Ylidylphosphanes and -diphosphanes

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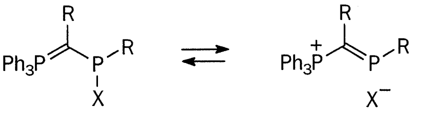
Chlorophosphanyl and dichlorophosphanyl alkylidene- and benzylidenephosphoranes **6** and **8** are converted by reaction with $LiAlH_4$ to the respective phosphanes **7** and **9**. The former can be isolated, but decompose on heating or on protonation to give the ylidyl diphosphane **11** and the phosphonium ylide or phosphonium salt, respectively. The final products are the cyclooligophosphanes **15**–**17**. Only the *C-tert*-butyl derivative **7c** is stable in both regards. The conformation of the RPH group in **7** as compared to that of the RPCl group in **6** clearly reflects their different interaction with the ylide moiety.

The most notable feature of ylide-substituted halophosphanes **1** (X = Cl, Br) is the elongated P–X bond and the ease of dissociation of this bond[1][2][3].



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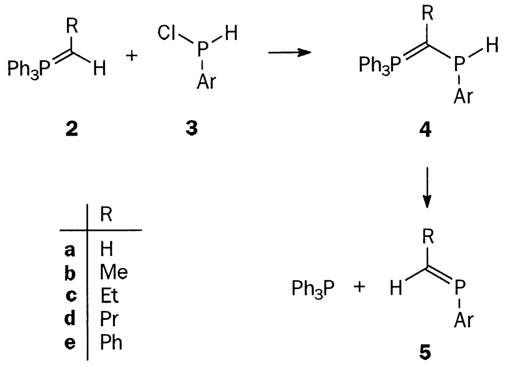
In these compounds, the electron-accepting halophosphane moiety matches the electron-donating ylide moiety. As a consequence, the system is stabilized and in particular the C–P^{III} bond is strengthened. The exchange of the halogen for hydrogen will, in contrast result in a mismatch of the two moieties and consequently in labile P–C bonds. With the exception of **7e**[4] (see below), no primary or secondary phosphanes with an ylide substituent are known. Special examples of secondary ylidylphosphanes **4** with Ar = 2,4,6-$tBu_3C_6H_2$ are proposed as intermediates from the 2:1 reaction of triphenylphosphonium ylide **2** and the monochlorophosphane **3**. The final products of this reaction are triphenylphosphane and the phosphaalkenes **5** [mixtures of (*E*/*Z*) isomers][5].

We report here the synthesis of ylidylphosphanes by a Cl/H-substitution and on their thermal decomposition, which is different to the one described for **4**.

Synthesis of Ylidylphosphanes

By reaction with $LiAlH_4$ at −40°C in THF solution, the chlorophosphanyl benzylidenephosphoranes **6** are converted to the phosphanyl derivatives **7**, which are stable at room temperature and can be isolated as orange (R = alkyl) or yellow (R = Ph) crystals. The compounds are readily



	R
a	H
b	Me
c	Et
d	Pr
e	Ph

soluble in THF and benzene but hardly soluble in pentane, and, except for **7c**, they are unstable in dichloromethane. This synthesis could not be extended, however, to examples with Me in place of Ph as the substituent at the ylidic carbon atom. In this case, from the analogous reaction, no ylidylphosphanes could be identified. A further example of type **7**, with two ylide substituents (**7e**, R = Ph_3PCPh) is formed as stable red crystals from the reaction of the bis(ylidyl)phosphenium chloride $(Ph_3PCPh)_2P^+Cl^-$ with $LiAlH_4$[4].

Under the same conditions, dichlorophosphanyl benzylidenephosphoranes **8a**, **b** and dichlorophosphanyl trimethylsilylmethylenephosphorane **8c** are converted by $LiAlH_4$ to the respective ylidylphosphanes **9**. They can be identified in solution at −40°C by their NMR spectra and can be observed for a short time at room temperature, but due to their thermal instability they cannot be isolated. In the reaction of **8c**, the bis(ylidyl)diphosphane **10c** is observed as a second, slightly more thermally-stable product.

Of particular interest among the ^{31}P-NMR data (Table 1) are the coupling constants $^2J_{PP}$ of the ylidylphosphanes

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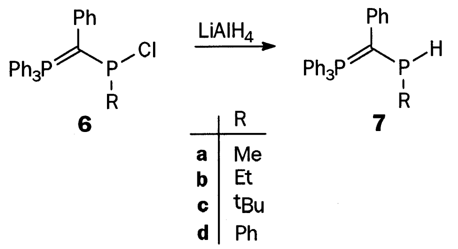
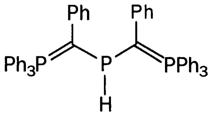
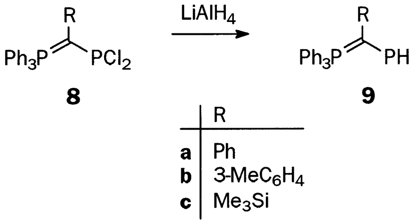
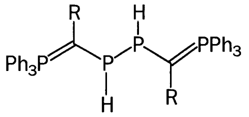




7e

9 and 7. They are considerably smaller than those of the dichlorophosphanes **8** (around 227 Hz) and the chlorophosphanes **6** (around 179 Hz). A value around 159 Hz as found for most compounds **9** and **7** still corresponds, however, to a synperiplanar orientation of the electron lone pair at P^{III} and the phosphonio group (as it is also observed in the crystal, see below). The much smaller constants of **9c** and **7e**, however, indicate that the antiperiplanar conformer has a large predominance in these cases.





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The ^{13}C-NMR spectra of compounds **7** as compared to those of compounds **6** reflect the Cl/H exchange by a highfield chemical shift of the ylidic carbon signal as well as by a slight increase in $^1J_{P(V)C}$ and a sharp decrease in $^1J_{P(III)C}$. These changes correspond well to a reduced electron transfer from the ylide to the P^{III} moiety.

Like other secondary phosphanes, the ylidylphosphane **7d** can be converted to the corresponding lithium phosphide by reaction with butyllithium in tetrahydrofuran.

