The interaction of phosphavinyl Grignard reagents with group 15 halides: synthesis and structural characterisation of novel heterocyclic and heterocage compounds

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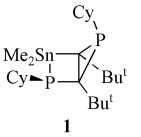
The reactions of a phosphavinyl Grignard reagent, $[CyP{=}C(Bu^t)MgCl(OEt_2)]$, Cy = cyclohexyl, with a variety of group 15 halide compounds in a number of stoichiometries have been investigated. When the Grignard reagent is reacted with Ph_2PCl or $CyPCl_2$, Cy = cyclohexyl, in a 1:1 and 2:1 stoichiometry respectively, the 1,3-diphosphapropene, $Ph_2PC(Bu^t){=}PCy$, and triphosphabicyclo[2.1.0]pentane compound, $CyP\{C_2(Bu^t)_2P_2Cy_2\}$, are formed. The 2:1 and 3:1 reactions of the Grignard reagent with either PCl_3 or $AsCl_3$ lead to the strained triphospha- and arsadiphosphabicyclo[1.1.1]pentanes, $Bu^tC\{\mu\text{-}P(Cy)\}_2\{\mu\text{-}ECl\}CBu^t$, E = P or As in moderate yield. The related 1:1 reaction of the Grignard reagent with PCl_3 affords two products, a phosphino-substituted phosphorus ylide, $Cl_2PC(Bu^t){=}P(Cy)(Cl)_2$, and a tetraphosphabicyclo[2.1.1]hexane, $Bu^tC\{\mu\text{-}P(Cl)P(Cy)\}\{\mu\text{-}P(Cy)\}\{\mu\text{-}P(Cl)\}CBu^t$, the mechanism of formation of which is discussed. An analogous 1:1 reaction of the Grignard reagent with $SbCl_3$ led to an unusual heterocyclic compound, $(Cl_2Sb)(Bu^t)CSb(Cl)C(Bu^t){=}P(Cl)(Cy)P(Cy)$, which quantitatively decomposes in solution to yield the known 1,2-dihydro-1,2-diphosphete, $P_2(Cy)_2C_2(Bu^t)_2$. All prepared compounds have been crystallographically characterised.

Introduction

Several years ago we developed a high yielding, stereo- and regiospecific synthetic route to a range of phosphavinyl Grignard reagents, *Z*-$[RP{=}C(Bu^t)MgCl(OEt_2)]$, R = alkyl or aryl.[1] Since that time we have been systematically investigating the utility of these compounds as transfer reagents in reactions with main group and transition metal halide complexes. We have found that phosphavinyl Grignard reagents generally behave significantly differently to their widely exploited vinyl counterparts. These differences include the ease with which the phosphavinyl fragment undergoes coupling reactions at the metal centre to give a variety of novel metallocage, heterocyclic and other coupled products, *e.g.* **1**[2] and **2**.[3] In addition, oxidative coupling of the phosphavinyl fragment can occur in these reactions to give strained heterocyclic systems such as **3**[4] and **4**.[5] Despite the facility of such coupling reactions, complexes containing 1 or 2 terminal phosphavinyl ligands can be prepared, *e.g.* $[(o\text{-}C_6H_4O_2)B\text{–}C(Bu^t){=}PCy]$[6] and $[Me_2Sn\{\text{–}C(Bu^t){=}PCy\}_2]$,[2] and their utility as ligands has been explored.

Given the wide applicability of vinyl group 15 compounds to several areas of synthesis, *e.g.* organo–group 15 synthesis,[7] macrocycle formation[8] *etc.*, and the ever increasing importance of phosphorus containing heterocycle and cage compounds,[9] we wished to extend our study to the preparation of phosphavinyl–group 15 compounds. This has led to the formation of a number of novel and often unexpected heterocyclic and heterocage compounds as described herein.



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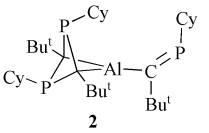

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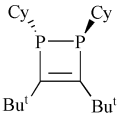

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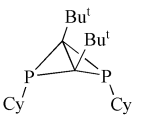

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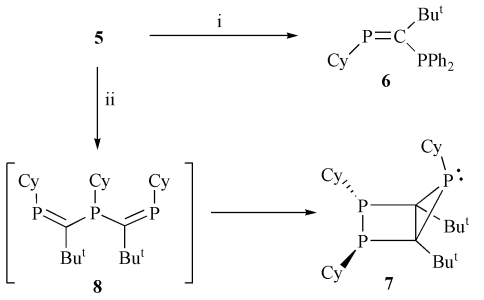
Results and discussion

In the initial stages of this work attempts were made to prepare heteroleptic group 15–phosphavinyl complexes *via* the reaction of $[CyP{=}C(Bu^t)MgCl(OEt_2)]$ **5** with either Ph_2PCl or *in situ* generated $CyPCl_2$ (Scheme 1). In the former reaction the expected 1,3-diphosphapropene, **6**, was formed in high yield (75%) with retention of the stereochemistry of the phosphavinyl fragment, whilst in the latter reaction a phosphavinyl coupling occurred to give a high yield (62%) of the triphosphabicyclo[2.1.0]pentane compound, **7**. The intermediate in this reaction is presumably **8** though this was not observed when the reaction was followed by ^{31}P NMR spectroscopy as **7** rapidly formed, even at −50 °C.

The spectroscopic data for both compounds are consistent with their proposed structures. In the case of **6** the $^{31}P\{^1H\}$



Scheme 1 *Reagents and conditions:* i, Ph_2PCl, Et_2O; ii, 1/2 $CyPCl_2$, Et_2O.

NMR spectrum displays a low field signal (350.1 ppm) for the phosphaalkene P-centre and a higher field signal (23.6 ppm) for the PPh_2 fragment with a large mutual two bond coupling of 140 Hz. The $^{31}P\{^1H\}$ NMR spectrum of **7** displays 3 signals, one at −104.3 ppm in the region normally associated with 3-membered phosphirane rings and the other two at lower field (−16.3 and 11.2 ppm), corresponding to the phosphorus centres in the 4-membered ring. The one bond coupling constant (86 Hz) between these two centres is low but can be explained by the likely high degree of p-character in the bond between these two centres.

