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Anatomy of Phobanes. Diastereoselective Synthesis of the Three Isomers of *n*-Butylphobane and a Comparison of their Donor Properties

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Abstract: Three methods for the large scale (50−100 g) separation of the secondary phobanes 9-phosphabicyclo[3.3.1]nonane (*s*-PhobPH) and 9-phosphabicyclo[4.2.1]nonane (*a*-PhobPH) are described in detail. Selective protonation of *s*-PhobPH with aqueous HCl in the presence of *a*-PhobPH is an efficient way to obtain large quantities of *a*-PhobPH. Selective oxidation of *a*-PhobPH in an acidified mixture of *a*-PhobPH and *s*-PhobPH is an efficient way to obtain large quantities of *s*-PhobPH. The crystalline, air-stable phosphonium salts [*s*-PhobP$(CH_2OH)_2$]Cl and [*a*-PhobP$(CH_2OH)_2$]Cl can be separated by a selective deformylation with aqueous NaOH. *a*-PhobPH is shown to be a_5-PhobPH in which the H lies over the five-membered ring. The isomeric a_7-PhobPH has been detected but isomerizes to a_5-PhobPH rapidly in the presence of water. *s*-PhobPH is more basic than *a*-PhobPH by about 2 pK_a units in MeOH. Treatment of *s*-PhobPH with BH_3·THF gives *s*-PhobPH(BH_3) and similarly *a*-PhobPH gives a_5-PhobPH(BH_3). Isomerically pure *s*-PhobPCl and a_5-PhobPCl are prepared by reaction of the corresponding PhobPH with C_2Cl_6. The *n*-butyl phobane *s*-PhobPBu is prepared by nucleophilic (using *s*-PhobPH or *s*-PhobPLi) and electrophilic (using *s*-PhobPCl) routes. Isomerically pure a_5-PhobPBu is prepared by treatment of *a*-PhobPLi with ^{n}BuBr and a_7-PhobPBu is prepared by quaternization of *a*-PhobPH with ^{n}BuBr followed by deprotonation. From the rates of conversion of a_7-PhobPBu to a_5-PhobPBu, the $\Delta G^{\ddagger}$ (403 K) for P-inversion is calculated to be 38.1 kcal mol^{-1} (160 kJ mol^{-1}). The donor properties of the individual isomers of PhobPBu were assessed from the following spectroscopic measurements: (i) $^1J_{PSe}$ for PhobP(Se)Bu; (ii) ν(CO) for *trans*-[RhCl(CO)(PhobPBu)$_2$], (iii) $^1J_{PtP}$ for the PEt_3 in *trans*-[$PtCl_2(PEt_3)$(PhobPBu)]. In each case, the data are consistent with the order of σ-donation being a_7-PhobPBu > *s*-PhobPBu > a_5-PhobPBu. This same order was found when the affinity of the PhobPBu isomers for platinum(II) was investigated by determining the relative stabilities of [Pt(CH_3)(*s*-PhobPBu)(dppe)][BPh_4], [Pt(CH_3)(a_5-PhobPBu)(dppe)][BPh_4], and [Pt(CH_3)(a_7-PhobPBu)(dppe)][BPh_4] from competition experiments. Calculations of the relative stabilities of the isomers of PhobPH, [$PhobPH_2]^+$, and PhobPH(BH_3) support the conclusions drawn from the experimental results. Moreover, calculations on the frontier orbital energies of PhobPMe isomers and their binding energies to H^+, BH_3, $PdCl_3^-$, and $PtCl_3^-$ corroborate the experimental observation of the order of σ-donation being a_7-PhobPR > *s*-PhobPR > a_5-PhobPR. The calculated He_8 steric parameter shows that the bulk of the isomers increases in the order a_7-PhobPR < *s*-PhobPR < a_5-PhobPR. The crystal structures of [*a*-PhobP$(CH_2OH)_2$][*s*-PhobP$(CH_2OH)_2$]Cl_2, *cis*-[$PtCl_2$(a_5-PhobP$CH_2OH)_2$], *trans*-[$PtCl_2$(*s*-PhobPBu)$_2$], and *trans*-[$PtCl_2$(a_7-PhobPBu)$_2$] are reported.

Introduction

The 9-phosphabicyclononanes known collectively as Phobanes (Chart 1) were first reported in 1966.[1] They are rare examples of ligands that have achieved prominence in a highly successful industrial process, namely Shell's cobalt-catalyzed alkene hydroformylation,[2,3] long before any reports of their coordination chemistry. Indeed, 30 years after the original Shell patent, Togni et al.[4] referred to phobanes as the "forgotten ligands". Doubtless, part of the reason for the lack of fundamental studies on the secondary phobanes, denoted here as *s*-PhobPH and *a*-PhobPH (Chart 1, R = H), has been that their synthesis requires handling PH_3 under pressure at high temperature.[5] Tertiary phobanes (Chart 1, R = hydrocarbyl) have been synthesized as mixtures of isomers by radical-initiated additions

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(1) (a) Mulders, J. P. *Neth. Patent* **1966**, *6*, 604 09 to Shell. (b) Winkle, J. L. V.; Mason, R. F. *U.S. Patent* **1968**, *3*, 400 163 to Shell.
(2) Winkle, J. L. V.; Morris, R. C.; Mason, R. F. *Ger. Patent* **1969**, *1*, 909 620 to Shell.
(3) Bungu, P. N.; Otto, S. *Dalton Trans.* **2007**, 2876.
(4) Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Koelner, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 759.

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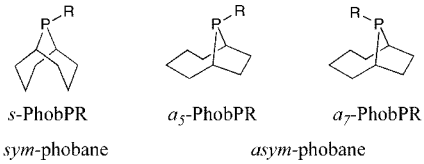
Chart 1



of *s*-PhobPH/*a*-PhobPH mixtures to alkenes[1,6] or RPH_2 to 1,5-cyclooctadiene.[6,7] There are two isomers of *a*-PhobPR which differ in whether the P−R substituent lies over the five-membered ring (a_5-PhobPR) or the seven-membered ring (a_7-PhobPR).[8,9]

Many applications of tertiary phobanes in catalysis have emerged recently, including olefin metathesis (Ru),[10−12] asymmetric hydrogenation (Rh),[13] carbonylation of alkenes (Pd),[14,15] ethylene oligomerization (Ni),[16] allylic substitution (Pd),[4,17−19] heterocyclic C−H arylation (Rh),[9,20] asymmetric hydroboration (Rh),[18] hydroformylation (Pd),[21] and atom transfer radical addition reactions (Ru).[22] In view of the catalytic utility of their complexes, it is surprising that there have been only a few reports concerning the coordination chemistry of phobane derivatives.[4,23−26]

It is known that there are significant differences between *sym*- and *asym*-phobane isomers in terms of their spectroscopic properties,[3,6] reactivity,[6,27,28] coordination chemistry,[4,11,22,23] and not surprisingly, their catalytic performance.[9,13,15] However, we are aware of only one previous catalytic study of all three isomeric phobanes: Bergman et al.[9] showed that *a*-PhobPCy gave superior results to *s*-PhobPCy in a Rh-catalyzed C−H arylation but the chromatographically separated isomers a_5-PhobPCy and a_7-PhobPCy gave similar catalytic results because, under the high temperature reaction conditions (250 °C), inversion at P was rapid and a_7-PhobPCy was quantitatively converted to the more stable a_5-PhobPCy.

One likely reason for the paucity of information on the individual PhobPR isomers is the lack of stereoselective routes to them. We report here full details of efficient methods for the separation of *s*-PhobPH and *a*-PhobPH (pivotal precursors to monodentate and bidentate phobane isomers), their protonation, boranation, chlorination, and stereoselective conversion to the *n*-butyl phobanes: *s*-PhobPBu, a_7-PhobPBu, and a_5-PhobPBu. An experimental and computational comparison of the donor properties of the alkyl phobanes is presented. Preliminary accounts of parts of this work have been given.[15,28]

Results and Discussion

Three convenient methods for the separation of *s*-PhobPH and *a*-PhobPH have been developed on the basis of the selective protonation of *s*-PhobPH, the selective oxidation of *a*-PhobPH, and the selective deformylation of [*a*-PhobP$(CH_2OH)_2$]Cl.

Protonation Studies of PhobPH Isomers. Mixtures of *s*-PhobPH and *a*-PhobPH dissolve readily in aqueous HCl or HBr to give [*s*-PhobPH_2]$^+$ and [*a*-PhobPH_2]$^+$, characterized by broad ^{31}P NMR signals in the vicinity of −17 and −2 ppm, respectively, the precise δ_P depending on the phosphonium ion concentration but not the counterion (Cl or Br). In the proton-coupled ^{31}P NMR spectra, no P−H coupling was observed, showing that proton exchange was rapid on the NMR time scale. The isolated salts [*s*-PhobPH_2]Cl and [*a*-PhobPH_2]Cl are only sparingly soluble in water but dissolve readily in aqueous HCl or methanol.

