) are in the range of 1806–1906 Hz (1–6, R = ⁱPr, ^tBu) or 2322– 2522 Hz (7–13, R = Et₂N, ⁱPr₂N). This trend is similar to those observed in Pt complexes of tertiary phosphanes with nitrogen ligands.^{15,16} Generally, ¹J(Pt,P1) are slightly smaller than those reported for [*trans*-(R'₃P)₂PtCl₂]¹⁴ or for Pt(0) complexes [L₄Pt] (L = tertiary phosphane),¹⁵ but significantly larger than reported for side-on bonded diphosphene complexes.⁷ The P2 atoms resonate at higher field than P1; a similar effect is observed in [(η^2 -P=P^tBu₂)Ni(PEt₃)₂].²⁰ In all other known phosphanylphosphinidene complexes^{4,5,19} the resonances of the phosphinidene phosphorus atoms are shifted to lower field. The striking phenomena here are very small and negative ¹J(Pt,P2) values. The chemical shifts of P3 and P4 are close to the values reported for [(R'₃P)₂PtCl₂].¹⁴

The values of ¹J(Pt,P3) of **1–6** are close to the values for [*cis*-(R'₃P)₂PtCl₂]¹⁶ but R'₃P3 is in mutual *trans* position to R₂P1, thus the *trans* influence exerted by the P1 atom is only humble. For R = Et₂N and ⁱPr₂N a significant decreasing of the ¹J(Pt,P3) values was observed compared to **1–6**. This is accompanied by increasing values of ¹J(Pt,P1) for **7–13**, probably due to strong σ donor properties of the P1 atom bearing two NR₂ groups as observed

for tertiary phosphanes.¹⁶ This should decrease the σ acceptor properties of the Pt centre and thus should lead to a weakening of the *trans* Pt–P3 bond.¹⁸ Similarly, the values of ¹J(Pt,P4) are close to the values for [*cis*-(R'₃P)₂PtCl₂]¹⁶ in spite of the P2 atom in *trans* position. The values of ²J(P1,P3) are significantly larger in **7–13** than in **1–6**. This is probably due to the electronegative nitrogen substituents on phosphorus P1.¹⁷ The values of ¹J(P1,P2) are in the range of 609–672 Hz and suggest a multiple bond character of the P1–P2 bond. The related values in other complexes of early transition metals with side-on bonded R₂P–P ligands are in the range of 425–520 Hz.^{4,5,19}

2.3. X-Ray crystallographic studies

The structures of $[(\eta^2-P=P^iPr_2)Pt(p-Tol_3P)_2$ ·toluene] (4·toluene), $[(\eta^2-P=P^iBu_2)Pt(p-Tol_3P)_2$ ·toluene] (6·toluene) and $[\{\eta^2-P=P-(N^iPr_2)_2\}Pt(p-Tol_3P)_2$ ·toluene] (13·toluene) were studied by X-ray diffraction.²¹⁻²³ 4·toluene crystallized in the triclinic system, space group $P\overline{1}$. The molecular structure of this compound is shown in Fig. 1.



Fig. 1 The molecular structure of $[\{\eta^2-P=P^iPr_2\}Pt(p-Tol_3P)_2\cdot toluene]$ (4-toluene). Displacement ellipsoids 50%, hydrogen atoms and toluene not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.2893(14), Pt1–P2 2.4072(15), Pt1–P3 2.2915(13), Pt1–P4 2.2653(14), P1–P2 2.052(2), P1–Pt1–P2 51.75(5), P2–Pt1–P3 95.30(5), P3–Pt1–P4 106.27(5), P1–Pt1–P4 106.81(5).

6-toluene crystallized in the triclinic system, space group P1. The molecular structure of this compound is shown in Fig. 2.