X-Ray crystal structure analyses of **6** and **7** were carried out to confirm their proposed structures (Figs. 1 and 2, Table 1). Compound **6** was found to be monomeric and to crystallise in the *Z*-isomeric form. The bond lengths P(1)–C(1) [1.678(3) Å] and P(2)–C(1) [1.855(3) Å] are significantly different but normal for localised double and single bonds respectively.[10] These bond lengths are close to those reported recently in the first crystallographically characterised 1,3-diphosphapropene complexes, $[W(CO)_5\{\eta^1\text{-}Z\text{-}P(Ph)_2C(Cl)=PMes^*\}]$ and $[W(CO)_4\{\eta^2\text{-}P,P\text{-}Z\text{-}P(Ph)_2C(Cl)=PMes^*\}]$, Mes* = $C_6H_2Bu^t_3$-2,4,6.[11] Compound **7** is the first structurally characterised example of a 2,3,5-triphosphabicyclo[2.1.0]pentane. It is monomeric and all bond lengths within the bicyclic framework are normal for single bonded interactions. The cyclohexyl

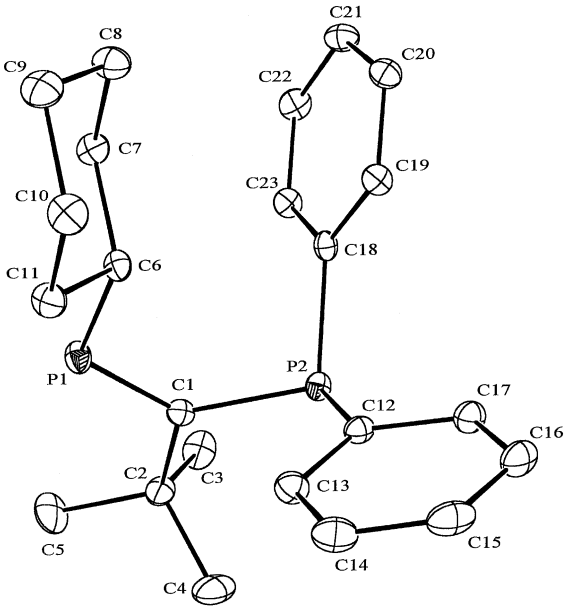


Fig. 1 Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.678(3), P(2)–C(1) 1.855(3), P(1)–C(6) 1.856(3), P(2)–C(12) 1.835(3), P(2)–C(18) 1.835(3), P(1)–C(1)–P(2) 129.80(16), C(1)–P(1)–C(6) 111.18(13), C(2)–C(1)–P(1) 118.1(2), C(2)–C(1)–P(2) 112.0(2).

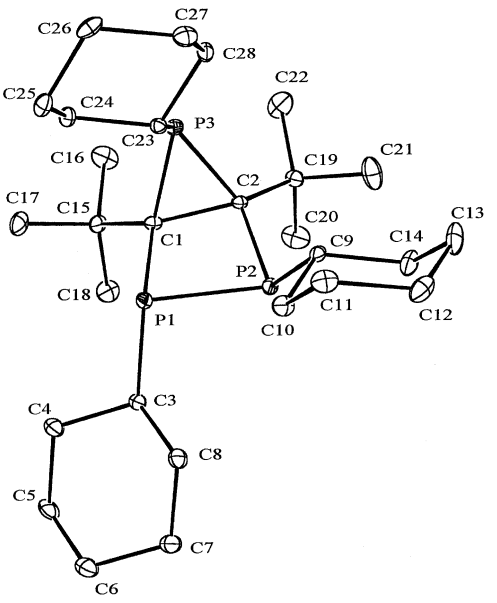


Fig. 2 Molecular structure of compound **7**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.902(4), P(1)–P(2) 2.1986(17), P(2)–C(2) 1.860(4), P(3)–C(1) 1.854(4), P(3)–C(2) 1.864(4), C(1)–C(2) 1.576(5), C(1)–P(1)–P(2) 78.17(13), C(2)–P(2)–P(1) 81.79(13), C(1)–P(3)–C(2) 50.17(17), C(2)–C(1)–P(3) 65.25(19), C(2)–C(1)–P(1) 99.8(2), P(3)–C(1)–P(1) 109.06(19), C(1)–C(2)–P(2) 97.8(2), C(1)–C(2)–P(3) 64.59(19), P(2)–C(2)–P(3) 120.6(2).

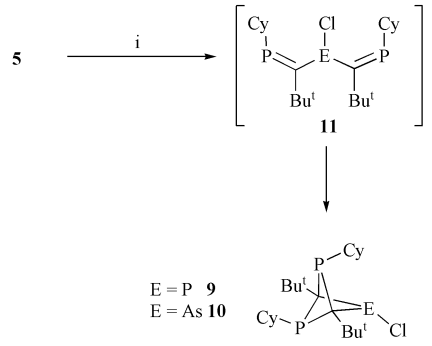
substituents at P(1) and P(2) are *trans* to each other and the P(3) substituent is in the *endo*-position. It is noteworthy that a similar bicyclic framework was observed for the stannadiphosphabicyclopentane, **1**,[2] and in that case the phosphirane cyclohexyl substituent is also *endo*.