From the ^{31}P NMR spectra of mixtures of methanolic solutions of *s*-PhobPH and [*s*-PhobPH_2]$^+$ (0.050 M total phosphorus), it was found that δ_P is a linear function of mole

(5) Elsner, G.; Heymer, G.; Stephan, H.-W. *German Patent* **1978**, *2*, 703 802 to Hoechst. Mixtures of *s*-PhobPH and *a*-PhobPH are now commercially available as solutions in toluene. The proportions of the isomers depend on the supplier.
(6) Bungu, P. N.; Otto, S. *J. Organomet. Chem.* **2007**, *692*, 3370.
(7) Robertson, A. J. *World Patent* 2000, WO 00/52017 to Cytec.
(8) The notation *a*-PhobP will be used throughout this article when the particular a_5 or a_7 stereoisomer is not specified. The IUPAC recommendations for the naming of compounds such as the phobanes are given by Moss, G. P. *Pure Appl. Chem.* **1996**, *68*, 2193. Application of the rules gives: for *s*-PhobPBu, 9-butyl-9-phosphabicyclo[3.3.1]nonane; for a_5-PhobPBu, 9-*syn*-butyl-9-phosphabicyclo[4.2.1]nonane; for a_7-PhobPBu, 9-*anti*-butyl-9-phosphabicyclo[4.2.1]nonane.
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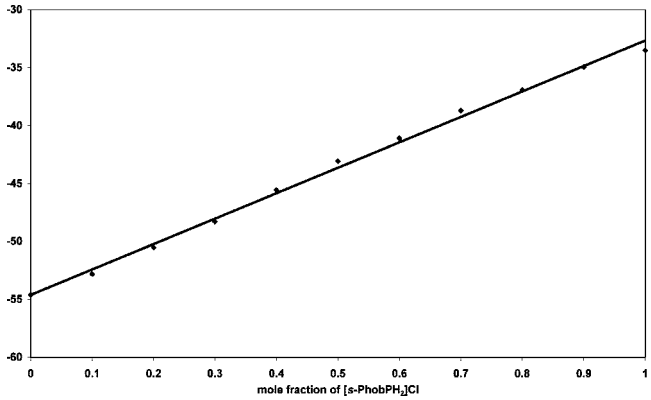
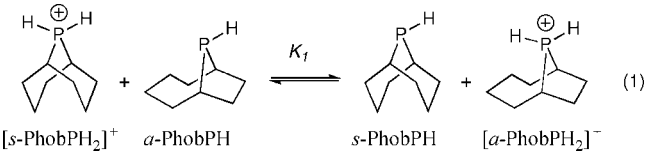


Figure 1. δ_P as a function of proportion of *s*-PhobPH and [*s*-PhobPH$_2$]Cl (0.050 M methanolic solutions with 10% C_6D_6 for lock).

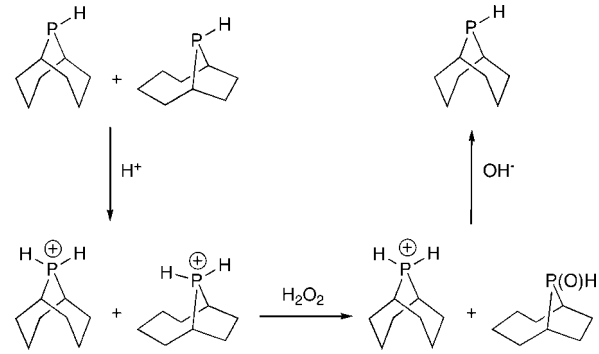
fraction (Figure 1). This was used to estimate the relative proton affinity of *s*-PhobPH and *a*-PhobPH in methanolic solution as follows. [*s*-PhobPH$_2$]$^+$ and *a*-PhobPH were mixed in 1:1 and 1:2 proportions to establish the equilibrium shown in eq 1 for which the equilibrium constant, K_1 is K_a(*a*-PhobPH$_2^+$)/K_a(*s*-PhobPH$_2^+$). The δ_P values for the *sym*-phobane component were used to estimate the concentrations of [*s*-PhobPH$_2$]$^+$ present (Figure 1) from which a K_1 of ca. 110 was calculated which corresponds to the pK_a for [*a*-PhobPH$_2$]$^+$ being about 2 units lower than for [*s*-PhobPH$_2$]$^+$ in methanol.[29] This confirms that *s*-PhobPH is considerably more basic than *a*-PhobPH and this feature is key to the separations based on selective protonation and selective oxidation.



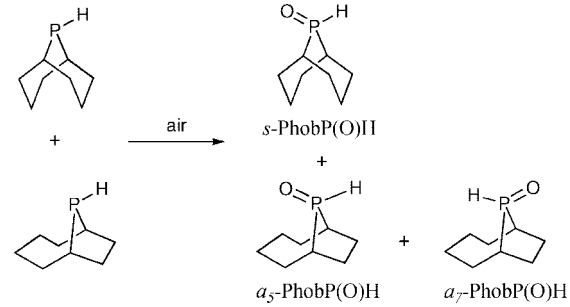
(1)

When a 1 M solution of HCl in diethyl ether was added to a mixture of *s*-PhobPH and *a*-PhobPH, a white precipitate formed which was predominantly [*s*-PhobPH$_2$]Cl. A similar precipitation occurs when HCl gas is bubbled through a diethyl ether solution of *s*-PhobPH and *a*-PhobPH. However, this approach to the separation was marred by difficulties in isolating the voluminous and sticky precipitate and its subsequent purification. Nevertheless, the difference in the aqueous basicities of *s*-PhobPH and *a*-PhobPH was exploited in their separation in a two-phase water/diethyl ether system. We have previously reported this method of separation[15,30] and an improved protocol is given in the Experimental Section. This procedure is the most convenient for separating large quantities of pure *a*-PhobPH. Both isomers can be recovered in high yields although multiple ether extractions are involved and sublimation of the *s*-PhobPH is required to obtain pure product.

Scheme 1



Oxidation Studies of PhobPH Isomers. A toluene solution of a 2:1 mixture of *s*-PhobPH and *a*-PhobPH was stirred in air to give predominantly the secondary phosphine oxides *s*-PhobP(O)H (δ_P 32.0 ppm, *J*(PH) 459 Hz) and *a*-PhobP(O)H as a 3:1 mixture of a_5- and a_7-isomers (δ_P 47.2 ppm, *J*(PH) 438 Hz) and 53.3 ppm, *J*(PH) 470 Hz) (eq 2). The oxidation was monitored by ^{31}P NMR spectroscopy and under these conditions, both isomers were ca. 90% oxidized in 5 h. Concentrations were estimated from integration of the ^{31}P NMR signals and plots of log[PhobPH] against time were linear (indicating first-order kinetics) with the slope for *s*-PhobPH ca. 1.25 times that for the *a*-PhobPH, consistent with *s*-PhobPH being the more susceptible isomer to aerial oxidation.



(2)

When a 2:1 mixture of phobanes was dissolved in aqueous HCl and then enough H_2O_2 added to oxidize the *a*-PhobPH component, the product was essentially a mixture of [*s*-PhobPH$_2$]$^+$ and *a*-PhobP(O)H. Protonation thus provides more effective protection to oxidation for *s*-PhobPH than for *a*-PhobPH which is consistent with the greater acidity of [*a*-PhobPH$_2$]$^+$ (see above). Neutralization, followed by hexane extraction gave pure *s*-PhobPH in 92% yield with the hydrophilic *a*-PhobP(O)H remaining in the aqueous phase (along with other unidentified oxidation products). This method is efficient for obtaining large quantities of *s*-PhobPH (see Scheme 1 and Experimental Section).

Hydroxymethyl Phobanes. A mixture of phosphonium salts [*s*-PhobP(CH$_2$OH)$_2$]Cl and [*a*-PhobP(CH$_2$OH)$_2$]Cl was prepared by treatment of *s*-PhobPH and *a*-PhobPH with aqueous formaldehyde in the presence of HCl (Scheme 2). This reaction was carried out on a 50 g scale in 80% yield and the white, crystalline product is air stable; these salts provide a convenient way of storing and manipulating the phobane mixture since the formaldehyde hydrophosphination is reversible (see below).

Slow diffusion of diethyl ether into a methanol solution of a mixture of [*s*-PhobP(CH$_2$OH)$_2$]Cl and [*a*-PhobP(CH$_2$OH)$_2$]Cl

(29) The ^{31}P NMR chemical shifts are sensitive to concentration, solvent and temperature. In the equilibrium studies, changes in chemical shift of <0.5 ppm were observed and so 10% C_6D_6 was added to provide a lock. The concentrations were kept low (0.050 M in phosphorus) in order to minimize the effects of H-bonding by the [*s*-PhobPH$_2$]Cl solute. Nevertheless, significant errors in the equilibrium constants are likely although the measured values of K_1 at two different concentrations were within 10% of each other. Since pK_a is logarithmic, the conclusion of a difference of ~2 units between *a*-PhobPH and *s*-PhobPH should be robust.

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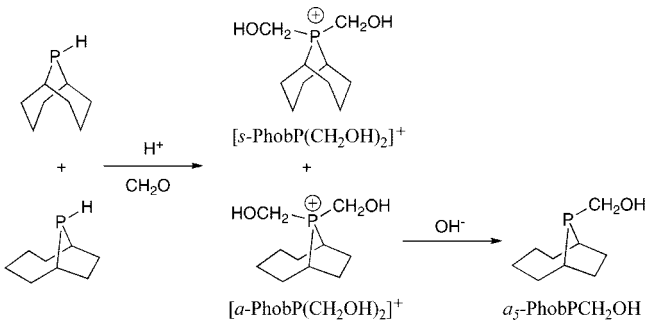
Scheme 2



produced crystals of the double salt $[a\text{-PhobP}(CH_2OH)_2][s\text{-PhobP}(CH_2OH)_2]Cl_2$ suitable for X-ray single crystal structure determination (see Figures 2−5). The structure contains a hydrogen bonded chain of ions with the $[a\text{-PhobP}(CH_2OH)_2]^+$ and $[s\text{-PhobP}(CH_2OH)_2]^+$ cations each forming two OH···Cl hydrogen bonds to chloride anions (see Figure 4).

In both cations the tetrahedral geometry at the quaternized phosphorus atom is distorted, less in the *sym*-cation (intraring C−P−C 100°) but markedly so in the *asym*-cation (intraring C−P−C 96°).

There is clear evidence for strain in the structure of the $[a\text{-PhobP}(CH_2OH)_2]^+$ cation (see Figure 2) as manifested in the short transannular contact between the hydroxymethyl hydrogen H2B and H17A in the seven-membered ring (see Figure 5). The C−P−C values for the hydroxymethyl groups in the $[a\text{-PhobP}(CH_2OH)_2]^+$ cation are substantially different (121° and 116° for C2 compared to 107° and 111° for C1) and even so the short H···H contact persists. These data are therefore consistent with greater strain involving adducts at phosphorus above the seven-membered ring in *asym*-phobane derivatives.