Fig. 2 The molecular structure of $[\{\eta^2-P=P^tBu_2\}Pt(p-Tol_3P)_2\cdot toluene]$ (6-toluene). Displacement ellipsoids 50%, hydrogen atoms and toluene not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.3059(17), Pt1–P2 2.4088(18), Pt1–P3 2.2906(16), Pt1–P4 2.2864(16), P1–P2 2.062(2), P1–Pt1–P2 51.82(6), P2–Pt1–P3 91.92(6), P3–Pt1–P4 106.82(6), P1–Pt1–P4 109.86(6).

13-toluene crystallized in the monoclinic system, space group $P2_1/c$. The molecular structure of this compound is shown in Fig. 3.



Fig. 3 The molecular structure of $[{\eta^2-P=P(N^iPr_2)_2}Pt(p-Tol_3P)_2$ toluene] (13-toluene). Displacement ellipsoids 50%, hydrogen atoms and toluene not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.2916(11), Pt1–P2 2.4024(9), Pt1–P3 2.3131(10), Pt1–P4 2.2773(9), P1–P2 2.0590(12), P1–Pt1–P2 51.97(3), P2–Pt1–P3 92.71(3), P3–Pt1–P4 98.74(3), P1–Pt1–P4 116.86(3).

The Pt atoms in 4-toluene, 6-toluene and 13-toluene are in an almost planar environment defined by P1, P2, P3 and P4.

The distance Pt1-P1 in 4-toluene is 2.2893(14) Aring;, in 13-toluene 2.2916(11) Aring;, and in 6-toluene 2.3059(17) Aring;. In other known complexes with the ^tBu₂P-P ligand these distances are in the range of 2.309(12)-2.3351(13) Aring;.1,24,25 Thus, it seems probable that the steric properties of R_2P fragments exert a substantial impact on these distances. The most significant feature of these X-ray structures are long distances Pt1-P2 in the range of 2.4024(9)-2.4088(18) Aring; (weak single bonds). Quite differently, in complexes of early transition metals with side-on bonded R_2P-P ligands the M-PR₂ distances are distinctly longer than the M–P ones. The distances Pt1–P3 are 2.2915(13) Aring; (4-toluene) and 2.2906(16) Å (6·toluene), but in $[\{\eta^2 - P = P^t Bu_2\} Pt(dppe)]$ this distance is 2.262(2) Å,²⁴ and in 13-toluene the distance Pt1-P3 is 2.3131(10) Aring; due to the *trans* effect of the $({}^{i}Pr_{2}N)_{2}P$ group. The distances Pt1-P4 are relatively short, 2.2653(14)-2.2864(16) Aring; probably due to the weak trans effect exerted by the P2 atoms. They are in the range typical for $[cis-(R'_{3}P)_{2}PtCl_{2}]$. This finding is supported by other X-ray studies.^{1,24,25}

The P1–P2 distances are found to be in the range of 2.052(2)– 2.062(2) Aring; The values of R₂P–P distances in side-on bonded phosphanylphosphinidene complexes of early transition metals are slightly larger: 2.073(2), 2.0888(15)⁴ and 2.0973(12) Å.⁵

The geometries around the P1 atoms in 4-toluene, 6-toluene and 13-toluene show a tendency to planarity. The sums of angles around P1, taking into account the P2–P1–R–R groups are in the range of 344.9–345.9°. This suggests²⁶ that the Pt–P1 π -bonding is only of limited importance in this class of compounds. The sums of angles around the N atoms in 13-toluene are 352.2° and 357.0°. This almost planar geometry around the N atoms is not due to the (¹Pr₂N)₂P–P ligand. In (¹Pr₂N)₂P–P(SiMe₃)Li and in (¹Pr₂N)₂P– P(SiMe₃)₂^{13,27} the geometries around the N atoms and the P–N distances are very similar to those in 13-toluene.

Additional intramolecular π - π interactions in 4-toluene, 6-toluene and 13-toluene are evident between the phenyl rings of neighbouring *p*-Tol₃P ligands.