Molecular Structures of Ylidylphosphanes

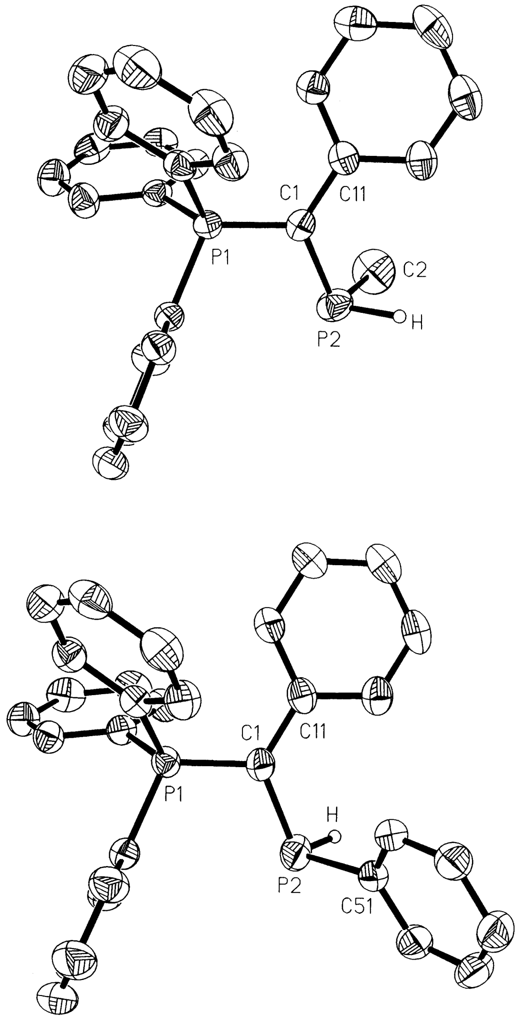
Crystals of **7a**·THF and **7d**·0.5 THF, suitable for X-ray structure analyses were obtained from THF solutions saturated at ambient temperature, to which pentane was added. The results of the structure determinations are shown in Figure 1 and Table 2. In both cases, the ylidic carbon atom C1 has a planar coordination sphere and the electron lone pair at P2 shows a roughly synperiplanar orientation with respect to the phosphonio center P1. This conformation has been found, in general, for ylidylphosphanes[1]. The bond lengths and angles of the two structures do not differ significantly and are in agreement with standard values.

For comparison, Table 2 also shows the structural data of the chlorophosphane **6a**. While the pyramidal P^{III}-coordination (sum of angles 302±1°) and the average of the two dihedral angles (130±2°) is essentially the same in all three cases, the conformation and the individual dihedral angles P1−C1−P2−C2 and P1−C1−P2−H/Cl in the hydrogen derivatives **7** are quite different from those in the chloro compound **6**. The angle P−C−P−Cl in **6** is, in fact, much smaller than the average, resulting in a near-ecliptic alignment of the P−Cl bond and the ylidic electron pair and allowing an effective charge transfer into the P−Cl bond. The corresponding dihedral angles P−C−P−H in **7** are, in contrast, larger than the average value and the P−H bond seems to avoid the described alignment. The dihedral angles are thus inversely ordered to the substituent's electronegativity Cl > C and C > H. The different charge transfer connected to the different conformation can also be monitored from the bond P2−C1 which is much shorter in the chloro derivative **6** than in the hydrogen derivatives **7**. Finally the

Table 1. ^{31}P-NMR data of ylidylphosphanes **9** and **7** (in THF) and the protonation products **19** (Cl^-) and **20** (BF_4^-) of **7c**, **d** (in CH_2Cl_2) as well as ^{13}C-NMR data of the ylidic carbon atom of **7** (in C_6D_6, coupling constants J in Hz)

	C−R	*P*−R	$\delta^{31}P^V$	$\delta^{31}P^{III}$	$^2J_{PP}$	$^1J_{PH}$	d^{13}C	$^1J(P^VC)$	$^1J(P^{III}C)$
9a	Ph	H	21.5	−133.4	159.6	194.8			
9b	3-MeC$_6$H$_4$	H	21.7	−133.0	159.6	194.1			
9c	SiMe$_3$	H	28.1	−129.0	91.5				
7a	Ph	Me	20.7	−88.0	160.9	203.5	26.6	115.2	22.9
7b	Ph	Et	20.9	−67.5	152.6	201.9	25.9	114.4	24.4
7c	Ph	*t*Bu	21.5	−33.2	154.9	207.1	27.7	111.0	31.3
7d	Ph	Ph	22.5	−51.8	167.7	219.1	26.2	114.5	19.2
7e	Ph	Ph$_3$PCPh	17.2	−55.8	87.4	236.6			
19c	Ph	*t*Bu	26.7	−19.9	24.9	203.0			
			26.2	−0.2	76.6	216.4			
19d	Ph	Ph	25.0	−47.4	42.5				
			24.9	−19.7	51.9				
20c	Ph	*t*Bu	26.8	−21.0	26.0	216.9			
			26.4	−1.3	76.8	222.9			
20d	Ph	Ph	24.7	−46.1	42.4				
			24.2	−22.0	58.8				

Figure 1. Molecular structures of **7a** (top) and **7d** (bottom) in the crystal (thermal ellipsoids with 50% probability). The hydrogen atoms, except the *P*-bonded one are omitted for clarity



difference in bonding is also of significant influence on the P−C−P-angles.

Table 2. Relevant bond lengths [pm], bond and dihedral angles [°] of **7a** and **7d** and of **6a** for comparison