When a two-phase mixture of toluene and an aqueous solution of $[s\text{-PhobP}(CH_2OH)_2]Cl$ and $[a\text{-PhobP}(CH_2OH)_2]Cl$ (ca. 1:1) was treated with 0.5 equiv of NaOH, the outcome, as shown by ^{31}P NMR spectroscopy, was that the aqueous phase contained exclusively $[s\text{-PhobP}(CH_2OH)_2]Cl$ and the toluene phase contained exclusively $a\text{-PhobPCH}_2OH$ (see Scheme 2). The deformylation of $[a\text{-PhobP}(CH_2OH)_2]Cl$ in the presence of $[s\text{-PhobP}(CH_2OH)_2]Cl$ is stereoselective: only one signal for the $a\text{-PhobPCH}_2OH$ product was observed despite the possibility of a_5- and a_7-isomers being formed. Treatment of the $a\text{-PhobPCH}_2OH$ product with $[PtCl_2(cod)]$ gave $[PtCl_2(a_5\text{-PhobPCH}_2OH)_2]$ as shown by X-ray crystallography (see below) confirming that it is the CH_2OH group over the seven-membered ring that is eliminated. As discussed above, the site over the seven-membered ring is relatively crowded and the removal of the hydroxymethyl from this site allows the seven-membered ring to adopt a less strained geometry.

The structure determination of *cis*-$[PtCl_2(a_5\text{-PhobPCH}_2OH)_2]$ confirms the cis disposition of the two $a_5\text{-PhobPCH}_2OH$ ligands at the square planar Pt(II) (see Figure 6). The phobane C_8 moieties are oriented in an anti fashion which minimizes steric clashing. The $a_5\text{-PhobPCH}_2OH$ ligand shows substantial distortion from tetrahedral geometry at the P atom (intraring C−P−C 93°). The hydroxymethyl groups are all involved in intermolecular hydrogen bonding (lengths O1A···O1 2.792 Å, O1A′···O1 2.779 Å, and O2A···O2 2.767 Å; O2A···Cl1 3.155 Å, O1···Cl2A 3.072 Å).

Treatment of the separated $[s\text{-PhobP}(CH_2OH)_2]Cl$ and $a\text{-PhobPCH}_2OH$ with an excess of NaOH in the presence of

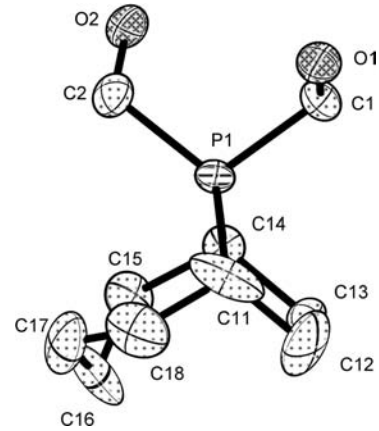


Figure 2. Structure of the $[a\text{-PhobP}(CH_2OH)_2]^+$ cation in crystals of $[a\text{-PhobP}(CH_2OH)_2][s\text{-PhobP}(CH_2OH)_2]Cl_2$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg); P(1)−C(1) 1.831(4), P(1)−C(2) 1.819(4), P(1)−C(11) 1.827(6), P(1)−C(14) 1.801(4), C(1)−P(1)−C(2) 104.7(2), C(11)−P(1)−C(14) 96.4(2), C(1)−P(1)−C(11) 107.4(2),C(14)−P(1)−C(1)111.2(2),C(2)−P(1)−C(11)120.9(3),C(2)−P(1)−C(14) 116.0(2).

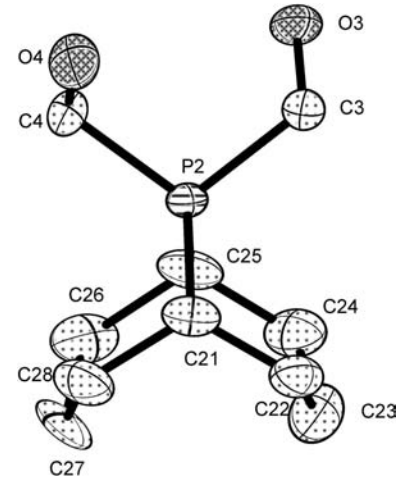


Figure 3. Structure of the $[s\text{-PhobP}(CH_2OH)_2]^+$ cation in crystals of $[a\text{-PhobP}(CH_2OH)_2][s\text{-PhobP}(CH_2OH)_2]Cl_2$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg); P(2)−C(3) 1.816(4), P(2)−C(4) 1.820(4), P(2)−C(21) 1.804(4), P(2)−C(25) 1.799(4), C(3)−P(2)−C(4) 105.2(2), C(21)−P(2)−C(25) 100.1(2), C(3)−P(2)−C(21) 113.0(2),C(3)−P(2)−C(25)111.3(2),C(4)−P(2)−C(21)114.3(2),C(4)−P(2)−C(25) 113.1(2).

$NaHSO_3$ (to trap the formaldehyde) gave the desired *s*-PhobPH and *a*-PhobPH. We previously reported the development of this chemistry into a separation protocol[28] and in the Experimental Section, a modified procedure is described which gives high purity *s*-PhobPH and *a*-PhobPH.

The ^{31}P NMR spectrum of *s*-PhobPH was a doublet at δ_P −54.1 with J_{PH} = 192 Hz. For *a*-PhobPH, one ^{31}P NMR signal was observed at −48.4 (d, J_{PH} = 188 Hz) that was assigned to a_5-PhobPH on the basis of its boranation/alkylation chemistry and its greater calculated stability (see below). Treatment of a_5-PhobPH with ^{n}BuLi in THF followed by H_2O gave two secondary phosphines in the ratio 2:1 according to the ^{31}P NMR spectrum. The major signal was the expected a_5-PhobPH and the minor species (δ_P −54.3 with J_{PH} = 192 Hz) was assigned to a_7-PhobPH (Scheme 3). It is striking how similar the ^{31}P NMR parameters are for a_7-PhobPH and *s*-PhobPH.[31] A mixture of the deuterated species a_5-PhobPD and a_7-PhobPD was generated by treat-

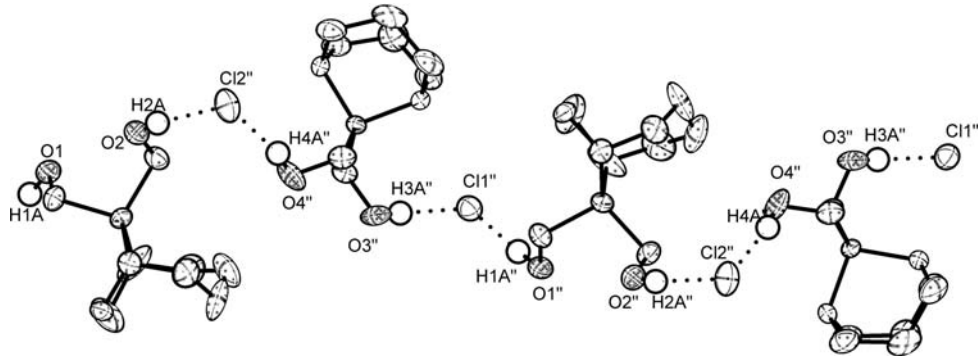


Figure 4. Chain of hydrogen bonded ions in crystals of [*a*-PhobP($CH_2OH)_2$][*s*-PhobP($CH_2OH)_2$]Cl_2. All bar hydroxyl hydrogen atoms have been omitted for clarity. Hydrogen bond lengths (Å): H(1)···Cl(1) 2.139, H(2)···Cl(2) 2.369, H(3)···Cl(1) 2.345, H(4)···Cl(2) 2.171.

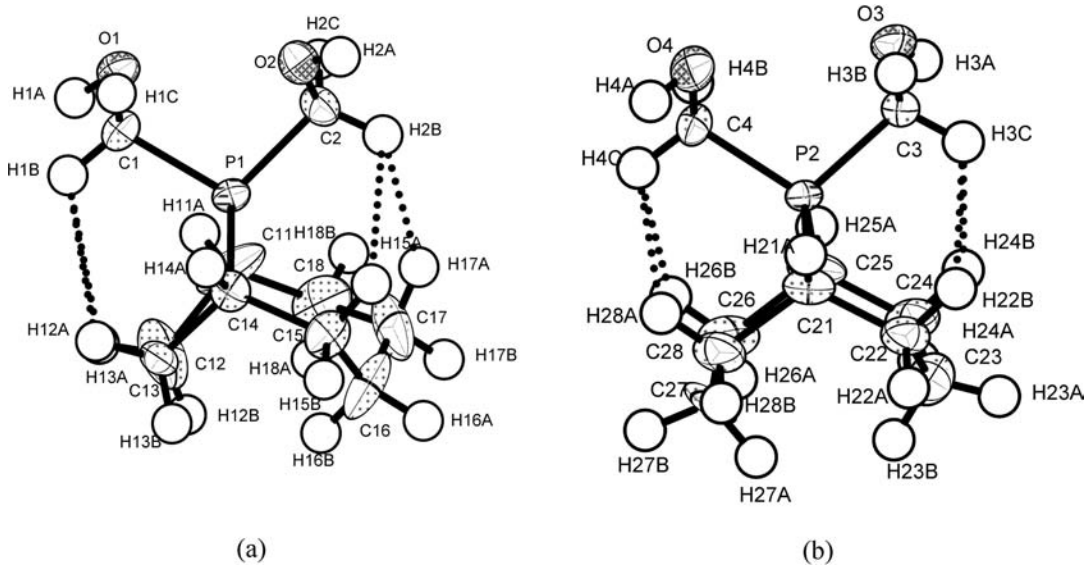


Figure 5. Transannular H···H contacts involving hydroxymethyl groups in the [*a*-PhobP($CH_2OH)_2$]$^+$ and [*s*-PhobP($CH_2OH)_2$]$^+$ cations. All other hydrogen atoms omitted for clarity. Distances (Å): (a) [*a*-PhobP($CH_2OH)_2$]$^+$ H(1B)···H(12A) 2.80, H(1B)···H(13A) 2.54, H(2B)···H(17A) 2.15, H(2B)···H(15A) 2.52. (b) [*s*-PhobP($CH_2OH)_2$]$^+$ H(3C)···H(22B) 2.41, H(3C)···H(24B) 2.36, H(4C)···H(26B) 2.50, H(4C)···H(28A) 2.42.

ment of PhobPLi with D_2O (Scheme 3). When a mixture of a_5-PhobPH and a_7-PhobPH was dissolved in dry THF at 20 °C, the amount of a_7-PhobPH only slightly decreased from 30% to 26% after 24 h. However, when this THF solution was saturated with water, the a_7-PhobPH signal was undetectable after 5 h, indicating that water catalyzes the inversion of a_7-PhobPH to a_5-PhobPH. Wild et al.[32] have previously shown that inversion at P in secondary phosphines is slow in the absence of traces of acid. Inspection of the ^{31}P NMR spectrum of the equilibrated mixture showed that K_2 in Scheme 3 is $>10^3$.