As an extension of this work attempts were made to prepare homoleptic phosphavinyl–group 15 complexes by reacting 3 equivalents of **5** with ECl_3, E = P, As, Sb and Bi. The reactions with PCl_3 and $AsCl_3$ led to the formation of the triphospha- and arsadiphosphabicyclo[1.1.1]pentanes, **9** and **10** respectively, in moderate yields after crystallisation from hexane (Scheme 2). Presumably these are formed *via* the bisphosphavinyl phosphorus or arsenic intermediates, **11**, which undergo facile phosphavinyl coupling reactions to give the bicyclic product. The intermediates were not observed when the reactions were followed by ^{31}P NMR spectroscopy and even at −50 °C **9** and **10** rapidly formed. It is worth noting that the proposed intermediate, **11**, is closely related to **8** but the framework of the phosphavinyl coupled product derived from the former is significantly different to that of the latter. It is also interesting that only two equivalents of the phosphavinyl Grignard react with the element halides and the remaining chloride ligands in **9** and **10** are not open to substitution. This contrasts with the formation of **2** from the reaction of 3 equivalents of **5** with $AlCl_3$. It is thought that in that case an intermediate analogous to **9**, *i.e.* E = Al, is involved though the likely trigonal planar Al centre in this intermediate is more open to nucleophilic attack than the pyramidal P or As centres in **9** and **10**. When the reactions of **5** with PCl_3 or $AsCl_3$ were carried out in a 2:1 stoichiometry, **9** and **10** were again formed in similar yields. In addition, it should be mentioned that related trihalotriphosphabicyclo[1.1.1]pentanes, $Bu^tC\{\mu\text{-}P(X)\}_3CBu^t$, X = Cl, Br or I, have been reported to be formed by a very different route involving treatment of the 1,3-diphosphabicyclobutanediyl complex, $[Cp_2Zr\{\eta^2\text{-}C_2(Bu^t)_2P_2\}]$, with PX_3.[12]

The spectroscopic data for **9** and **10** are as expected in that the $^{31}P\{^1H\}$ NMR spectra of both compounds display signals

Table 1 Crystal data for compounds **6**, **7**, **9**, **10**, **12**, **13**, **14** and **16**

	6	**7**	**9**	**10**	**12**	**13**	**14**	**16**
Chemical formula	$C_{23}H_{30}P_2$	$C_{28}H_{51}P_3$	$C_{22}H_{40}ClP_3$	$C_{22}H_{40}AsClP_2$	$C_{27}H_{40}O_5P_2W$	$C_{22}H_{40}Cl_2P_4$	$C_{11}H_{20}Cl_4P_2$	$C_{22}H_{40}Cl_4P_2Sb_2$
FW	368.41	480.60	432.90	476.90	690.38	499.32	356.01	751.78
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbcn*	*Pbcn*	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	9.7667(8)	10.012(4)	10.124(2)	10.1511(11)	10.441(2)	9.4270(19)	8.1380(16)	10.367(2)
b/Å	9.8576(5)	10.877(4)	23.941(5)	24.438(3)	18.702(4)	16.555(3)	12.136(2)	23.930(6)
c/Å	12.5778(9)	15.047(7)	9.791(2)	9.8440(11)	15.226(3)	16.512(3)	16.208(3)	10.889(2)
α/°	87.871(5)	72.31(3)	90	90	90	90	90	90
β/°	69.191(6)	89.79(3)	90	90	103.99(3)	93.34(3)	95.58(3)	114.71(3)
γ/°	69.303(6)	66.25(3)	90	90	90	90	90	90
V/Å^3	1053.47(13)	1415.7(10)	2373.1(8)	2442.1(5)	2885.0(10)	2572.6(9)	1593.2(5)	2864.2(10)
Z	2	2	4	4	4	4	4	4
T/K	293(2)	150(2)	150(2)	223(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo-K$_\alpha$)/mm^{-1}	0.21	0.22	0.37	1.64	4.15	0.51	0.92	2.38
Reflections collected	4017	5977	4176	10121	5653	48132	27552	30376
Unique reflections (R_{int})	3777 (0.0223)	5751 (0.0835)	2135 (0.0841)	1725 (0.0771)	5199 (0.0478)	5884 (0.0361)	3647 (0.0499)	5560 (0.0800)
$R1$ ($I > 2\sigma(I)$)	0.0425	0.0574	0.0670	0.0923	0.0394	0.0286	0.0256	0.0488
w$R'2$ (all data)	0.1176	0.1449	0.1877	0.2470	0.1366	0.0700	0.0643	0.1207



Scheme 2 *Reagents and conditions:* i, 1/3 ECl_3, Et_2O.

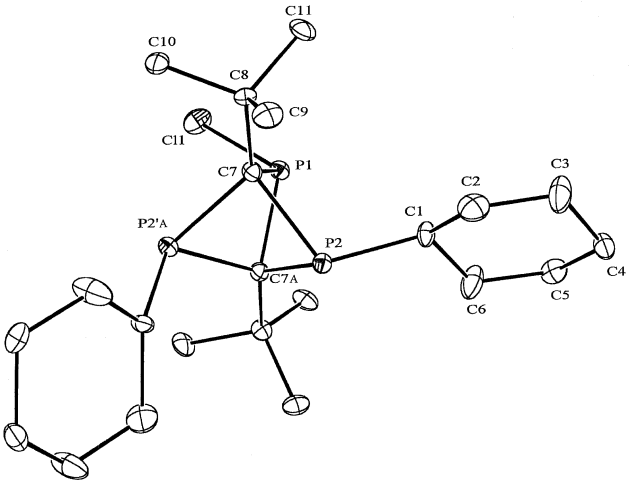


Fig. 3 Molecular structure of compound **9**. Selected bond lengths (Å) and angles (°): Cl(1)–P(1) 2.095(3), P(1)–C(7) 1.848(5), P(2)–C(7) 1.926(5), P(2′A)–C(7) 1.931(5), C(7A)–P(1) 1.816(5), C(7A)–P(2) 1.898(5), C(7)–P(1)–C(7A) 76.5(3), C(7)–P(2)–C(7A) 72.8(3), C(7)–P(2′A)–C(7A) 72.2(2), Cl(1)–P(1)–C(7) 110.7(2), P(1)–C(7)–P(2) 84.2(2), P(1)–C(7)–P(2′A) 89.0(2), P(2)–C(7)–P(2′A) 87.6(2). Symmetry transformation A: $-x$, y, $-z+1/2$.

for 3 or 2 chemically inequivalent phosphorus centres with no measurable two bond P–P couplings, again most likely because of the acute nature of the C–P–C angles in the strained cages. As expected, only one Bu^t signal is seen in the ^{1}H NMR spectra and both compounds exhibit molecular ion peaks in their APCI mass spectra.