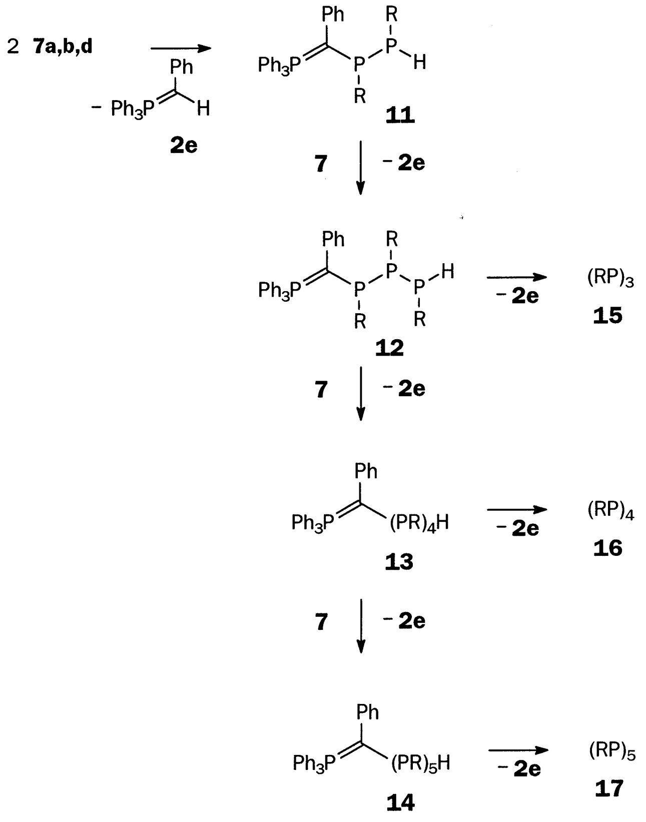
	6a	7a	7d
P1−C1	173.0(2)	171.2(3)	172.2(3)
C1−C11	149.8(2)	146.6(4)	146.6(4)
P2−C1	172.5(2)	178.6(3)	177.6(3)
P2−C2	183.6(2)	183.7(4)	183.5(3)[b]
P2−H	–	137(4)	116
P1−C1−C11	116.8(1)	120.4(2)	119.5(2)
P2−C1−C11	122.7(1)	123.5(2)	125.3(2)
P1−C1−P2	118.7(1)	115.2(2)	114.5(1)
C1−P2−C2	101.3(1)	103.9(2)	107.7(1)[b]
C1−P2−H	107.2(1)[a]	101(2)	101
C2−P2−H	92.2(1)[a]	96(2)	93[b]
P1−C1−P2−C2	163.8	121.8	126.5[b]
P1−C1−P2−H	100.8[a]	139.0	137.2

[a] Cl in place of H. – [b] C51 in place of C2.

Thermolysis of Ylidylphosphanes

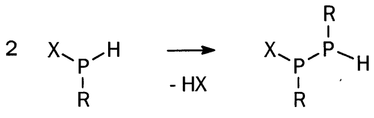
If the ylidylphosphanes **7a**, **b**, **d** are heated in solution to 60 °C for several hours, they completely decompose to the ylide **2e** and a mixture of the cyclotri-, cyclotetra-, and cyclopentaphosphanes **15**, **16**, and **17**. The formation of this mixture seems to be kinetically determined and requires a pathway consistent with the formation of small cyclophosphanes off the thermodynamic equilibrium. Such a pathway is proposed in Scheme 1. If the heating is interrupted after a few minutes, besides unreacted ylidylphosphanes **7**, the ylidyldiphosphanes **11** can in fact be clearly identified by their ^{31}P-NMR spectra and, somewhat less clearly, also the ylidyltriphosphanes **12**.

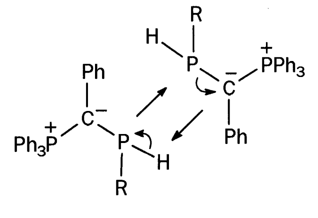
Scheme 1



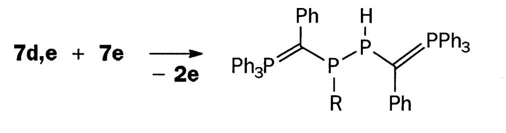
A condensation of the general type shown below, as it is observed here for the case of X = Ph_3PCPh (e.g. in the reaction 2 × **7** → **2e** + **11**) is unknown in the case of other organo substituents X, but is well known in case of amino substituents X[6] and phosphino substituents X. The latter reaction has been described as a disproportionation of a diphosphane[7]. All these reactions may be understood by a four-centred mechanism involving a proton transfer and a nucleophilic/electrophilic interaction of the two tervalent phosphorus atoms.

The bis(ylidyl)phosphane **7e** (R = Ph_3PCPh) also decomposes rapidly at 60 °C. As a primary product, the respective diphosphane **18e** can be detected in the ^{31}P-NMR spectrum. In addition, however, the primary ylidylphosphane **9a** and the bis(ylidyl)diphosphane **10a** are observed. As ylidyl-





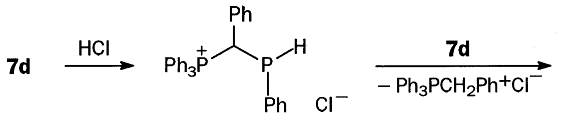
substituted cyclophosphanes seem not to be stable, the thermolysis finally yields a complex mixture which cannot be analyzed. If an equimolar mixture of **7e** and **7d** is heated, only the 1,2-bis(ylidyl)diphosphane **18d** is observed as product and not its 1,1-isomer. This suggests that the course of the reaction is determined by the proton transfer step; in the case under discussion the course is thus decided by the higher basicity of the ylidic carbon atoms of **7e** as compared to that of **7d**. In contrast to **7a**,**b**, and **d**, the *tert*-butyl derivative **7c** is thermally stable and remains unchanged in refluxing benzene for at least one week.



18d R = Ph
18e R = CPhPPh$_3$

Protonation and Alkylation of Ylidylphosphanes

Instead of warming, the formation of ylidyldiphosphanes from **7** can also be initiated by adding half an equivalent of HCl. From a 2:1 reaction of **7d** with HCl in ether, the benzylphosphonium chloride precipitates and the ylidyldiphosphane **11d** remains in solution. With more HCl added, the ylidyldiphosphane is converted to more phosphonium chloride and a mixture of cyclophosphanes. In addition, a minor amount of PhPH$_2$ is observed as a product of further reduction.



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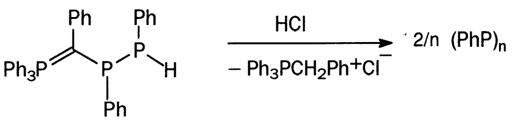
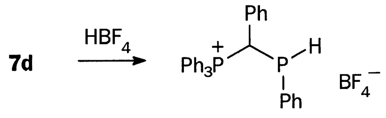


11d

The ylidyldiphosphane obviously results from the condensation of the primary product of protonation **17** with more ylidylphosphane **7d**. Consequently, the protonation of an ylidylphosphane **7** without a concomitant condensation can be achieved, if any temporary excess of **7** is avoided, i.e. if **7d** is added to HBF$_4$. In this way the phosphanyl benzylphosphonium tetrafluoroborate **20** precipitates from THF and is isolated as a mixture of two diastereomers. Followed with a second molecule of **7**, the cation of **20** enters the expected condensation and this way an access to mixed substituted ylidyldiphosphanes is provided. With **7b**, **c** the ylidyldiphosphanes **11f**, **g** are obtained. Their formation can be understood to result from a nucleophilic attack of the ylidylphosphane **7** on the cation of **20**.