Borane Derivatives of the PhobPH Isomers. Treatment of *s*-PhobPH with BH_3·THF gave *s*-PhobPH(BH_3) and similarly a_5-PhobPH with BH_3·THF gave a_5-PhobPH(BH_3) (Scheme 4) both of which have been fully characterized (see Experimental Section).

It was noted that after 24 h, THF solutions that were originally of pure a_5-PhobPH(BH_3) contained 14% of another secondary phosphine-borane adduct (J_{PH} = 356 Hz, J_{PB} = 45 Hz) assigned the structure a_7-PhobPH(BH_3). After 10 days the ratio of a_5/a_7 isomers settled on ca. 2:1 which is assumed to be the equilibrium position (K_3 = 0.5 in Scheme 5). The 2:1 ratio of the borane adducts contrasts with the $>10^3$:1 ratio in the precursor secondary phosphines and reflects the effect of putting a BH_3 group in the crowded site above the seven-membered ring; this will be further discussed in the light of the calculations below.

Wild et al.[32] have shown that secondary phosphine boranes of the type RR′PH(BH_3) are optically stable under ambient conditions and therefore intramolecular P-inversion is unlikely to be the mechanism for the isomerization of a_5-PhobPH(BH_3). Instead, the mechanism given in Scheme 5 is proposed. The following observations support the involvement of THF solvolysis (step i). (1) No isomerization was observed in C_6D_6 over 5 days. (2) The ^{31}P and ^{11}B NMR spectra of solutions of a_5-PhobPH(BH_3) in THF after a few hours showed the presence of ca. 5 mol% of a_5-PhobPH and BH_3·THF. (3) Solutions of a_5-PhobPH(BH_3) to which BH_3·THF had been added (to make the solution ca. 0.3 M in BH_3) did not show any evidence of isomerization after 24 h.

(31) The assignment of the minor species as a_7-PhobPH was validated by the addition of genuine *s*-PhobPH to a sample of the mixture of a_5-PhobPH and a_7-PhobPH and three distinct ^{31}P NMR signals were observed at −48.4, −54.1, and −54.3 ppm. Furthermore, addition of BH_3·THF to the 3:1:1 mixture of a_5-PhobPH, a_7-PhobPH, and *s*-PhobPH gave a 3:1:1 mixture of a_5-PhobPH(BH_3), a_7-PhobPH(BH_3), and *s*-PhobPH(BH_3).

(32) Bader, A.; Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1996**, *35*, 3874.

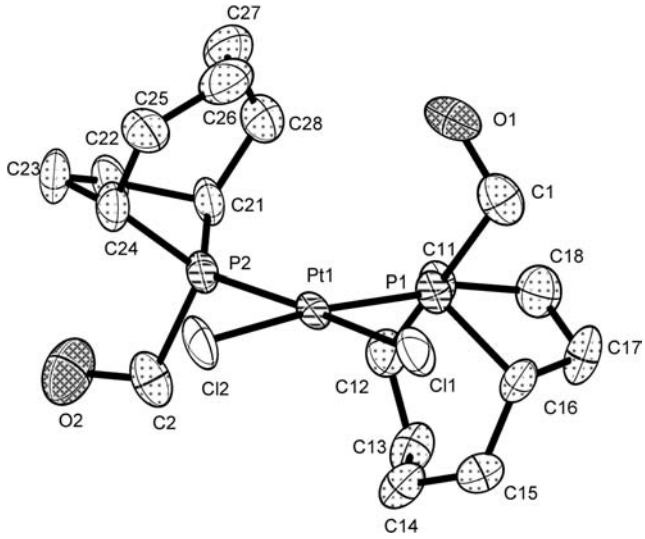
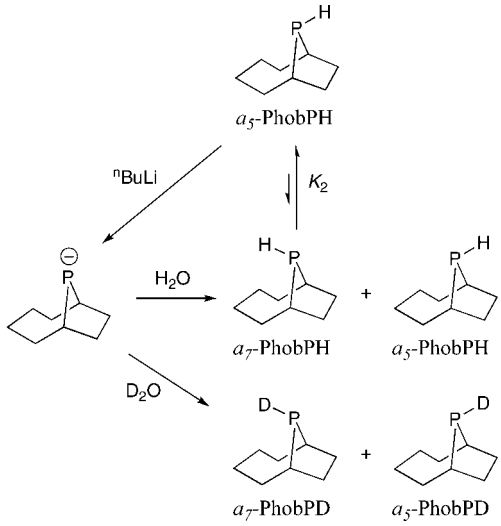
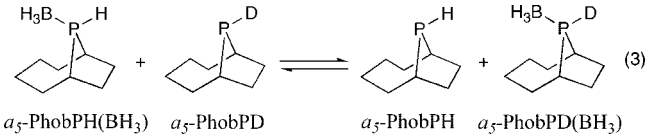


Figure 6. Structure of the ordered one of the two independent molecules of *cis*-[$PtCl_2$(a_5-$PhobPCH_2OH$)$_2$]. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) (values in second independent molecule shown in square brackets). Pt(1)−Cl(1) 2.356(3) [2.353(4)], Pt(1)−Cl(2) 2.361(2) [2.373(2)], Pt(1)−P(1) 2.240 (2) [2.237(2)], Pt(1)−P(2) 2.245(2) [2.236(2)], P(1)−C(1) 1.861(9) [1.851(22)], P(2)−C(2) 1.865(9) [1.863(9)], P(1)−Pt(1)−P(2) 103.3(1) [102.2(1)], Cl(1)−Pt(1)−Cl(1) 87.5(1) [88.0(1)], C(11)−P(1)−C(16) 93.6(4) [93.1(5)] C(21)−P(2)−C(24) 92.6(4) [91.8(4)].

Scheme 3

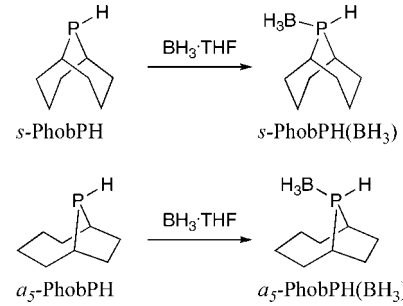


The equilibrium in step i is not rate limiting in the isomerization since addition of 1 equiv of the labeled compound a_5-PhobPD to a_5-PhobPH(BH_3) in THF led to complete equilibration (eq 3) within 12 h. Step ii is proposed to be rate determining since the a_5-PhobPH to a_7-PhobPH isomerization has been shown to be very unfavorable (see above).

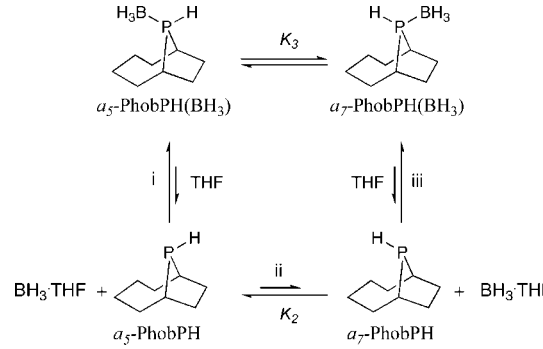


Addition of 1 equiv of *s*-PhobPH to a_5-PhobPH(BH_3) in THF led to BH_3 exchange and the establishment of the equilibrium

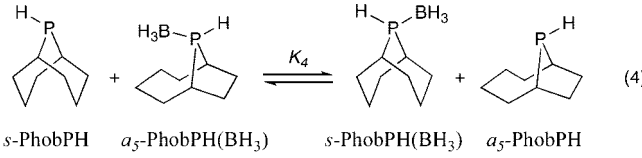
Scheme 4



Scheme 5



shown in eq 4 within 24 h with a K_4 (THF) of 1.0×10^2; the equilibrium position was confirmed by approaching it in the other direction, i.e., addition of 1 equiv of a_5-PhobPH to *s*-PhobPH(BH_3) in THF.

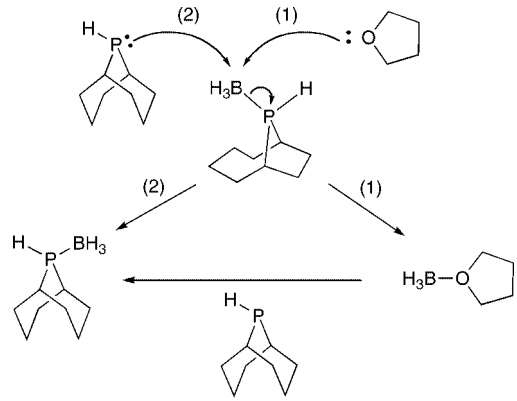


Detailed kinetic analysis of the BH_3 exchange between the *s*- and a_5-PhobPH isomers was not carried out, but the following qualitative trends were noted. The rate of equilibration (eq 4) in THF was significantly faster than in benzene; equilibrium was established within 24 h in THF and took ca. 36 h in benzene. Doubling the concentration from 0.1 to 0.2 M total P-reagents had little effect on the rate of equilibration in THF but reduced the time to establish equilibrium in C_6D_6 to 24 h. These observations are consistent with the parallel nucleophilic mechanisms shown in Scheme 6 operating (1) a solvolysis pathway (dominating in THF) and (2) direct attack on B by the P-nucleophile pathway (dominating in benzene).

We are in a position to list the secondary phobane isomers in order of their affinity for BH_3. For Scheme 7, the equilibrium constants K_3 and K_4 have been determined (see above) and a lower limit to the value for K_2 has been obtained. Therefore, for the hypothetical equilibrium shown Scheme 7, K_5 ($= K_2K_3/K_4$) is calculated to be >5 which means that the order of affinity of the secondary phobane isomers for BH_3 is a_7-PhobPH > *s*-PhobPH > a_5-PhobPH.