The X-ray crystal structures of **9** and **10** are isomorphous and show the hetero-atoms of each to be disordered over two sites. In addition, there is a disorder within the cyclohexyl substituents. Each disordered molecule lies on a 2-fold axis containing Cl(1) and the mid point between C(7) and C(7A). Only one disordered set is shown in Figs. 3 and 4 (see Table 1). The strained nature of these bicyclic compounds becomes clear when the angles within the cages are examined. In the case of **9** the average framework C–P–C angle is 74.7° whilst the average P–C–P angle is 86.9°. Similar angles are seen in **2** and the closely related compound, Bu^{t}C{μ-P(Cl)}$_3$CBu^t, in which the C–P–C and P–C–P angles are 74.1(3)° and 87.5(3)° respectively.[12] All the group 15 centres in **9** and **10** have distorted pyramidal geometries and the bond lengths to the neighbouring C or Cl centres are in the normal range.[10]

The 3:1 reactions of **5** with $SbCl_3$ or $BiCl_3$ were not clean and led to oily mixtures which $^{31}P\{^1H\}$ NMR spectroscopy suggested comprised a multitude of phosphorus containing products. One of the more prominent peaks seen in these mixtures occurred at −52 ppm which was assigned to the known 1,2-dihydro-1,2-diphosphete, **3**, which most likely forms *via* an oxidative coupling of two phosphavinyl fragments. Evidence for such a coupling comes from the fact that elemental antimony or bismuth were deposited in these reactions. Moreover, when the product mixture from the antimony reaction was treated with [W(CO)$_5$(THF)] the W(CO)$_5$ complex of **3**, namely [W(CO)$_5${η^1-P$_2$(Cy)$_2$C$_2$(Bu^t)$_2$}] **12**, was formed, albeit in very low yield (< 1%). The low yield of **12** prevented its spectroscopic characterisation but its X-ray crystal structure was obtained and is included here. Its molecular structure (Fig. 5, Table 1) shows it to be monomeric with one P-centre coordinated to a W(CO)$_5$ fragment through its lone pair. The geometry of the 1,2-dihydro-1,2-diphosphete ligand is very close to that seen in the structure of the uncoordinated ligand[4] and other related compounds, *e.g.* $Ph_2P_2C_2Bu^t_2$.[13]

Considering the unexpected formation of **9** and **10** from the 2:1 and 3:1 reactions of **5** with PCl_3 and $AsCl_3$ it was thought of particular interest to attempt analogous 1:1 reactions of **5** with group 15 halides. Again the outcome of these reactions was unpredictable and led to novel results (Scheme 3). When the PCl_3 reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy signals due to two major products appeared in the reaction mixture at temperatures above −50 °C. Both products were isolated from the mixture as crystalline solids, though not in as high yields as the NMR spectrum of the reaction mixture

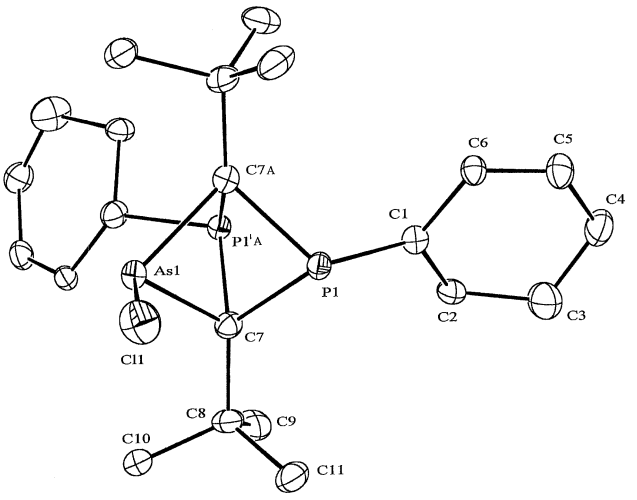


Fig. 4 Molecular structure of compound **10**. Selected bond lengths (Å) and angles (°): Cl(1)–As(1) 2.201(3), As(1)–C(7) 1.980(7), P(1)–C(7) 1.907(8), P(1′A)–C(7) 1.923(9), C(7A)–As(1) 1.959(8), C(7A)–P(1) 1.878(8), C(7)–As(1)–C(7A) 71.0(4), C(7)–P(1)–C(7A) 74.4(5), C(7)–P(1′A)–C(7A) 73.5(4), Cl(1)–As(1)–C(7) 110.7(2), As(1)–C(7)–P(1) 85.6(3), As(1)–C(7)–P(1′A) 89.4(3), P(1)–C(7)–P(1′A) 89.1(4). Symmetry transformation A: $-x, y, -z+1/2$.

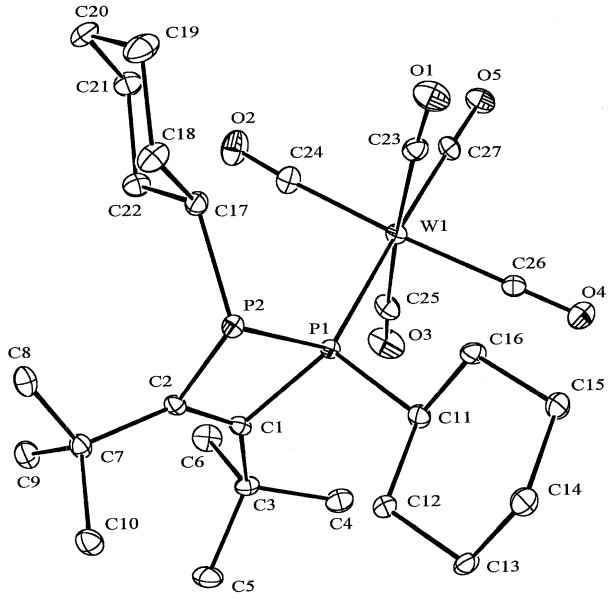
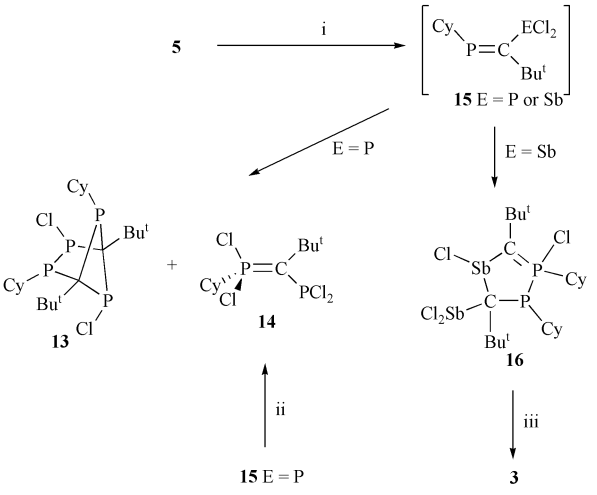