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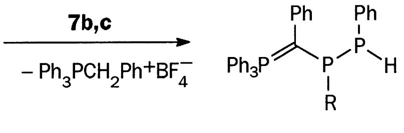
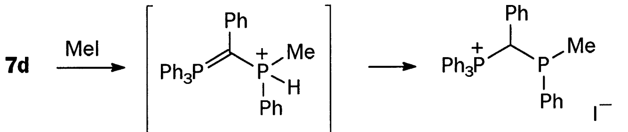


11f R = Et
11g R = ^{t}Bu

The *tert*-butylsubstituted ylidylphosphane **7c**, which resists the thermal condensation (see above), does not undergo an HCl-initiated condensation either. Its hydrochloride **19c** and hydrotetrafluoroborate **20c** therefore are stable even in presence of excess **7c**.

Methyl iodide alkylates **7d** at the phosphorus atom with a concomitant shift of the proton to the carbon atom to give the phosphonium iodide **21** which corresponds to the product **17** from the initial protonation step. With a chlorophosphane such as MePCl$_2$ **7d** reacts in a way analogous to HCl yielding the phosphonium chloride **22** and a mixture of phenyl cyclophosphanes.



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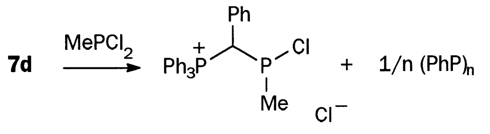

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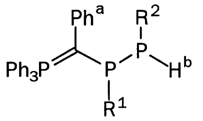
NMR Spectra of Ylidyl Di- and Triphosphanes

For most of the diphosphanes **10**, **11**, and **18**, two diastereomers are observed in the ^{31}P-NMR spectrum with slightly different coupling constants $^1J_{PP}$ (Table 3). For the phenyl derivative **11d**, this difference is quite large and allows a tentative assignment of the signals to the individual diastereomers. Due primarily to the steric interaction of the ylidyl substituent at the one phosphorus atom with the phenyl substituent at the other phosphorus atom, the share of the *trans* conformation should be smaller for the (*R*,*R*)- than for the (*R*,*S*)-isomer and consequently $^{1}J_{PP}$ should be larger for the (*R*,*R*)- than for the (*R*,*S*)-isomer. In all cases a $^{3}J_{PP}$ coupling is observed for only one of the two diastereomers. In agreement with the phenyl derivative **11d**, this is assigned to the (*R*,*S*)-isomer for all the other derivatives too. For the ylidyltriphosphane **12b** all four diastereomers can be identified in the ^{31}P-NMR spectrum (Table 3).

Table 3. ^{31}P-NMR data of ylidyldiphosphanes **10**, **11**, and **18** and ylidyltriphosphanes **12** (in C_6H_6 or THF, coupling constants J in Hz)

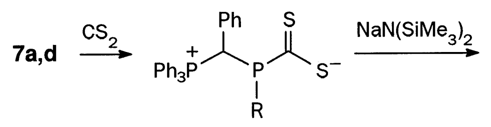


Fraction [%]		R^1	R^2		δ_A	δ_B	δ_C	δ_D	$^{2}J_{AB}$	$^{3}J_{AC}$	$^{1}J_{BC,\,BB'}$	$^{3}J_{BD}$	$^{1,2}J_{CD}$	$^{1}J_{PCH}$
10a		H	CPhPPh$_3$	AA′BB′	20.1[a]	−82.0	–							
10c[b]	74	H	CSiMe$_3$-PPh$_3$	AA′BB′	26.6	−70.0	–		114.1		−128.0			
	26			AA′BB′	25.6	−71.9	–		–					
11a	51	Me	Me	ABC	20.0	−44.8	−95.8		187.8	–	206.6			201.3
	49			ABC	20.8	−45.1	−89.8		187.8	11.7	199.5			183.1
11b	49	Et	Et	ABC	19.8	−30.1	−66.7		186.7	–	208.4			209.1
	51			ABC	20.8	−33.0	−65.2		185.4	11.4	222.5			202.3
11d	68	Ph	Ph	ABC	21.6	−13.9	−60.5		204.0	–	301.0			194.6
	32			ABC	22.5	−19.1	−52.4		208.9	9.6	223.4			203.5
711f	52	Et	Ph	ABC	20.5	−15.4	−60.5		186.9	–	222.1			
	48			ABC	21.1	−18.2	−49.1		187.9	7.8	251.2			
11g	57	*t*Bu	Ph	ABC	21.1	12.1	−64.0		200.3	–	253.3			
	43			ABC	22.0	6.6	−69.8		202.4	10.4	272.9			
18d		Ph	CPhP^{D}Ph$_3$	ABCD	20.7	−27.6	−62.4	20.5	191.0	–	227.3		177.5	205.5
18e[c]		CPhP^{E}Ph$_3$	CPhPPh$_3$	ABCDE	15.2	−36.7	−76.7	25.2	200.9	16.1	125.6		172.3	
12b	24	Et	P^{D}HEt[d]	ABCD		−26.6	−48.1	−79.5	187.8	5.3	200.7	80.4	241.2	
	18			ABCD		−21.2	−39.9	−80.7	187.8	5.9	218.9	70.4	209.5	
	22			ABCD		−15.9	−43.5	−83.4	187.8	4.7	228.9	29.1	194.3	
	36			ABCD		−16.4	−47.3	−78.2	185.8	2.4	195.4	65.7	216.6	

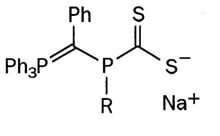
[a] Superimposed. – [b] For **10c** SiMe$_3$ in place of Ph. – [c] δ_E = 19.3, J_{BE} = 220.1, J_{CE} = 16.1, $^{1}J_{P^{E}H}$ = 189.9, $^{2}J_{P^{E}H}$ = 38.4. – [d] For **12b** Et in place of H.