Complex 14 crystallized in the monoclinic system, space group $P2_1/c$. The molecular structure of $[{(Ph_2EtP)_2Pt}_2](14)$ is shown in Fig. 4. Similar compounds were obtained by us in the reactions of $R_2P-P(SiMe_3)_2$ with $[(R'_3P)_2PtCl_2]$ and were studied with X-ray diffraction.8 The molecule of 14 consists of two distorted square planar arrangements P1-P2-P3-P4-Pt1 and P1-P2-P5-P6-Pt2, respectively, almost perpendicular to each other, which form a "roof" framework. The bond between the phosphorus atoms in the bridging P_2 unit is short, 2.121(10) Aring; The mean distance R'₃P-Pt in 14 is 2.270(8) Aring; and the mean angle R'₃P-Pt- PR'_{3} is 106.6(3)°. Thus, the P1 atom in 14 exerts almost as small *trans* effect as the Cl atoms in $[cis-(Ph_2EtP)_2PtCl_2]$, Pt-P (mean) = 2.2575(9) Aring; and the related P-Pt-P angle is 100.23(3)°.28 In 14 the Pt-P(1,2) mean distance of 2.382(7) Aring; is in the range of P–P distances in diphosphenes bonded side-on to a $Pt(PR'_3)_2$ centre.29



Fig. 4 The molecular structure of $[\{(Ph_2EtP)_2Pt\}_2P_2]$ (14). Displacement ellipsoids 50%, hydrogen atoms not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.388(7), Pt1–P2 2.377(6), Pt1–P3 2.280(6), Pt1–P4 2.265(8), P1–P2 2.121(10), Pt2–P1 2.395(7), Pt2–P2 2.367(6), Pt2–P5 2.270(7), Pt2–P6 2.264(7), P1–Pt1–P2 52.8(2), P3–Pt1–P4 108.4 (2). The dihedral angle between mean planes defined by P1–P2–Pt1–P3–P4 and P1–P2–Pt2–P5–P6 = 101.32(12)°.

The unit cell of **14** contains two relatively large voids of *ca*. 184 Aring;³ centered at (0,0,0) and (0, 1/2, 1/2), Wyckoff position *a*, containing *ca*. 29 e⁻ each. This space can be occupied (or partly occupied) by disordered THF or pentane molecules, however, no well-defined electron density peaks can be found in the Fourier map. The presented data are uncorrected for this effect which probably increased the value of the R_1 index (the PLATON-SQUEEZE program failed before normal ending due to numerical instability).

2.4. Discussion

The reactions of $R_2P-P(SiMe_3)Li$ with $[(R'_3P)_2PtCl_2]$ open an efficient entry to phosphanylphosphinidene complexes of platinum. So far, we have isolated only four compounds as crystals because the other compounds are highly soluble in hydrocarbons. Nevertheless, this is a more general and therefore preferable way than the reaction of ${}^{t}Bu_2P-P=P{}^{t}Bu_2(Me)$ with $[(C_2H_4)Pt(PR'_3)_2]^{t4}$ because of a broader scope of groups R which can be introduced as R_2P-P ligands in these reactions.

X-Ray studies upon 4-toluene, 6-toluene and 13-toluene together with NMR studies upon compounds 1–13 provide some insight into the electronic properties of the side-on bonded R_2P-P ligand. The R_2P1-P2 group behaves, to a certain extent, like a tertiary phosphane with substituents R, R and P2. The coupling constant ¹J(P1,Pt) is smaller than in the case of a genuine tertiary phosphane in spite of a relatively short distance Pt–P1. The *trans* influence of the R₂P group is weak. Very small values of ¹J(Pt,P2) of -52 Hz to -124 Hz are diagnostic and in accord with very long Pt–P2 distances. The *trans* influence of the P2 atom is weak, too. There are similar NMR properties and notable structural analogies between the complexes $[(\eta^2-P=PR_2)Pt(PR'_3)_2]$ and complexes³⁰⁻³⁴ with ligands which can be seen as side-on bonded phosphanylphosphenium cations $[RR'P=PR"]^+$.¹⁰ Even complexes with phosphinomethanide ligands $RR'P=CR"_2$ ³⁵ display similar properties. We have compared the sterical alignments of $Pt(\eta^2-iBu_2P=P-P^iBu_2)$ in $[(1,2-\eta^-iBu_2P=P-P^iBu_2)Pt(PPh_3)Br]^{34}$ with the $Pt(\eta^2-iBu_2P=P)$ group in 6. Fig. 5 shows the best overlap of these two fragments.