Fig. 5 Molecular structure of compound **12**. Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.5845(14), P(1)–C(1) 1.847(5), P(1)–P(2) 2.2063(19), P(2)–C(2) 1.849(5), C(1)–C(2) 1.366(8), C(1)–P(1)–W(1) 126.68(17), P(2)–P(1)–W(1) 126.82(7), C(2)–P(2)–P(1) 75.64(18), C(2)–C(1)–P(1) 101.3(4), C(1)–C(2)–P(2) 104.5(4).

suggested. The first of these, **13** (15% isolated yield), is a tetraphosphabicyclo[2.1.1]hexane in which two P-centres have Cl substituents and two have cyclohexyl substituents. The second product is the phosphino-substituted phosphorus ylide, **14** (5% isolated yield).

Although no intermediates were observed in this reaction it seems likely that the expected product, a dichlorophosphinophosphaalkene **15**, E = P, initially forms. A reductive coupling reaction then occurs in which two molecules of **15** transfer a chlorine atom to another molecule of **15** by an unknown process to yield the observed ylide, **14**. This would allow the two reduced fragments, "$CyP{=}C(Bu^t)PCl^{\bullet}$", to couple to give the bicyclic compound, **13**. It was postulated that the chlorine



Scheme 3 *Reagents and conditions:* i, $1/3\ ECl_3$, Et_2O; ii, SO_2Cl_2, Et_2O; iii, 2 days, $-Sb_{(s)}$, $-SbCl_3$.

transfer reaction could be mimicked by treating *in-situ* generated **15** with a suitable chlorinating agent. To this end an ethereal solution of **5** was reacted with one equivalent of PCl_3 at $-90\,^{\circ}C$. One equivalent of SO_2Cl_2 was quickly added to the mixture which was then warmed to room temperature. The ^{31}P NMR spectrum of the reaction mixture showed that **14** was the only phosphorus containing product which was subsequently isolated in moderate yield.

The spectroscopic data for **13** are suggestive of its proposed structure as its ^1H NMR spectrum displays two signals due to chemically inequivalent *tert*-butyl groups. In addition, its $^{31}P\{^1H\}$ NMR spectrum exhibits two low field signals arising from the chlorine substituted P-centres and two higher field signals due to the cyclohexyl substituted P-centres. There is a characteristic one bond P–P coupling (296 Hz) between P(2) and P(4) (see Fig. 6 for numbering scheme) and a very large

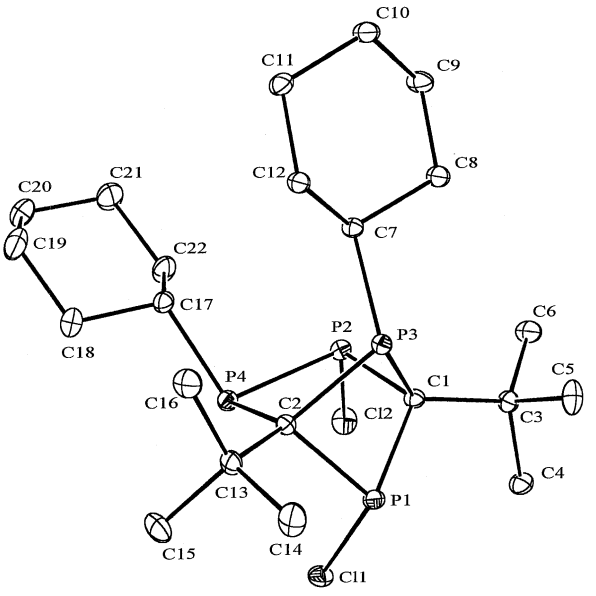


Fig. 6 Molecular structure of compound **13**. Selected bond lengths (Å) and angles (°): Cl(1)–P(1) 2.0848(6), Cl(2)–P(2) 2.0943(7), P(1)–C(1) 1.8660(14), P(1)–C(2) 1.8873(14), P(2)–C(1) 1.8500(14), P(2)–P(4) 2.2334(6), P(3)–C(2) 1.9146(14), P(3)–C(1) 1.9411(14), P(4)–C(2) 1.8989(14), C(1)–P(1)–C(2) 83.19(6), C(1)–P(1)–Cl(1) 109.60(5), C(2)–P(1)–Cl(1) 106.77(5), C(1)–P(2)–Cl(2) 105.81(5), C(1)–P(2)–P(4) 94.42(5), Cl(2)–P(2)–P(4) 101.45(3), C(2)–P(3)–C(1) 80.51(6), C(2)–P(4)–P(2) 91.35(5), P(2)–C(1)–P(1) 114.57(7), P(2)–C(1)–P(3) 100.91(6), P(1)–C(1)–P(3) 82.34(6), P(1)–C(2)–P(4) 103.78(7), P(1)–C(2)–P(3) 82.50(6), P(4)–C(2)–P(3) 113.08(7).