Adduct and Complex Formation of Ylidylphosphanes

As it is well known of other phosphanes, the ylidylphosphanes **7** also add to carbon disulfide. The adduct undergoes a proton shift to the ylidic carbon atom to give the betaine **23** which can be deprotonated, yielding the ylidylphosphanyl dithioformate **24**.



23a R = Me
23b R = Ph



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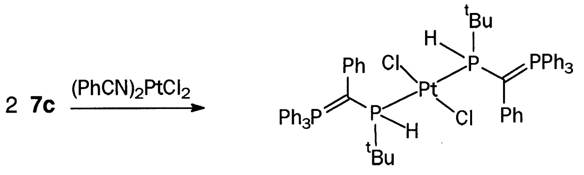
The ylidylphosphane **7c** adds in a 2:1 ratio to platinum dichloride. The complex **25** contains the unchanged ligand in a *trans*-coordination and is formed as a roughly equimolar mixture of two diastereomers. Their ^{31}P-NMR data are almost identical and result, therefore, in overlapping spectra which could, however, be analyzed by calculation[8]. The coordination to platinum is demonstrated by the coordination shift from $\delta^{31}P^{III}$ = −33.2 to 6.0, by the increase in P–H-coupling from $^{1}J_{PH}$ = 207.1 to 379.0 Hz, and the decrease of P–P-coupling from $^{2}J_{PP}$ = 154.9 to 14.5 and 16.6 Hz as well as by the satellite signals originating from the ^{195}Pt-containing isotopomer with $^{1}J_{PtP}$ = 2331.4 Hz. The coupling constant $^{2}J_{PP}$ = 513.6 Hz between the coordinated phosphorus atoms of the two ligand molecules is characteristic of a *trans* coordination[9].



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Complex formation in which an ylidylphosphane makes use not only of its phosphane site is exemplified by the complex of **7c** with the 16-electron fragment CpMn(NO)CO^{+}. Through an additional nucleophilic interaction of the ylidic carbon atom with the carbonyl group, a four-membered ring is formed in this case[10].

Experimental Section

All manipulations were carried out in flame-dried glassware under argon using Schlenk tube techniques. Dry dichloromethane and benzene were used as obtained (Fluka). Pentane was dried over molecular sieves (4 Å). Tetrahydrofuran was dried by refluxing with sodium/benzophenone and subsequent distillation. Melting points were determined in sealed capillaries. – NMR: JEOL GSX 270 (^{7}Li, ^{31}P), JEOL EX 400 (^{1}H, ^{13}C) with Me_4Si (int.), 85% H_3PO_4 (ext.), and aqueous LiCl (ext.) as standards. The aromatic hydrogen atoms in *ortho*, *meta*, and *para* positions of C-Ph are identified as 2-, 3-, 4-H, those of P^{III}-Ph as 6-, 7-, 8-H and those of Ph_3P as *o*-, *m*-, *p*-H. – The ylidyl chlorophosphanes **6**[2] and **8**[1] were prepared as described.

[α-(Methylphosphanyl)benzylidene]triphenylphosphorane (**7a**): To a stirred suspension of $LiAlH_4$ (0.76 g, 20.0 mmol) in 20 ml of THF, a solution of **6a** (8.65 g, 20.0 mmol) in 175 ml of THF was added dropwise at −40°C over 2 h. After cooling the grey suspension for an additional 6 h, it was warmed up to ambient temperature over 2 h. The precipitate was filtered off, and the orange filtrate was concentrated to 50% of its original volume. After standing at room temperature for 12 h, orange crystals were filtered off, washed with THF, and dried in vacuo. By concentration of the filtrate to about 20% of its original volume a second crop could be obtained. Yield 6.78 g (78%) of **7a**·0.5 THF, dec. > 60–63°C. – ^{1}H NMR (C_6D_6): δ = 1.35 (t, $^{2}J_{PH}$ = 6.0 Hz, $^{3}J_{HH}$ = 6.0 Hz, CH_3), 5.04 (ddq, $^{1}J_{PH}$ = 205.8 Hz, $^{3}J_{PH}$ = 24.3 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1 H, P-H), 6.75 (tm, *J* = 7.3 Hz, *J* = 0.7 Hz, 1 H, 4-H), 6.93–7.09 (m, 11 H, arom. H), 7.42 (d, $^{4}J_{PH}$ = 7.9 Hz, 2 H, 2-H), 7.62–7.69 (m, 6 H, *o*-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 8.6 (dd, $^{1}J_{PC}$ = 15.3 Hz, $^{3}J_{PC}$ = 3.8 Hz, CH_3), 26.6 (dd, $^{1}J_{PC}$ = 115.2, 22.9 Hz, C=PPh_3), 118.5 (s, 4-C), 126.7 (d, $^{4}J_{PC}$ = 10.7 Hz, 3-C), 128.5 (d, $^{3}J_{PC}$ = 11.4 Hz, *m*-C), 130.1 (dd, $^{1}J_{PC}$ = 86.2 Hz, $^{3}J_{PC}$ = 5.0 Hz, *i*-C), 131.4 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-C), 133.2 (d, $^{3}J_{PC}$ = 9.2 Hz, 2-C), 134.5 (dd, $^{2}J_{PC}$ = 9.2 Hz, $^{4}J_{PC}$ = 2.3 Hz, *o*-C), 145.5 (d, $^{2}J_{PC}$ = 11.5 Hz, 1-C). – $C_{26}H_{24}P_2 \cdot 1/2\ C_4H_8O$ (434.48): calcd. C 77.41, H 6.50; found C 77.12, H 6.35.