Fig. 5 The best overlap of 6-toluene (black) and $[(1,2-\eta-{}^{t}Bu_{2}P=P-P{}^{t}Bu_{2})-Pt(PPh_{3})Br]$ (dashed line).

The root-mean-square deviation of coordinates of atoms C1, C5, P1, P2 and Pt1 is only 0.0807 Aring;, what indicates an excellent congruence of the two alignments.

Thus, the properties of $[(\eta^2-P=PR_2)Pt(PR'_3)_2]$ are best explained with two resonance structures (Scheme 2):



The P1-P2 distances in the side-on bonded 'Bu2PP ligands 2.062(2) Aring; (6 toluene), 2.071(1),¹ 2.072 (2)²⁴ and 2.067(2) Aring;²⁵ are shorter than in complexes with phosphanylphosphenium cations [^tBu₂PPP^tBu₂]⁺ as ligands, 2.149(2),³⁴ 2.128(10)⁹ and 2.1368(5) Aring;.⁹ The shortening of this bond is due to a zwitterionic structure of the $R_2P=P$ ligands (Scheme 2a). Considerations of the bonding variations (side-on vs. terminal) suggest that the ability of the R₂P1 group to coordinate to a metal center can be an important factor. It seems very probable that late transition metals at low oxidation states,26 capable to act as π -donors, can support the side-on bonding. Early transition metals at high oxidation states should favor the terminal bonding of the R₂P-P group and the multiple bond character of a metalphosphinidenephosphorus bond. The side-on bonded complexes of early transition metals synthesized by the Cummins group have amido groups (strong π and σ donors) as additional ligands.^{4,5} This can enhance the π donor ability of these metal centers and thus can favor the side-on bonding of the R₂P–P group.

3. Experimental

All reactions and manipulations were performed in an inert atmosphere of ultra-high purified argon employing standard Schlenk vacuum line techniques. Solvents were purified, dried and distilled prior to use, from dark blue potassium (THF) or sodium (toluene) diphenylketyl solutions. Pentane was distilled from a blue ketyl solution in a mixture of pentane and diglyme.

The known lithium derivatives of diphosphanes R_2P – P(SiMe₃)Li (R = Ph, 'Bu, 'Pr₂N) were prepared according to published methods,¹³ (Et₂N)₂P–P(SiMe₃)Li was prepared according to ref. 36, [(R'₃P)₂PtCl₂] (R'₃P = Me₃P, Et₃P, Et₂PhP, EtPh₂P and *p*-Tol₃P) were prepared according to known procedures.³⁷

 31 P NMR spectra were recorded on Bruker AC250, Bruker Av400, Bruker AMX300 and Varian Unity+ 500 spectrometers (external standard 85% H₃PO₄) at ambient temperature.

General comments

All reactions of $R_2P-P(SiMe_3)Li$ with $[(R'_3P)_2PtCl_2]$ were carried out in the same way. Therefore, only those ones which resulted in crystalline products are described in more detail.