two bond coupling (269 Hz) between P(1) and P(3). The magnitude of this coupling could be due to a cross ring interaction between the two P-centres which both have *endo*-substituents with the P-lone pairs, presumably in close proximity to each other. There is precedent for such large couplings between P-centres in the 1- and 3-positions of puckered 4-membered rings contained within organophosphorus cage compounds.[14] The $^{31}P\{^{1}H\}$ NMR spectrum of the ylidic compound, **14**, exhibits an AB spin system, the lower field signal of which is derived from the P(III) centre. The very large two bond coupling (377 Hz) between the P-centres is not unexpected as similar couplings have been observed in closely related ylidic systems, *e.g.* $Ph_3P{=}C(Me)PCl_2$.[15]

The molecular structure of **13** (Fig. 6, Table 1) confirms its bicyclic formulation and shows the substituents at P(2) and P(4) to be *trans* to each other whilst the P(1) and P(3) substituents are in *endo*-positions. It is clear that the P(1)C(1)P(3)C(2) 4-membered ring is puckered and has a short cross ring P(1)···P(3) distance of 2.507 Å which is well within the sum of the van der Waals radii for two phosphorus centres (3.8 Å).[16] This close interaction likely gives rise to the large mutual coupling between these P-centres observed in the $^{31}P\{^{1}H\}$ NMR spectrum of this compound. The molecular structure of **14** (Fig. 7, Table 1) shows it to be monomeric and to contain one phosphorus centre, P(1), in the +5 oxidation state and one, P(2), in the +3 oxidation state. The C(1)–P(1) distance of 1.6925(14) Å supports this proposal and is normal for an ylidic P–C bond.[10] Although the P(2)–C(1) distance at 1.7460(15) Å is short for a single bond it can be explained by the fact that C(1) is sp^2-hybridised (Σ angles 359.8°).

The 1:1 reactions of **5** with either $AsCl_3$ or $BiCl_3$ were not clean and gave inseparable mixtures of products which in the latter reaction included significant amounts of **3**. Interestingly, the corresponding 1:1 reaction with $SbCl_3$ was very clean and gave a completely different result (Scheme 3). The ^{31}P NMR spectrum of the reaction mixture showed only one phosphorus containing product, **16**, that was isolated in good yield (66%) after recrystallisation from hexane. This unusual heterocycle contains an antimony and a phosphorus centre in the +3 oxidation state and another phosphorus(V) centre that forms part of an ylidic system. In addition, there is a terminal, exocyclic $SbCl_2$ fragment. Despite many attempts, we have not been able

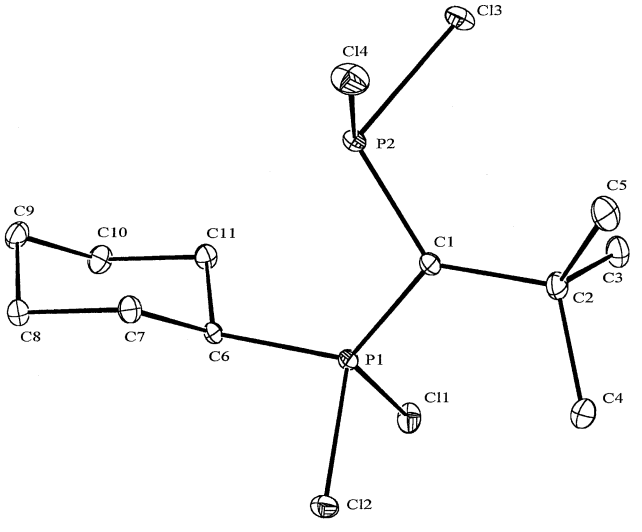


Fig. 7 Molecular structure of compound **14**. Selected bond lengths (Å) and angles (°): Cl(1)–P(1) 2.0343(6), Cl(2)–P(1) 2.0378(6), Cl(3)–P(2) 2.0934(6), Cl(4)–P(2) 2.1179(6), P(1)–C(1) 1.6925(14), P(2)–C(1) 1.7460(15), C(1)–C(2) 1.5659(19), P(1)–C(6) 1.8269(14), P(1)–C(1)–P(2) 106.76(8), P(1)–C(1)–C(2) 122.74(10), P(2)–C(1)–C(2) 130.31(10), Cl(3)–P(2)–Cl(4) 96.18(3), Cl(1)–P(1)–Cl(2) 99.20(3).

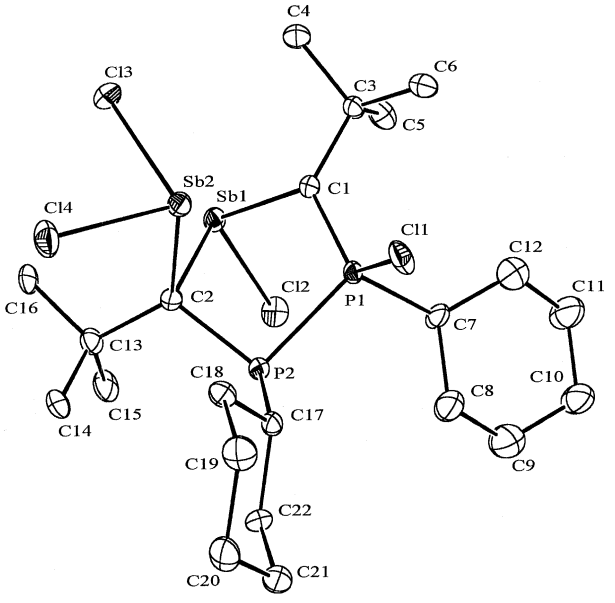


Fig. 8 Molecular structure of compound **16**. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.128(6), Sb(1)–C(2) 2.225(6), Sb(1)–Cl(2) 2.4467(19), Sb(2)–C(2) 2.215(6), Sb(2)–Cl(3) 2.4041(19), Sb(2)–Cl(4) 2.484(2), Cl(1)–P(1) 2.069(2), P(1)–C(1) 1.714(6), P(1)–P(2) 2.217(2), P(2)–C(2) 1.878(6), C(1)–Sb(1)–C(2) 86.3(2), C(1)–P(1)–P(2) 106.9(2), C(2)–P(2)–P(1) 96.3(2), P(1)–C(1)–Sb(1) 109.4(3), P(2)–C(2)–Sb(1) 101.8(3), Sb(2)–C(2)–Sb(1) 94.9(2), Sb(2)–C(2)–P(2) 107.0(3), Cl(3)–Sb(2)–Cl(4) 89.99(8), Cl(3)–Sb(2)–C(2) 98.82(17), Cl(4)–Sb(2)–C(2) 100.29(17), Cl(2)–Sb(1)–C(2) 100.04(16), Cl(2)–Sb(1)-C(1) 101.14(17).