Chlorophobanes. The chlorophobanes *s*-PhobPCl and *a*-PhobPCl are potentially useful electrophilic sources of the phobane moiety. It has been reported that a mixture of chlorophobanes can be generated from the reaction of a

Scheme 6



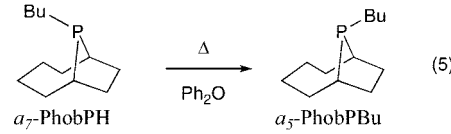
s-PhobPH/*a*-PhobPH mixture with C_2Cl_6[33] or PCl_3.[6] We have prepared *s*-PhobPCl and *a*-PhobPCl separately (Scheme 8), and these have been fully characterized (see Experimental Section). Only one isomer was observed in the ^{31}P NMR spectrum for *a*-PhobPCl which is tentatively assigned, on steric grounds, as a_5-PhobPCl. Interestingly in the ^{31}P NMR spectra of both *s*-PhobPCl and *a*-PhobPCl, two signals separated by 0.03 ppm are clearly discerned (in the ratio of ca. 3:1) corresponding to the P−^{35}Cl and P−^{37}Cl isotopomers.[34]

***n*-Butylphobanes.** The greater nucleophilicity of *s*-PhobPH than *a*-PhobPH can be exploited in the selective synthesis of tertiary *sym*-phobanes. Hence, quaternization of a 1:1 mixture of *s*-PhobPH and *a*-PhobPH with ^{n}BuBr in refluxing MeCN gave predominantly (ca. 80%) [*s*-PhobPHBu]Br. Pure tertiary *sym*-phobanes have been obtained previously by using a large excess of *s*-PhobPH/*a*-PhobPH mixture but yields based on *s*-PhobPH were reportedly less than 10%.[4] Moreover, pure tertiary *asym*-phobanes cannot be obtained by these competitive nucleophilic routes. The separation of the phobanes has opened up access to single isomers of *s*-PhobPR, a_5-PhobPR, and a_7-PhobPR, as demonstrated here for the *n*-butylphobanes.

The isomers of *n*-butylphobane have been prepared by the routes shown in Schemes 9 and 10 (see Experimental Section for details). Thus pure *s*-PhobPBu was prepared using nucleophilic or electrophilic sources of the *s*-PhobP group by the three routes shown in Scheme 9: Route A, quaternization of *s*-PhobPH with ^{n}BuBr followed by deprotonation with NaOH; Route B, treatment of *s*-PhobPH with ^{n}BuLi to generate *s*-PhobPLi followed by addition of ^{n}BuBr; Route C, substitution of the Cl in *s*-PhobPCl using ^{n}BuLi.

A 1:1 mixture of a_5-PhobPBu and a_7-PhobPBu was obtained when *a*-PhobPCl was reacted with ^{n}BuLi (Route I in Scheme 10).[35] The stereoselectivity of the lithiation route (Route II in Scheme 10) was much greater (94% in favor of a_5-PhobPBu). The most stereoselective routes were via boranation (Route III in Scheme 10) which gave 100% pure a_5-PhobPBu and via quaternization (Route IV in Scheme 10) which gave 96% pure a_7-PhobPBu. The stereochemistry of these products was confirmed by the crystal structure of *trans*-[$PtCl_2$(a_7-PhobPBu)$_2$] (**5a$_7$**, see below). The formation of the a_7-PhobPBu via quaternization and the a_5-PhobPBu via the borane adduct validate the assignment of the predominant isomer of *a*-PhobPH as the a_5-isomer.

When a solution of pure a_7-PhobPBu in toluene is refluxed for 2 days, no change (<0.1%) was observed by ^{31}P NMR spectroscopy. Isomerization of a_7-PhobPBu to a_5-PhobPBu (eq 5) proceeded smoothly at 210 °C and after 22 h, conversion to a_5-PhobPBu was >99.9% showing that a_5-PhobPBu is the thermodynamically more stable *asym*-isomer. This would be expected on steric grounds and agrees with calculations (see below); Bergman et al.[9] came to similar conclusions for the *asym*-isomers of PhobPCy. The first-order rate constants for the isomerization (eq 5) were measured at five temperatures with concentrations obtained from integration of the ^{31}P NMR signals. From an Eyring plot, the activation parameters were calculated (see Experimental Section) and $\Delta G^{\ddagger}$ (at 403 K) was determined to be 38.1 kcal mol^{-1} (160 kJ mol^{-1}). This is higher than the previously determined $\Delta G^{\ddagger}$ (at 403 K) values by Mislow et al.[36] of 29−36 kcal mol^{-1} for P-inversion in a variety of tertiary phosphines (including monocyclic phosphines) and may reflect the extra strain imposed by the bicycle on the trigonal transition state for the isomerization (see discussion of computational results below).



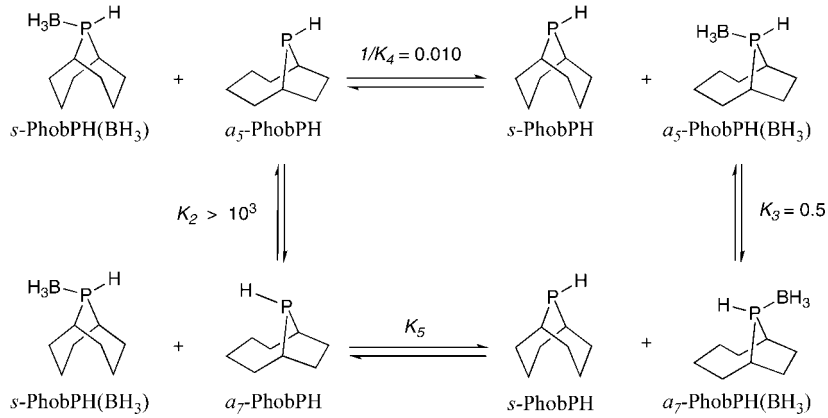
Experimental Measures of the Donor Properties of *n*-Butylphobane Isomers. The spectroscopic properties of the three series of compounds **1**−**3** shown in Scheme 11 have been investigated in order to probe the donor characteristics of the *n*-butylphobanes.

The magnitude of J_{PSe} in $R_3P(Se)$ is inversely correlated with the σ-donor strength of PR_3.[3,6,37] The isomers of PhobP(Se)Bu (**1**) were generated quantitatively by treatment of the isomers of PhobPBu with KSeCN in methanol (see Experimental Section).[37] The J_{PSe} values in $CDCl_3$[38] increase in the order **1a$_7$** (662 Hz) < **1s** (684 Hz) < **1a$_5$** (707 Hz) (cf. 683 Hz for PBu_3 and 733 Hz for PPh_3 analogues)[3] indicating that the σ-donor strength decreases in the order a_7-PhobPBu > *s*-PhobPBu > a_5-PhobPBu.

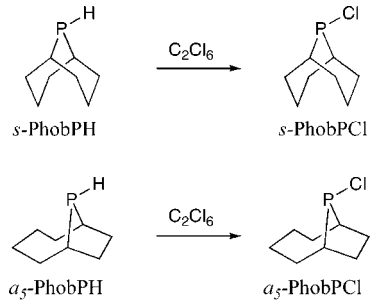
The value of ν(CO) in *trans*-[RhCl(CO)(PR_3)$_2$] is a measure of the net donor strength of the PR_3 ligand.[39] The complexes *trans*-[RhCl(CO)(PhobPBu)$_2$] (**2**) were made quantitatively in situ by treatment of [$Rh_2Cl_2(CO)_4$] with the isomers of PhobPBu in CH_2Cl_2 (see Experimental Section). The ν(CO) values increase in the order **2a$_7$** (1947 cm^{-1}) < **2s** (1950 cm^{-1}) < **2a$_5$** (1954 cm^{-1}) (cf. 1953 cm^{-1} for PBu_3 and 1965 cm^{-1} for PPh_3 analogues)[39] indicating that the donor strength decreases in the order a_7-PhobPBu > *s*-PhobPBu > a_5-PhobPBu.

(33) Weferling, N. *Z. Anorg. Allg. Chem.* **1987**, *548*, 55.
(34) Buckingham, M. J.; Hawkes, G. E.; Ismail, I. M.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1982**, *6*, 1167.
(35) The lack of stereoselectivity in the *a*-PhobPCl substitution reaction may be due to frontside and backside nucleophilic attack, see for example van Bochove, M. A.; Swart, M.; Bickelhaupt, F. M. *ChemPhysChem* **2007**, *8*, 2452.
(36) (a) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090. (b) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 1442.
(37) Muller, A.; Otto, S.; Roodt, A. *Dalton Trans.* **2008**, 650.
(38) To compare J_{PSe} values with those from ref 3 it is important to use the same solvent since the values obtained in MeOH (**1a$_7$**, 649 Hz; **1s**, 671 Hz; **1a$_5$**, 696 Hz) are significantly lower than in $CDCl_3$ but are in the same descending order.
(39) (a) Clarke, M. L.; Holliday, G. L.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1093. (b) Roodt, A.; Otto, S.; Steyl, G. *Coord. Chem. Rev.* **2003**, *245*, 121.