[α-(Ethylphosphanyl)benzylidene]triphenylphosphorane (**7b**): Prepared as described above from (0.53 g, 14.0 mmol) of $LiAlH_4$ and **6b** (6.19 g, 13.9 mmol). Yield 4.97 g (80%) of **7b**·0.5 THF, dec. > 66°C. – ^{1}H NMR (C_6D_6): δ = 1.06 (dt, $^{3}J_{PH}$ = 17.1 Hz, $^{3}J_{HH}$ = 7.8 Hz, 3 H, CH_3), 1.42 (m, 2 H, THF), 1.78–1.96 (m, 2 H, CH_2), 3.56 (m, 2 H, THF), 4.91 (dddd, $^{1}J_{PH}$ = 204.6 Hz, $^{3}J_{PH}$ = 20.0 Hz, $^{3}J_{HH}$ = 7.8, $^{3}J_{HH}$ = 3.4 Hz, 1 H, P-H), 6.72 (tt, *J* = 7.3 Hz, *J* = 1.0 Hz, 1 H, 4-H), 6.95–7.07 (m, 11 H, arom. H), 7.42 (d, $^{4}J_{PH}$ = 8.3 Hz, 2 H, 2-H), 7.63–7.69 (m, 6 H, *o*-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 11.8 (d, $^{2}J_{PC}$ = 16.8 Hz, CH_3), 16.7 (dd, $^{1}J_{PC}$ = 10.6 Hz, $^{3}J_{PC}$ = 3.0 Hz, CH_2), 25.8 (s, THF), 25.9 (dd, $^{1}J_{PC}$ = 114.4 HZ, $^{1}J_{PC}$ = 24.4 Hz, C=PPh_3), 67.8 (s, THF), 118.5 (s, 4-C), 126.6 (d, $^{4}J_{PC}$ = 10.2 Hz, 3-C), 128.5 (d, $^{3}J_{PC}$ = 10.7 Hz, *m*-C), 130.1 (dd, $^{1}J_{PC}$ = 87.0 Hz, $^{3}J_{PC}$ = 6.1 Hz, *i*-C), 131.4 (s, *p*-C), 133.2 (d, $^{3}J_{PC}$ = 10.7 Hz, 2-C), 134.6 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-C), 146.0 (d, $^{2}J_{PC}$ = 10.7 Hz, 1-C). – $C_{27}H_{26}P_2.1/2\ C_4H_8O$ (448.50): calcd. C 77.66, H 6.74; found C 76.84, H 7.07.

[α-(tert-Butylphosphanyl)benzylidene]triphenylphosphorane (**7c**): Prepared as described above from (0.84 g, 22.1 mmol) of $LiAlH_4$ and **6c** (10.56 g, 22.2 mmol). Yield 6.53 g (67%) of **7c**, m.p. 124–126°C. – ^{1}H NMR (C_6D_6): δ = 1.53 (d, $^{3}J_{PH}$ = 12.5 Hz, CH_3), 5.27 (dd, $^{1}J_{PH}$ = 210.7 Hz, $^{3}J_{PH}$ = 25.6 Hz, P-H), 7.01 (t, *J* = 7.1 Hz, 1 H, 4-H), 7.26–7.37 (m, 11 H, arom. H), 7.85 (d, $^{4}J_{PH}$ = 8.6 Hz, 2 H, 2-H), 7.95–8.01 (m, 6 H, *o*-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 27.7 (dd, $^{1}J_{PC}$ = 111.0 Hz, $^{1}J_{PC}$ = 31.3 Hz, C=PPh_3), 30.9 (d, $^{2}J_{PC}$ = 15.6 Hz, CH_3), 32.6 [dd, $^{1}J_{PC}$ = 15.6 Hz, $^{3}J_{PC}$ = 4.2 Hz, C-$(CH_3)_3$], 119.3 (s, 4-C), 127.6 (s, 3-C), 128.4 (d, $^{3}J_{PC}$ = 11.8 Hz, *m*-C), 130.4 (dd, $^{1}J_{PC}$ = 85.8 Hz, $^{3}J_{PC}$ = 4.6 Hz, *i*-C), 131.4 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-C), 134.1 (d, $^{3}J_{PC}$ = 19.8 Hz, 2-C), 134.8 (dd, $^{2}J_{PC}$ = 8.8 Hz, $^{4}J_{PC}$ = 1.9 Hz, *o*-C), 146.4 (dd, $^{2}J_{PC}$ = 11.1, 1.1 Hz, 1-C). – $C_{29}H_{30}P_2$ (440.50): calcd. C 79.07, H 6.86; found C 78.40, H 6.99.

[α-(Phenylphosphanyl)benzylidene]triphenylphosphorane (**7d**): Prepared as described above from (0.82 g, 21.6 mmol) of $LiAlH_4$ and **6d** (10.75 g, 21.7 mmol). Yield 9.53 g (89%) of **7d**·0.5 THF, dec. > 84°C. – ^{1}H NMR (C_6D_6): δ = 1.42 (m, 2 H, THF), 3.56 (m, 2 H, THF), 5.86 (dd, $^{1}J_{PH}$ = 220.6 Hz, $^{3}J_{PH}$ = 21.4 Hz, P-H), 6.69 (tt, *J* = 7.3 Hz, *J* = 1.0 Hz, 1 H, 4-H), 6.91–7.21 (m, 14 H, arom. H), 7.45 (d, $^{3}J_{PH}$ = 8.1 Hz, 2 H, 2-H), 7.68–7.74 (m, 8 H, *o*-H/6-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 25.6 (s, THF), 26.2 (dd, $^{1}J_{PC}$ = 114.5 Hz, $^{1}J_{PC}$ = 19.2 Hz, C=PPh_3), 67.6 (s, THF), 118.4 (s, 4-C), 125.8 (d, $^{4}J_{PC}$ = 11.5 Hz, 3-C), 126.0 (s, 8-C), 127.8 (C_6D_6), 128.1 (superimposed, *i*-C), 128.2 (d, superimposed, 7-C), 128.4 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*-C), 129.8 (d, $^{2}J_{PC}$ = 15.4 Hz, 6-C), 131.4 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-C), 132.2 (d, $^{3}J_{PC}$ = 10.0 Hz, 2-C), 134.3 (dd, $^{2}J_{PC}$ = 9.2 Hz, $^{4}J_{PC}$ = 1.5 Hz, *o*-C), 143.9 (dd, $^{1}J_{PC}$ = 20.0 Hz, $^{3}J_{PC}$ = 6.9 Hz, 5-C), 146.2 (d, $^{2}J_{PC}$ = 12.3 Hz, 1-C). – $C_{31}H_{26}P_2 \cdot 1/2\ C_4H_8O$ (496.55): calcd, C 79.82, H 6.09; found C 79.57, H 5.57.