 $\begin{array}{l} R_2P-P(SiMe_3)Li \text{ were used as THF solvates: } ^{t}Bu_2P-P(SiMe_3)Li \cdot 2THF, \ (^{t}Pr_2N)_2P-P(SiMe_3)Li \cdot 2.6THF, \ Ph_2P-P(SiMe_3)Li \cdot 3THF, \ (Et_2N)_2P-P(SiMe_3)Li \cdot 1.7THF \ and \ ^{t}Pr_2P-P(SiMe_3)Li \cdot 2THF. \end{array}$

Synthesis of $[(\eta^2 - iPr_2P - P)Pt(p - Tol_3P)_2]$ (4)

A solution of ⁱPr₂P–P(SiMe₃)Li·2THF (0.145 g; 0.377 mmol) in THF (1.5 cm³) was added to a suspension of $[(p-Tol_3P)_2PtCl_2]$ (0.150 g; 0.171 mmol) in THF (1.5 cm³) at -40 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The suspension dissolved, and the color of the solution gradually changed to dark orange. After one day the reaction mixture was evaporated to dryness in vacuo (1 mTorr, 5 h). The residue was dissolved in toluene (10 cm³), filtered, concentrated to a volume of 1 cm³ and kept at -70 °C for one month. Colorless crystals of p-Tol₃P were obtained (X-ray analysis). After filtration and subsequent concentration (to 0.5 cm³) in vacuo, the resulting orange solution was kept at -70 °C for 6 months to isolate orange crystals of 4-toluene. The crystals were filtrated, washed with a small amount of cold toluene and evacuated for 6 h at 1 mTorr. Yield 62 mg (38%). Dissolving of 4 in C₆D₆ leads to its decomposition.

Anal. calcd. for $C_{48}H_{56}P_4Pt$ (951.9): C 60.56, H 5.13; found: C 60.8, H 5.4%.

Synthesis of $[\eta^2 - {}^tBu_2P - P]Pt(p-Tol_3P)_2]$ (6)

A solution of ${}^{t}Bu_{2}P-P(SiMe_{3})Li\cdot2THF$ (0.121 g; 0.346 mmol) in THF (1.5 cm³) was added to a suspension of $[(p-Tol_{3}P)_{2}PtCl_{2}]$ (0.138 g; 0.158 mmol) in THF (1.5 cm³) at -40 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The suspension dissolved, and the color of the solution gradually changed to dark orange. After one day the reaction mixture was evaporated to dryness *in vacuo* (1 mTorr, 5 h). The residue was dissolved in toluene (10 cm³), filtered and concentrated to a volume

of 2 cm³. Pentane (10 cm³) was diffused to this solution and orangered crystals of 6-toluene were deposited. The crystals were filtrated, washed with a small amount of pentane and evacuated for 6 h at 1 mTorr. Yield 76 mg (49%).

¹H NMR: 7.80 ppm, m*, 6H, C₆H₄; 7.71 ppm, m*, 6H, C₆H₄, 6.79 ppm, m**, 12H, C₆H₄, 1.997 ppm, s, 9H, CH₃C₆H₄; 1.993 ppm, s, 9H, CH₃C₆H₄; 1.47 ppm, d, ³J_{P-H} 15.2 Hz, 18H, C(CH₃)₃. Small signals of *p*-Tol₃P were visible.

¹³C NMR (δ ppm): 21.76, 21.82, 21.89, 34.24, 36.25, 36.45, 134.87, 135.15, 135.57, 135.78, 135.92, 136.10, 136.25, 139.21, 139.69, 139.89.

Anal. calcd. for $C_{50}H_{60}P_4Pt$ (980.00): C 61.28, H 6.17; found: C 61.0, H 6.4%.