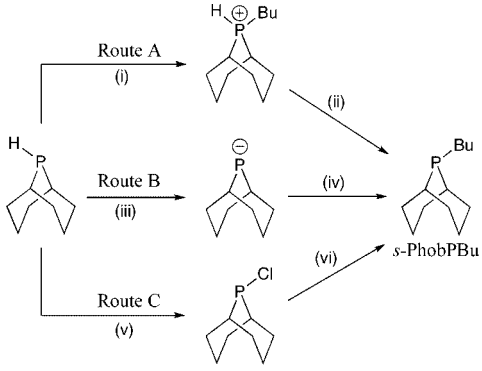
Scheme 7



Scheme 8

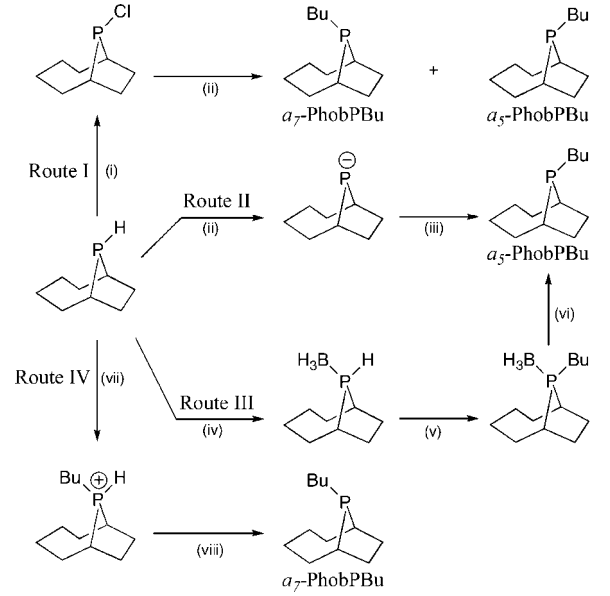


Scheme 9[a]



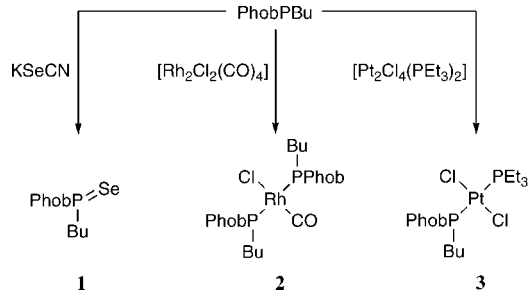
[a] (i) ^{n}BuBr, MeCN, reflux, 20 h; (ii) 1 M NaOH, 30 min; (iii) ^{n}BuLi, 0 °C, 20 min; (iv) ^{n}BuBr, −78 °C, 20 h; (v) C_2Cl_6, toluene, 115 °C, 90 min; (vi) ^{n}BuLi, 0 °C, 3 h.

Scheme 10[a]



[a] (i) C_2Cl_6, toluene, 24 h, reflux; (ii) ^{n}BuLi, 20 min, 0 °C; (iii) ^{n}BuBr, −78 °C, 20 h; (iv) BH_3·THF, 20 h, 0 °C; (v) ^{n}BuLi, 20 min, 0 °C, and then ^{n}BuBr, −78 °C, 20 h; (vi) pyrrolidine, 20 h; (vii) ^{n}BuBr, MeCN, reflux, 48 h; (viii) 1 M NaOH, 30 min.

Scheme 11



The unsymmetrical *trans*-[$PtCl_2(PEt_3)$(PhobPBu)] (**3**) were generated in situ by the bridge cleavage reactions shown in Scheme 11 (see Experimental Section) in order to determine the relative trans influences of the isomers of PhobPBu from the J_{PtP} values for the trans PEt_3. The J_{PtP} values for the coordinated PEt_3 increase in the order **3a$_7$** (2406 Hz) < **3s** (2423 Hz) < **3a$_5$** (2456 Hz), indicating that the order of trans influence is a_7-PhobPBu > *s*-PhobPBu > a_5-PhobPBu.

All the spectroscopic data for compounds **1**−**3** therefore support the conclusion that the strength of ligation of the PhobPBu isomers is in the order a_7-PhobPBu > *s*-PhobPBu > a_5-PhobPBu.

To assess the relative affinities of the *n*-butylphobane isomers for platinum(II), the relative stabilities of the isomers of [$Pt(CH_3)$(dppe)(PhobPBu)]BPh_4 (**4**) were determined. Complexes **4** were prepared according to eq 6 and fully characterized (see Experimental Section). The equilibria shown in Scheme 12 were established over 48 h, as confirmed by approaching the equilibria in both directions. For example the same values of K_A were calculated when either **4s** was mixed with a_7-PhobPBu or **4a$_7$** was mixed with *s*-PhobPBu. The equilibrium constants were estimated from integration of the ^{31}P NMR signals for the components; the error in the value of K_C is significant because of the tiny amounts of **4a$_5$** present but the estimated value is approximately equal to K_AK_B as expected.

Scheme 12

$$\mathbf{4s} + a_7\text{–PhobPBu} \underset{}{\overset{K_A = 13}{\rightleftharpoons}} \mathbf{4a_7} + s\text{–PhobPBu}$$

$$\mathbf{4a_5} + s\text{–PhobPBu} \overset{K_B = 58}{\rightleftharpoons} \mathbf{4s} + a_5\text{–PhobPBu}$$

$$\mathbf{4a_5} + a_7\text{–PhobPBu} \overset{K_C = 720}{\rightleftharpoons} \mathbf{4a_7} + a_5\text{–PhobPBu}$$

The values clearly show that the order of stability is **4a$_7$** > **4s** > **4a$_5$** indicating the order of affinity for platinum(II) is a_7-PhobPBu > s-PhobPBu > a_5-PhobPBu which is the same as the order of strength of ligation of these ligands determined spectroscopically and discussed above.

$$[PtCl(CH_3)(cod)] \xrightarrow[\text{ii PhobPBu}\\ \text{iii } NaBPh_4]{\text{i dppe}} \left[\begin{array}{c} Ph_2 \\ P \\ Pt(CH_3) \\ P \\ Ph_2 \end{array}\right] BPh_4 \qquad (6)$$

4

Structural Studies of PhobPBu Isomers. Treatment of $[PtCl_2(NC^tBu)_2]$ with the isomers of PhobPBu in CH_2Cl_2 gave *trans*-$[PtCl_2(PhobPBu)_2]$ (**5**) (eq 7). The crystal structures of **5s** and **5a$_7$** have been determined but frustratingly, for **5a$_5$** we have been unable to grow crystals that are suitable for X-ray crystallography.

$$[PtCl_2(NC^tBu)_2] \xrightarrow{2\ \text{PhobPBu}} \left[\begin{array}{c} Bu \\ Cl \quad PPhob \\ Pt \\ PhobP \quad Cl \\ Bu \end{array}\right] \qquad (7)$$

5

The structure of *trans*-$[PtCl_2(s\text{-PhobPBu})_2]$ (**5s**) has the s-PhobPBu ligands mutually trans with square planar coordination at the Pt(II) center (which has exact inversion symmetry). In addition, the C_8 moieties are in the sterically least hindered anti conformation (see Figure 7). As in previous cases, the phobane ligand shows considerable distortion from tetrahedral geometry at the phosphorus atom (intraring C−P−C 96°).

The structure of *trans*-$[PtCl_2(a_7\text{-PhobPBu})_2]$ (**5a$_7$**) contains two independent (half-) molecules in the asymmetric unit with the platinum lying at an inversion center in each case (see Figure 8). In both cases, the molecules differ with respect to the conformation of the butyl substituent on the phosphine. The a_7-PhobPBu ligands are mutually trans at the square planar Pt(II) center with the C_8 moieties anti. The a_7-PhobPBu ligand in **5a$_7$** shows even greater distortion from tetrahedral geometry at the phosphorus atom (intraring C−P−C 91°) than does the s-PhobPBu ligand in **5s**.

Computational Study of Phobanes. Studying synthetically relevant, realistically sized transition metal complexes computationally is more viable now than when an early computational study was carried out on the charge distribution in PhobPPh ligands.[40] Here we have optimized the geometries of representative PhobPR ligands and their complexes with density functional theory (BP86, see Experimental Section for details of the computational method). Optimizations of s-PhobPH, a_5-PhobPH and a_7-PhobPH confirm that the s-PhobPH is the lowest energy isomer, with a_5-PhobPH lying about 1 kcal mol^{-1} higher in energy and a_7-PhobPH a further 3 kcal mol^{-1} above a_5-PhobPH, supporting the experimental conclusion of the greater stability of a_5-PhobPH than a_7-PhobPH.

The gas-phase proton affinities for PhobPH were calculated as the energy difference between the protonated and neutral species, E(PhobPH) − E([PhobPH$_2$]$^+$), and are thus influenced by the relative stabilities of the PhobPH isomers. Both a-PhobPH isomers give the same product on protonation ([a-PhobPH$_2$]$^+$) which is 4 kcal mol^{-1} higher in energy than [s-PhobPH$_2$]$^+$. The differences in the relative energies of s-PhobPH, a_5-PhobPH, and a_7-PhobPH lead to the proton affinities for s- and a_7-PhobPH being the same at 229.5 kcal mol^{-1} and the proton affinity of a_5-PhobPH being lower at 226.5 kcal mol^{-1} (see Figure 9), in agreement with the higher acidity observed experimentally for [a-PhobPH$_2$]$^+$.

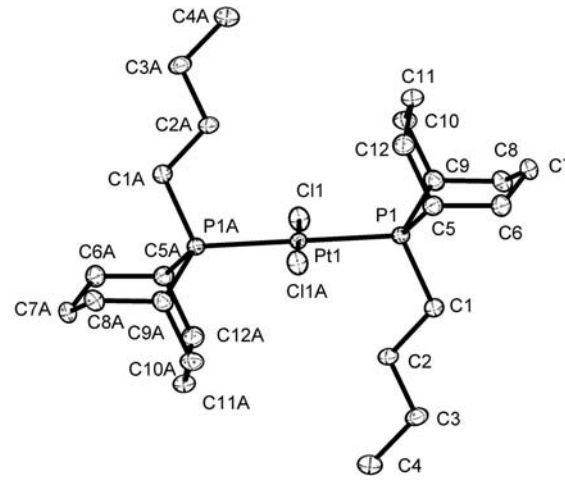


Figure 7. Structure of *trans*-[PtCl$_2$(s-PhobPBu)$_2$] (**5s**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg); Pt(1)−Cl(1) 2.3059(11), Pt(1)−P(1) 2.3121(11), P(1)−C(1) 1.834(4), P(1)−C(5) 1.844(4), P(1)−C(9) 1.823(4), C(5)−P(1)−C(9) 95.71(7).