[α-(Phosphanyl)benzylidene]triphenylphosphorane (**9a**): To a stirred suspension of $LiAlH_4$ (0.73 g, 19.2 mmol) in 20 ml of THF, a solution of **8a** (3.47 g, 7.7 mmol) in 20 ml of THF was added dropwise at −40°C over 30 min. The brown suspension was stirred for an additional 30 min. The precipitate was filtered off, and the orange filtrate was concentrated to 50% of its original volume. Compound **9a** is stable in solution below −40°C.

[(3-Methylphenyl)phosphanylmethylidene]triphenylphosphorane (**9b**): Prepared as described above from (112 mg, 2.9 mmol) of $LiAlH_4$ and **8b** (0.55 g, 1.2 mmol). **9b** is stable in solution below −40°C.

[(3-Methylphenyl)phosphanylmethylidene]triphenylphosphorane (**9c**): Prepared as described above from $LiAlH_4$ (0.12 mg, 3.2 mmol) and **8c** (0.71 g, 3.2 mmol). Compound **10c** is observed as a by-product. After standing at ambient temperature for 10 h, **9c** and **10c** can no longer be detected by ^{31}P NMR.

Deprotonation of **7d**: In an NMR tube, **7d** (105 mg, 0.2 mmol) was dissolved in 0.5 ml of THF. A 1.56 mol/l solution of *n*BuLi (0.13 ml, 0.2 mmol) in hexane was added. After 10 min, a ^{31}P-NMR spectrum of the deep red solution was recorded at room temp. ^{31}P{^{1}H} NMR (THF, hexane): AB (40%), δ_A = 21.6 δ_B = −54.9 (broad, superimposed), J_{AB} = 57.1 Hz, AB (21%), δ_A = 20.8, δ_B = −54.9 (broad, superimposed), J_{AB} = 57.6 Hz, δ = 8.6 (s, 7%), 4.5 (s, 11%), −6.5 (d, *J* = 187.9.5 Hz, 5%), −32.7 (d, *J* = 188.4 Hz, 4%). In the ^{1}H-coupled ^{31}P-NMR spectrum no $^{1}J_{PH}$ could be detected. – ^{7}Li{^{1}H} NMR (THF, hexane): δ = 2.3 (s).

Thermolysis of Ylidylphosphanes **7a**, **b**, **d**, **e**: In an NMR tube a solution of **7a**, **b**, **d**, **e** (0.3 mmol) in 0.05 ml of THF was warmed to 60°C for 120 seconds. After 5 min a ^{31}P-NMR spectrum of the red (**7d** orange) solution was recorded at room temp. (For results see text and Table 3). Further heating of **7a**, **b**, **d** to 60°C for an additional 5 h yielded a mixture of the cyclophosphanes **15**, **16**, and **17** and the ylide **2e**. A solution of **7c** in C_6H_6 remains unchanged after refluxing for 7 d.

Cothermolysis of **7d** *and* **7e**: In an NMR tube, a solution of **7d** (91 mg, 0.2 mmol) and **7e** (146 mg, 0.2 mmol) in 0.7 ml of THF was warmed at 60°C for 240 seconds. After 5 min, a ^{31}P-NMR spectrum of the red solution showed a mixture of **2e**, **18d**, and starting materials.

Ylidyl Diphosphane **11d**: To a stirred solution of **7d** (3.75 g, 7.6 mmol) in 60 ml of THF, a solution of 1.0 mol/l HCl (3.78 ml, 3.8 mmol) in diethyl ether and 20 ml of THF was added dropwise at 0°C over 30 min. The white precipitate of $Ph_3P-CH_2Ph^+Cl^-$ was filtered off, and 80 ml of pentane was added to the yellow solution. After cooling to −20°C for 12 h, the yellow precipitate was filtered off, washed twice with THF/pentane (1:1) and dried in vacuo. The ^{31}P NMR of the precipitate showed the signals for **11d** and for small residues of **7d**.

Reaction of **7d** *with HCl:* To a fresh solution of **7d** (210 mg, 04 mmol) in 5 ml of dichloromethane 1.0 mol/l HCl (0.47 ml, 0.5 mmol) in diethyl ether was added. After 5 min, a ^{31}P-NMR spectrum was recorded. It showed the signals of **19d**, $Ph_3P-CH_2Ph^+Cl^-$, **16d**, **17d**, and $PhPH_2$.

Preparation of **20d**: A solution of **7d** (2.10 g, 4.2 mmol) in 20 ml of THF was added dropwise to a solution of 54% HBF_4 (0.82 ml, 4.2 mmol) in diethyl ether and 8 ml of THF at −60°C over 10 min. After additional stirring for 10 min, the white precipitate was filtered off, washed twice with pentane and dried in vacuo. Yield: 2.09 g (91%) of **20d** (2 diastereomers), m.p. 162−165°C. − ^1H NMR ($CDCl_3$): δ = 4.41 (ddd, $^1J_{PH}$ = 222.9 Hz, $^3J_{PH}$ = 8.8 Hz, $^3J_{HH}$ = 7.8 Hz, PH), 4.89 (ddd, $^1J_{PH}$ = 216.9 Hz, $^3J_{HH}$ = 5.0 Hz, J = 1.2 Hz, PH), 4.98 (dd, $^2J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 7.7 Hz, CH), 5.42 (dd, $^2J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 4.9 Hz, CH), 6.69−7.74 (m, 50 H, arom. H). − $C_{31}H_{27}BP_2F_4$ (548.31): calcd. C 67.91, H 4.96; found C 67.38, H 4.82.

Reaction of **7c** *with HCl:* In an NMR tube, 1.0 mol/l HCl (0.25 ml, 0.3 mmol) in diethyl ether was added to a solution of **7c** (213 mg, 0.5 mmol) in 0.5 ml of THF. After 30 min, a ^{31}P-NMR spectrum was recorded and showed signals of equal amounts for **7c** and **20c**.

Ylidyldiphosphane **11f**: In an NMR tube, **20d** (158 mg, 0.3 mmol) and **7b** (126 mg, 0.3 mmol) were suspended in 0.5 ml of THF. After 10 min, a ^{31}P-NMR spectrum was recorded and showed the signals for **11f**, **3d**, $Ph_3P-CH_2Ph^+Cl^-$, and **2e**.