Synthesis of $[\{\eta^2 - (iPr_2N)_2P - P\}Pt(p-Tol_3P)_2]$ (13)

A solution of $({}^{1}Pr_{2}N)_{2}P-P(SiMe_{3})Li\cdot2.6THF$ (0.153 g; 0.289 mmol) in THF (1.5 cm³) was added to a suspension of $[(p-Tol_{3}P)_{2}PtCl_{2}]$ (0.119 g; 0.136 mmol) in THF (1.5 cm³) at -40 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The suspension dissolved and the color of the solution gradually changed to brown. After one day the reaction mixture was evaporated to dryness *in vacuo* (1 mTorr, 5 h). The residue was dissolved in toluene (10 cm³), filtered, concentrated to a volume of about 1 cm³ and kept at -30 °C for five months to isolate an orange powder which was dissolved in toluene again and kept at -4 °C for one day whereupon large, orange crystals of **13**-toluene were obtained. The crystals were filtrated, washed with a small amount of toluene and evacuated for 6 h at 1 mTorr. Yield 98 mg (68%).

Anal. calcd. for $C_{54}H_{70}N_2P_4Pt$ (1066.1): C 60.84, H 6.62; found: C 60.5, H 6.8%.

¹H NMR: 7.79 ppm, m*, 6H, C₆H₄; 7.65 ppm, m*, 6H, C₆H₄, 6.81 ppm, m**, 12H, C₆H₄; 4.13 ppm, hept, ²J_{H-H} 7.0 Hz, 4H, NCH(CH₃)₂; 1.989 ppm, s, 9H, CH₃C₆H₄; 1.984 ppm, s, 9H, CH₃C₆H₄; 1.984 ppm, d, ²J_{H-H} 6.8 Hz, 12H, NCH(CH₃)₂; 1.405 ppm, d, ²J_{H-H} 6.8 Hz, 12H, NCH(CH₃)₂; ³¹P NMR see Table 1, additionally weak signals of AA'XX' and of [{(*p*-Tol₃P)₂Pt}₂P₂] were seen: AA'XX' 79.22 ppm (psdd 18.8 + 23.0) J(Pt-P) = 465.3 Hz, 27.16 ppm (psdd 18.8 + 23.0) J(Pt-P) = 2890.2 Hz.

¹³C NMR (δ ppm): 21.78, 21.86, 24.69, 24.73, 25.24, 50.05, 50.07, 50.14, 50.16, 134.89, 135.09, 135.49, 135.63, 136.39, 136.50, 139.53 (d 1.4 Hz), 139.77 (d 1.4 Hz), m* AA'XX' pattern, pseudo dd, m** overlap of two AA'XX' patterns (overlap of two pseudo t).

Synthesis of $[{(EtPh_2P)_2Pt}_2P_2](14)$

A solution of $({}^{1}Pr_{2}N)_{2}P-P(SiMe_{3})Li\cdot2.6THF$ (0,112 g; 0,230 mmol) in THF (1 cm³) was added to a suspension of [(EtPh_{2}P)_{2}PtCl_{2}] (0,085 g; 0,122 mmol) in THF (1 cm³) at -40 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The suspension dissolved and the color of the solution gradually changed to brown. After one day the reaction mixture was evaporated to dryness *in vacuo* (1 mTorr, 5 h). The residue was dissolved in pentane (5 cm³), filtrated, concentrated to a volume of 1 cm³ and cooled at -4 °C for one month whereupon pale-brown crystals of **14** were obtained. Yield 32 mg.

Crystal structure determinations

Diffraction data were collected at 100 K (13-toluene) and 120 K (other compounds) on a KUMA KM4CCD diffractometer, Oxford Diffraction Ltd. Numerical absorption correction based on the multi-faceted crystal shape with empirical scaling was applied (CrysAlis RED, Oxford Diffraction²²). Details of crystal data, data collection and refinement are summarized in Table 2 (supplementary materials). The structures were solved by direct methods using the SHELX-97 program package^{23,24} and refined with fullmatrix least-squares on F². All atoms, excluding hydrogen, were refined with anisotropic displacement ellipsoids. Hydrogen atoms were positioned geometrically and refined as riding on their heavy atoms.

The toluene molecules were left isotropic for 4-toluene and 13-toluene. In the later case the solvent was refined as disordered over two positions. In both cases C-C bond lengths in toluene were restrained to have physically acceptable values.

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