to shed light on the mechanism of formation of **16** but it is thought that it probably forms *via* a coupling and subsequent rearrangement of two molecules of the supposed intermediate, **15**, E = Sb. One of the most interesting features of this compound is that although it is moderately thermally stable in the solid state, in toluene solutions it quantitatively decomposes to the diphosphete, **3**, over 2 days, depositing elemental antimony and presumably $SbCl_3$. Therefore compound **16** can be considered as a trapped intermediate in a phosphavinyl coupling reaction.

The $^{31}P\{^{1}H\}$ NMR spectrum of **16** displays an AB pattern with a large one bond coupling of 314 Hz between the low field ylidic phosphorus signal at 97.7 ppm and the resonance for the P(III) centre at 16.0 ppm. Its molecular structure (Fig. 8, Table 1) confirms the heterocyclic nature of the compound and displays a distorted tetrahedral geometry for P(1) with the P(1)–C(1) distance of 1.714(6) Å being in the expected region for an ylidic bond (*cf.* compound **14**).[10] All other bond lengths within the compound are normal for single bonded interactions. The geometry about P(2) is distorted pyramidal as are the geometries for Sb(1) and Sb(2). The angles about the antimony centres are, however, more acute than those about the phosphorus centre and are suggestive of considerable p-character to the bonding to their neighbouring atoms, as is common in tertiary antimony(III) compounds.

Conclusions

The reactions of a phosphavinyl Grignard reagent, **5**, with a variety of group 15 halide compounds in a number of stoichiometries have been carried out. These have led to the formation of a series of novel organo–group 15 compounds which include heterocycles, cages and acyclic unsaturated systems. The use of several of these compounds as ligands is currently being explored.

Experimental details

General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether and hexane were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. ^{1}H and ^{31}P NMR spectra were recorded on Bruker DPX400, Bruker AMX 360 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^{1}H resonances of the solvent used (^{1}H NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were obtained from the Warwick Microanalytical Service. Reproducible microanalyses of **6**, **7**, **9** and **10** could not be obtained due to small amounts of impurities in the crystalline samples. However, the NMR spectra of these samples suggested their purity was greater than 95%. The starting material **5** was prepared by a literature procedure.[1] All other reagents were used as received.

$Ph_2PC(Bu^t)$=PCy 6

A solution of **5** (0.54 g, 1.75 mmol) in diethyl ether (10 ml) was added over 10 min to a solution of Ph_2PCl (0.32 ml, 1.75 mmol) in diethyl ether (30 ml) at −78 °C. The resulting solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the yellow residue extracted into hexane (5 ml), whereupon the extract was slowly cooled to −30 °C to afford **6** as yellow prisms (75% yield) m.p. 98–103 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.20 (s, 9H, Bu^t), 0.92–1.82 (m, 11H, Cy), 6.86–7.70 (m, 10H, Ph); ^{31}P{^{1}H} NMR (145.8 MHz, C_6D_6) δ 350.1 (d, P=C, $^2J_{PP}$ 140 Hz), 23.6 (d, PPh_2, $^2J_{PP}$ 140 Hz); MS APCI: m/z (%) 368 [M^+, 100], 285 [M^+ − Cy, 5%]; IR (Nujol) ν/cm^{-1} 1280(s), 1105(m), 980(s).

$CyP\{C_2(Bu^t)_2P_2Cy_2\}$ 7

A 1 M solution of CyMgCl (1.10 ml, 1.1 mmol) was added to a solution of PCl_3 (0.10 ml, 1.1 mmol) in diethyl ether (20 ml) at 0 °C and the solution stirred for 15 min. This was then cooled to −78 °C and a solution of **5** (0.70g, 2.2 mmol) in diethyl ether (15 ml) added to it over 10 min. The resulting suspension was warmed to room temperature and stirred overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane (10 ml), filtered and the filtrate placed at −30 °C overnight to afford colourless crystals of **7**. (62% yield) m.p. 114–116 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.15–2.73 (m, 33H, Cy), 1.46 (s, 9H, Bu^t), 1.52 (s, 9H, Bu^t); ^{31}P{^{1}H} NMR (145.8 MHz, C_6D_6) δ 104.3 (s, CP(Cy) C), −16.3 (d, PP, $^1J_{PP}$ 86 Hz), 11.2 (d, PP, $^1J_{PP}$ 86 Hz); MS APCI: m/z (%) 481 [M^+, 100], 398 [M^+ − Cy, 12%]; IR (Nujol) ν/cm^{-1} 1280(s), 1110(m), 985(s).

$Bu^tC\{\mu\text{-}P(Cy)\}_2\{\mu\text{-}PCl\}CBu^t$ 9

To a solution of PCl_3 (71 µl, 0.8 mmol) in diethyl ether (20 ml) at −78 °C was added a solution of **5** (0.50 g, 1.62 mmol) in diethyl ether (10 ml) over 5 min. The resulting solution was warmed to room temperature overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane, filtered and the filtrate placed at −30 °C overnight to yield colourless crystals of **9**. (36% yield) m.p. 184–186 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.05–1.95 (m, 20H, CH_2), 1.36 (s, 18H, Bu^t), 2.85–2.95 (m, 2H, CH); ^{31}P{^{1}H} NMR (145.8 MHz, C_6D_6) δ −0.4 (s, PCy), 74.4 (s, PCy), 95.8(s, PCl); MS APCI: m/z (%) 433 [M^+, 72], 397 [M^+ − Cl, 100%]; IR (Nujol) ν/cm^{-1} 1260(s), 1140(m), 1093(m), 970(m).