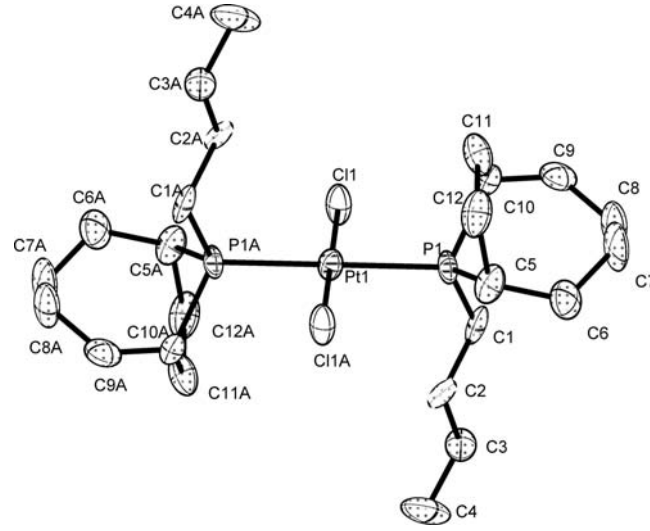


Figure 8. Solid-state structure of one of the two independent molecules of *trans*-[PtCl$_2$(a_7-PhobPBu)$_2$] (**5a$_7$**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) (values for second independent molecule are given in square brackets); Pt(1)−Cl(1) 2.307(4) [2.318(4)], Pt(1)−P(1) 2.302(4) [2.321(5)], P(1)−C(1) 1.839(16) [1.787(18)] P(1)−C(5)1.85(2)[1.833(17)],P(1)−C(10)1.891(18)[1.817(18)],C(5)−P(1)−C(10) 91.3(9) [96.8(8)].

(40) Howard, S. T.; Foreman, J. P.; Edwards, P. G. *Inorg. Chem.* **1996**, *35*, 5805.

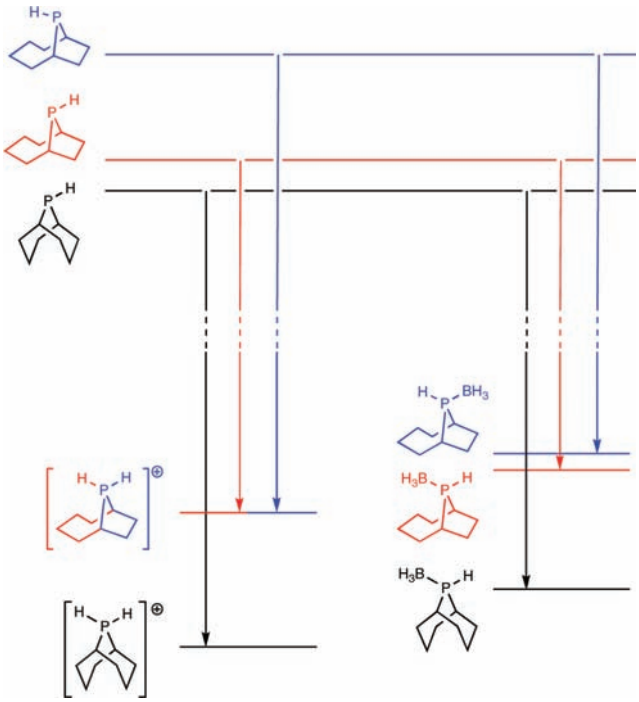


Figure 9. Schematic of the relative calculated energies of the isomers of PhobPH and their derivatives.

For the borane adducts PhobPH(BH_3), the a_5 isomer is 3.4 kcal mol^{-1} higher in energy than the *s* isomer, while the a_7 isomer remains 4.0 kcal mol^{-1} higher in energy than the *s* isomer and thus the a_5-to-a_7 gap shrinks to 0.6 kcal mol^{-1} (shown schematically in Figure 9). This change in relative isomer energies can be traced to unfavorable interactions between one of the BH_3 hydrogens and a hydrogen on the seven-membered ring in the a_5-isomer; in a_5-PhobPH(BH_3), there is an H···H contact of 2.247 Å which is particularly short compared to the closest H···H contacts of 2.592 Å in *s*-PhobPH(BH_3) and 2.730 Å in a_7-PhobPH(BH_3). This is a similar situation to that discussed above for the $[PhobP(CH_2OH)_2]^+$ isomers.

The ^1J(PB) values of 45 Hz for a_7-PhobPH and 38 Hz for a_5-PhobPH (cf. 47 Hz for *s*-PhobPH) imply a difference in the strength of the P−B σ-bond for the two *asym*-phobanes. The binding energy for coordination of the BH_3 fragment to the ligand can be estimated computationally as BE(BH_3) = [*E*(BH_3) + *E*(PhobPH)] − *E*(PhobPH(BH_3)). The BE(BH_3) value is similar for the *s*- and a_7-isomers (35.6 and 35.5 kcal mol^{-1}, respectively) but lower for the a_5-isomer (33.2 kcal mol^{-1}), at least in part due to the shorter H···H contact in the borane adduct. The calculated P−B bond is longer in a_5-PhobPH(BH_3) (1.945 Å) than in a_7-PhobPH(BH_3) (1.937 Å) or *s*-PhobPH(BH_3) (1.934 Å) presumably to reduce the unfavorable interactions between the BH_3 fragment and the seven-membered ring in the a_5-isomer. These results suggest that the difference in BH_3 binding energies for the two *a*-PhobPH isomers shifts the a_5-to-a_7 ratio in favor of the a_7-PhobPH(BH_3) compared to the uncomplexed isomers.

Differences in the stabilities of the ground-state isomers also need to be considered for the calculation of barriers to inversion at the phosphorus. Experimentally, we have observed a $\Delta G^{\ddagger}$ of 38.1 kcal mol^{-1} (at 403 K) for the inversion of a_7-PhobPBu, whereas the calculated inversion has a barrier of 33.8 kcal mol^{-1} (incl. ZPE), equivalent to a $\Delta G^{\ddagger}$ of 33.9 kcal mol^{-1} (at 298 K) for the conversion of a_7-PhobPBu to a_5-PhobPBu; barriers of 39.6 kcal mol^{-1} (incl. ZPE) and $\Delta G^{\ddagger}$ = 39.5 kcal mol^{-1} at 298 K for the reverse process. We have calibrated our calculated inversion barriers against some of experimental results of Mislow[36] for both cyclic and acyclic phosphine ligands, and generally found that our computational approach underestimated inversion barriers somewhat, especially those of strained ring systems.[41] A detailed investigation of this is beyond the scope of this work, but we note that both cumulative differences between calculated and experimental geometries, as well as the known problem of DFT approaches with reproducing relative isomer energies of strained hydrocarbons,[42] may be contributing to this discrepancy. Nevertheless, these calculations demonstrate a trend toward higher barriers for more strained ring systems, thus supporting our discussion of the experimental observations.

Table 1. LKB-P Descriptor Values for a Range of P-Donor Ligands[a]

L	E_{HOMO}	E_{LUMO}	PA	He_8 steric	BE (BH_3)	BE ($PdCl_3^-$)	BE ($PtCl_3^-$)
a_5-PhobPMe	−0.1870	0.0209	237.6	5.9	36.8	38.5	51.6
s-PhobPMe	−0.1829	0.0269	240.9	4.8	39.3	40.3	52.8
a_7-PhobPMe	−0.1791	0.0250	243.5	3.7	40.1	41.0	53.6
PMe_3	−0.1905	0.0327	233.0	3.0	39.2	38.5	
P^nBu_3	−0.1865	0.0274	243.3	6.1	39.1	37.2	

[a] See ref 43 for details of calculations, complexes, and analysis.

We have recently described the development of a database of structural and energetic data relating to P-donor ligands determined computationally, termed a ligand knowledge base (LKB-P).[43] The LKB-P can be used to compare the properties of the phobanes described here with more familiar ligands in a variety of coordination environments. Some of the LKB descriptors for *s*-, a_5-, and a_7-isomers of PhobPMe are collected, together with those for representative P-donor ligands, in Table 1. Although the chemistry described in this article is of PhobPBu, the computational work has concentrated on PhobPMe to limit conformational noise arising from the flexible butyl substituents and to reduce the associated computational cost. The similarity of PhobPMe and PhobPBu has been established by comparison of the isomer stabilities and the borane binding energies (see Table 2).

A comparison of the LKB descriptor values for the three phobane isomers highlights how these ligands are subtly different in their donor/acceptor properties, as captured by their frontier molecular orbital energies (E_{HOMO}, E_{LUMO}) and in their interactions with other fragments (schematically illustrated in Figure 10). The proton affinities and binding energies to BH_3, $PdCl_3^-$, and $PtCl_3^-$ fragments all show the same trend with a_7-PhobPMe > *s*-PhobPMe > a_5-PhobPMe. This concurs with the order arrived at on the basis of experimental data for the Se, Rh(I), and Pt(II) adducts discussed above. If it is assumed that σ-bonding dominates the binding of the PhobPMe isomers to each of the species, then this trend can be rationalized in terms of the E_{HOMO} which is also in the order a_7-PhobPMe > *s*-PhobPMe > a_5-PhobPMe.

The He_8 steric descriptors[43] suggest that, in terms of steric bulk, a_7-PhobPMe < *s*-PhobPMe < a_5-PhobPMe although the differences are small. Nevertheless, this order agrees well with our

(41) Compare the experimental values (from ref 32) and calculated values for the following: PMePh^{n}Pr, exptl $\Delta G^{\ddagger}$ = 32.1 kcal mol^{-1} (403 K), calcd $\Delta G^{\ddagger}$ = 30.2 kcal mol^{-1} (298 K); PMePh^{t}Bu, exptl $\Delta G^{\ddagger}$ = 32.7 kcal mol^{-1} (403 K), calcd $\Delta G^{\ddagger}$ = 30.4 kcal mol^{-1} (298 K); 3-methyl-1-phenylphospholane, exptl $\Delta G^{\ddagger}$ = ca. 36 kcal mol^{-1} (443 K), calcd $\Delta G^{\ddagger}$ = 31.1 kcal mol^{-1} (298 K).

(42) (a) Schreiner, P. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 4217. (b) Grimme, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4460.

(43) Fey, N.; Tsipis, A. C.; Harris, S. E.; Harvey, J. N.; Orpen, A. G.; Mansson, R. A. *Chem. Eur. J.* **2006**, *12*, 291.

Table 2. Comparison of Calculated Results for PhobPMe and PhobPBu[a]

	s-PhobPMe	a_5-PhobPMe	a_7-PhobPMe	*s*-PhobPBu	a_5-PhobPBu	a_7-PhobPBu
E_{rel} PhobPR	0.0	0.5	6.3	0.0	0.4	6.1
E_{rel} PhobPR(BH_3)	0.0	3.0	5.4	0.0	3.0	5.4
BE (BH_3)	39.3	36.8	40.1	39.2	36.7	39.9

[a] Energies are in kcal mol^{-1}; E_{rel} values are relative to energy of most stable isomer.