Ylidyldiphosphane **11g**: As described above from **20d** (103 mg, 0.2 mmol) and **7c** (81 mg, 0.2 mmol). A ^{31}P NMR showed the signals for **7c**, **11g**, and **20c**.

Reaction of **7d** *with MeI:* To a stirred solution of **7d** (0.16 g, 0.3 mmol) in 7 ml of THF, a solution of MeI (0.02 ml, 0.4 mmol) in 5 ml of THF was added dropwise. After 1 h, a white precipitate had formed. $^{31}P\{^1H\}$ NMR (THF, CH_2Cl_2): **7d**, AB (**21**), δ_A = 21.2, δ_B = 13.7, J_{AB} = 59.9 Hz, $(PhP)_3$.

Reaction of **7d** *with* $MePCl_2$*:* As described earlier from **7d** (0.20 g, 0.4 mmol) and methyldichlorophosphane (0.039 ml, 0.4 mmol). 5 ml of dichloromethane were added to the suspension to yield a colourless solution. $^{31}P\{^1H\}$ NMR (THF, CH_2Cl_2): AB (**22**), δ_A = 97.6, δ_B = 24.9, J_{AB} = 62.2 Hz, **16d**, **17d**.

Reaction of **7a** *with* CS_2*:* To a stirred suspension of **7a** (1.48 g, 3.4 mmol) in 25 ml of THF, a solution of carbon disulfide (0.21 ml, 3.5 mmol) in 10 ml of THF was added at 0°C over 15 min. After 10 min the pale red precipitate was filtered off, washed twice with THF/pentane (1:1) and dried in vacuo. − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): AB (**23a**), δ_A = 25.1, δ_B = 13.4, J_{AB} = 89.3 Hz, δ = 23.6 (s). In an NMR tube, 110 mg of the precipitate and $NaN(SiMe_3)_2$ (45 mg) were dissolved in 0.5 ml of THF, to yield a red solution. − $^{31}P\{^1H\}$ NMR (THF): AB (**24**), δ_A = 28.9, δ_B = 19.1, J_{AB} = 191.0 Hz, δ = 8.4 (s).

Reaction of **7d** *with* CS_2*:* As described above from **7d** (0.90 g, 1.8 mmol) and carbon disulfide (0.11 ml, 1.8 mmol). − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): AB (**23b**), δ_A = 25.7, δ_B = 18.2, J_{AB} = 98.1 Hz, δ = 23.1 (s). The product was recrystallized from dichloromethane/pentane (2:1). − ^1H NMR ($CDCl_3$): δ = 5.32 (m, broad, 1 H, CH), 6.69−6.91 (m, 4 H, arom. H), 6.96 (t, J = 7.81 Hz, arom. H), 7.21−7.50 (m, 9 H, arom. H, *m*-H), 7.57−7.74 (m, 10 H, arom. H, *o*-H). − $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 47.8 (dd, $^1J_{PC}$ = 54.2 Hz, 50.4 Hz, CH).

$PtCl_2$ Complex of **7c**: In an NMR tube, $PtCl_2(PhCN)_2$ (53 mg, 0.1 mmol) was added to a solution of **7c** (104 mg, 0.2 mmol) in 0.5 ml of THF. After 30 min, a ^{31}P-NMR spectrum of the yellow solution was recorded. − $^{31}P\{^1H\}$ NMR (THF): AB (**7c**, 57%), $[AB]_2$ (**25**, diastereomer I, 16%), $[AB]_2X$ (**25**, X = Pt, 7%), δ_A = 18.8, δ_B = 6.0 (superimposed), $^2J_{AB}$ = 16.6 Hz, $^1J_{BX}$ = 2331.4 Hz, $[AB]_2$ (**25**, diastereomer II, 10%), $[AB]_2X$ (**25**, X = Pt, 5%), δ_A = 18.6, δ_B = 6.0 (superimposed), $^2J_{AB}$ = 14.5 Hz, $^1J_{BX}$ = 2331.4 Hz.

Crystal Structure Determinations: Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å]. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied, but intensity data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-ma-

Table 4 Crystallographic data and details of data collection and structure refinement of compounds **7a**, **d**

	7a·THF	**7d**·0.5 THF
Crystal data		
Formula	$C_{30}H_{32}OP_2$	$C_{33}H_{30}O_{0.5}P_2$
M_r	470.54	496.51
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Crystal dimensions [mm]	0.4 × 0.45 × 0.45	0.15 × 0.45 × 0.45
a [Å]	9.057(1)	9.969(1)
b [Å]	14.423(2)	14.426(1)
c [Å]	19.788(2)	19.040(1)
β	94.34(1)	104.10(1)
V [Å^3]	2577.6(6)	2655.7(4)
r [g cm^{-3}]	1.212	1.242
Z	4	4
F (000) [e]	1000	1048
μ (Mo-K_α) [cm^{-1}]	1.83	1.86
Data collection		
T [°C]	− 62	− 68
Scan Mode	Θ-Θ	ω
h, k, l range	0/10, 0/17, −23/23	0/11, 0/17, −23/22
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.59	0.62
Measured refl.	4848	4754
Unique refl.	3989	4495
Observed refl.	4629	4489
Refinement		
Refined parameters	329	314
H atoms (found/calcd.)	1/23	1/29
$R1$[a]	0.0513	0.0492
$wR2$[b]	0.0652	0.1217
(shift/error)$_{max}$	<0.001	<0.001
ρ_{fin} (max/min) [eÅ^{-3}]	0.30/−0.26	0.93/−0.33

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. − [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0592 (**7a**·THF), 0.0627 (**7d**·0.5 THF); b = 2.91 (**7a**· THF), 2.02 (**7d**·0.5 THF).

trix-least squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the solvent THF molecules, which were disordered in both compounds. C−*H* atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{\mathrm{iso(fix)}} = 1.5 \times U_{\mathrm{eq}}$ of the attached C atom). The P−*H* atoms were found and included with isotropic (**7a**·THF) and fixed isotropic contributions (**7d**·0.5 THF, $U_{\mathrm{iso(fix)}} = 0.08$ Å^2). Further information on crystal data, data collection and structure refinement are summarized in Table 4. Important interatomic distances and angles are shown in Table 2. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-407613 (**7a**·THF), -407614 (**7d**·0.5 THF).

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