$Bu^tC\{\mu\text{-}P(Cy)\}_2\{\mu\text{-}AsCl\}CBu^t$ 10

To a solution of $AsCl_3$ (45µl, 0.54 mmol) in diethyl ether (20 ml) at −78 °C was added a solution of **5** (0.34 g, 1.10 mmol) in diethyl ether (10 ml) over 5 min. The resulting solution was warmed to room temperature overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane, filtered and the filtrate placed at −30 °C overnight to yield colourless crystals of **10**. (41% yield) m.p. 182–184 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.10–2.10 (m, 20H, CH_2), 1.21 (s, 18H, Bu^t), 2.95–3.06 (m, 2H, CH); ^{31}P{^{1}H} NMR (145.8 MHz, C_6D_6) δ 13.5 (s, PCy), 73.8 (s, PCy); MS APCI: m/z (%) 477 [M^+, 100], 442 [M^+ − Cl, 52%]; IR (Nujol) ν/cm^{-1} 1376(m), 1260(s), 1020(m), 800(m).

$Bu^tC\{\mu\text{-}P(Cl)P(Cy)\}\{\mu\text{-}P(Cy)\}\{\mu\text{-}P(Cl)\}CBu^t$ 13

To a solution of PCl_3 (140µl, 1.58 mmol) in diethyl ether (20 ml) at –78 °C was added a solution of **5** (0.50 g, 1.60 mmol) in diethyl ether (10 ml) over 5 min. The resulting orange solution was warmed to room temperature overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane, filtered and the filtrate placed at −30 °C overnight to yield colourless crystals of **13**. (15% yield) m.p. 119–121 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.30 (s, 9H, Bu^t), 1.54 (s, 9H, Bu^t), 0.98–2.72 (m, 22H, Cy); ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6) δ 25.8 (d, P(3), $^2J_{PP}$ 269 Hz), 66.6 (d, P(4), $^1J_{PP}$ 296 Hz), 120.3 (d, P(2), $^1J_{PP}$ 296 Hz), 140.0 (d, P(1), $^2J_{PP}$ 269 Hz); MS APCI: m/z (%) 499 [M^+, 100]; IR (Nujol) ν/cm^{-1} 1644(m), 1263(m), 1207(m), 1102(m), 997(w), 881(w); found C 52.55, H 8.17%; calc. for $C_{22}H_{40}Cl_2P_4$: C 52.92, H 8.07%.

$Cl_2PC(Bu^t)$=P(Cy)(Cl)$_2$ 14

To a solution of PCl_3 (84 µl, 0.95 mmol) in diethyl ether (20 ml) at −78 °C was added a solution of **5** (0.30 g, 0.95 mmol) in diethyl ether (10 ml) over 5 min. To the resulting orange solution was added SO_2Cl_2 (76 µl, 0.95 mmol). The reaction mixture was then warmed to room temperature overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane (10 ml), filtered and the filtrate placed at −30 °C overnight to yield colourless crystals of **14**. (26% yield) m.p. 90–92 °C; ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ 1.71 (s, 9H, Bu^t), 0.66–2.82 (m, 11H, Cy); ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6) δ 77.0 (d, P=C, $^2J_{PP}$ 377 Hz), 151.1 (d, PCl_2, $^2J_{PP}$ 377 Hz); MS APCI: m/z (%) 102 [PCl_2^+, 100], 83 [Cy^+, 62]; IR (Nujol) ν/cm^{-1} 1286 (m), 1243 (s), 1208 (m), 1162 (m), 1002 (m), 849(w); found C 37.91, H 5.81%; calc. for $C_{11}H_{20}Cl_4P_2$: C 37.11, H 5.66%.

$(Cl_2Sb)(Bu^t)CSb(Cl)C(Bu^t)$=P(Cl)(Cy)P(Cy) 16

To a solution of $SbCl_3$ (0.36 g, 1.58 mmol) in diethyl ether (20 ml) at −78 °C was added a solution of **5** (0.50 g, 1.60 mmol) in diethyl ether (10 ml) over 5 min. The resulting orange solution was warmed to room temperature overnight, filtered and volatiles removed *in vacuo*. The residue was extracted into hexane, filtered and the filtrate placed at −30 °C overnight to yield yellow crystals of **16**. (66% yield) m.p. 83–85 °C (dec.); ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ 1.38 (s, 9H, Bu^t), 1.72 (s, 9H, Bu^t), 0.88–2.49 (m, 22H, Cy); ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6) δ 16.0 (d, PCy, $^1J_{PP}$ 314 Hz), 97.7 (d, P=C, $^1J_{PP}$ 314 Hz); MS APCI: m/z (%) 559 [M^+ − $SbCl_2$, 100]; IR (Nujol) ν/cm^{-1} 1263 (s), 1207 (m), 1112 (m), 916 (w), 816 (m); found C 35.46, H 5.53%; calc. for $C_{22}H_{40}Cl_4P_2Sb_2$: C 35.14, H 5.36%.

Structure determinations

Crystals of **6**, **7**, **9**, **10**, **12**, **13**, **14** and **16** suitable for X-ray structure determination were mounted in silicone oil or epoxy resin. Crystallographic measurements were made using either Nonius CAD4, Nonius Kappa CCD or Siemens SMART CCD diffractometers. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[17] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). The quality of the X-ray data for compound **10** was poor but the fact that this compound is isomorphous to **9** leaves no doubt about its gross molecular framework. Crystal data, details of data collections and refinements are given in Table 1. The molecular structures of the complexes are depicted in Figs. 1–8 and show ellipsoids at the 30% probability level.

CCDC reference numbers 187286–187293. See http://www.rsc.org/suppdata/nj/b2/b204663f/ for crystallographic data in CIF or other electronic format.

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