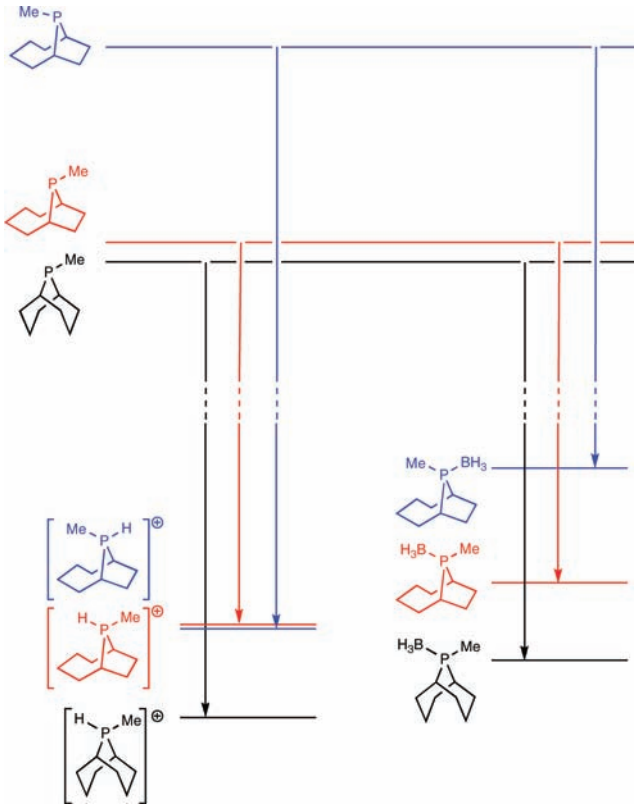


Figure 10. Schematic of the relative calculated energies of the isomers of PhobPMe and their derivatives by calculation.

observations of unfavorable close contacts in a_5-PhobPH(BH_3), but it may be less important in square planar coordination environments where the metal fragment can rotate to alleviate steric congestion.

It is notable that in each column in Table 1, the metric for a_7-PhobPMe is closer to the value for *s*-PhobPMe than the value for a_5-PhobPMe.

Conclusion

The extensive use of alkylphobane complexes in catalysis implies that these bicyclic phosphine ligands have special properties that deserve detailed study.[44] The reported catalyses have often employed mixtures of phobane isomers which complicates the discussion and interpretation of the results in terms of ligand stereoelectronics. Isolating the effects of the individual isomers should simplify the understanding of these systems. The separation of *s*-PhobPH and *a*-PhobPH held the key to the stereospecific synthesis of the isomeric tertiary phosphines *s*-PhobPR, a_5-PhobPR, and a_7-PhobPR. This has been demonstrated here with the synthesis of the archetypal *n*-butylphobane isomers via nucleophilic routes (using PhobPH or PhobP(BH_3)Li) or electrophilic routes (using PhobPCl).

The previous understanding has been that *s*-PhobPR compounds are more basic, more nucleophilic, and complex to metals more strongly than *a*-PhobPR isomers. It has been shown here experimentally, and supported computationally, that the situation is more complicated. The affinities of the isomers of PhobPBu for Se, Rh(I) and Pt(II) are consistently in the order $a_7 > s > a_5$. In addition, calculations have traced the source of these trends to the accessibility of the lone pair (E_{HOMO}) which is in the order $a_7 > s > a_5$. A comparative study of the catalytic performance of isomeric PhobPR ligands is currently underway.

Experimental Section

General Considerations. Unless otherwise stated, all work was carried out under a dry nitrogen atmosphere, using standard Schlenk line techniques. Dry N_2-saturated solvents were collected from a Grubbs system[45] in flame and vacuum-dried glassware. The complexes $[PtCl_2(NC^tBu)_2]$,[46] $[PtCl(CH_3)(cod)_2]$,[47] and $[Rh_2Cl_2(CO)_4]$[48] were made by literature methods. Isomeric mixtures of phobanes were obtained from Shell or Rhodia. All other chemicals were purchased from Aldrich. NMR spectra were measured on a Jeol Eclipse 300, Jeol Eclipse 400, or Jeol GX 400. Unless otherwise stated, ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300, 100, and 121 MHz, respectively, at +23 °C. Mass spectra were recorded on a MD800. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

Separation of *a*-PhobPH Isomer by Selective Protonation of the *s*-PhobPH Isomer. A 2:1 mixture of *sym*- and *asym*-phobane in toluene (50 cm^3) was concentrated under reduced pressure to give the colorless, oily solid phobane mixture (28.0 g, 0.20 mol). The solid was dissolved in diethyl ether (200 cm^3), and deoxygenated water (100 cm^3) was added. The biphasic mixture was stirred vigorously while deoxygenated 12 M HCl (100 cm^3) was added dropwise over 40 min. ^{31}P NMR spectroscopy of the ether phase showed that 96% *a*-PhobPH and 4% *s*-PhobPH was present. The organic phase (A) and aqueous phase (B) were separated and the aqueous phase was extracted with diethyl ether (7 × 50 cm^3). The organic phases were combined and concentrated to 100 cm^3, washed with 12 M HCl (4 cm^3), a saturated $NaHCO_3$ solution (30 cm^3), and then dried over $MgSO_4$. The solvent was removed under reduced pressure to give *a*-PhobPH as a colorless solid (6.00 g, 42.3 mmol, 63% yield and 99.4% pure, 0.6% *s*-PhobPH) as a colorless solid.

The *s*-PhobPH can be recovered from the aqueous phase as follows, but the purity was comparatively low (90%) prior to sublimation. Diethyl ether (200 cm^3) was added to the aqueous phase (B) and then 14.4 M aqueous NaOH solution (160 cm^3, 2.30 mol) was added dropwise over 1.5 h to the vigorously stirred two-phase mixture which was cooled in ice. The phases were separated and the aqueous phase extracted with diethyl ether (4 × 50 cm^3). The combined organic phase was dried over $MgSO_4$ and then the solvent was removed under reduced pressure to give solid *s*-PhobPH (19.79 g, 0.139 mol, 91% yield and 90% pure with 3% *a*-PhobPH and 7% unidentified impurity having δ_P 15). Sublimation of the

(44) Phosphacycles have recently attracted considerable attention in hydroformylation catalysis. For leading references see: (a) Müller, C.; Vogt, D. *Dalton Trans.* **2007**, 5505. (b) Haddow, M. F.; Middleton, A. J.; Orpen, A. G.; Pringle, P. G.; Papp, R. *Dalton Trans.* **2009**, 202.

(45) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(46) Fraccarollo, D.; Bertani, R.; Mozzon, M.; Belluco, U.; Michelin, R. A. *Inorg. Chim. Acta* **1992**, *201*, 15.

(47) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(48) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 84.

product at 60 °C and 2 mmHg gave 80% recovery of 98% pure *s*-PhobPH (2% *a*-PhobPH).

Separation of *s*-PhobPH Isomer by Selective Oxidation of the *a*-PhobPH Isomer. A 2:1 mixture of *sym*- and *asym*-phobane in toluene (500 cm^3, 1.58 mol) was concentrated under reduced pressure to give a colorless oily solid. Aqueous HCl (12 M, 415 cm^3) was added slowly over 2 h while the temperature of the mixture was maintained at ca. 30 °C. The solution was then cooled to 0 °C and stirred vigorously while H_2O_2 (109 cm^3, 30 wt %, ca. 1 mol) was added dropwise over 45 min. When the addition was complete, the mixture was stirred for another 30 min. Then deoxygenated hexane (250 cm^3) was added and the mixture again cooled to 0 °C and an ice cold solution of NaOH (160 g) in water (625 cm^3) was added dropwise. When the addition was complete, the hexane layer was separated and the water layer extracted with hexane (2 × 250 cm^3). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give *s*-PhobPH as a colorless solid (100.0 g, 92% yield and 96% pure, 0.5% *a*-PhobPH).[49]

Separation of Phobane Isomers via the bis(Hydroxymethyl)phosphonium Salts. A 1:1 mixture of *sym*- and *asym*-phobane in toluene (100 cm^3, 1.58 mol) was concentrated under reduced pressure to give a colorless oily solid. The resulting mixture of isomers (50 g, ca. 0.35 mol) was dissolved in 35% aqueous CH_2O (120 cm^3, 42.5 g, 1.41 mol) exothermically to give a cloudy, viscous solution. The stirred solution was then cooled in an ice bath while 7.5 M HCl (80 cm^3, 0.60 mol) was added dropwise over 1 h. A small amount of organic material (mainly residual toluene) was then separated from the aqueous layer (using a separating funnel, in air). The aqueous phase was concentrated on a rotary evaporator to give a viscous, cloudy oil. The oil was triturated with 2-propanol (200 cm^3) to give a colorless precipitate which was filtered off, washed with ice cold 2-propanol (50 cm^3), and diethyl ether (50 cm^3). The solid was recrystallized from boiling MeOH to give colorless crystals (53.4 g). By concentrating the filtrate, another crop of product was obtained (14.85 g). The combined yield (ca. 80%) was an air stable, 4:3 mixture of [*s*-PhobP$(CH_2OH)_2$]Cl (δ_P 23.4 in H_2O) and [*a*-PhobP$(CH_2OH)_2$]Cl (δ_P 55.2 in H_2O). A sample of this mixture of salts (55.0 g, 135 mmol of [*s*-PhobP$(CH_2OH)_2$]Cl and 95.5 mmol of [*a*-PhobP$(CH_2OH)_2$]Cl) was dissolved in deoxygenated water (130 cm^3) and pentane (230 cm^3) was added. A 1 M aqueous NaOH solution (93 cm^3, 93 mmol) was added over 7 h to the vigorously stirred two-phase mixture. The aqueous phase (C) and pentane phase (D) were then separated.

The aqueous phase (C), containing predominantly [*s*-PhobP$(CH_2OH)_2$]Cl was washed with pentane (2 × 35 cm^3). Then 1.5 M aqueous NaOH solution (7.0 cm^3) was added to remove the final traces of [*a*-PhobP$(CH_2OH)_2$]Cl. The aqueous phase was again washed with pentane (3 × 50 cm^3), and the pentane washings were discarded. Fresh pentane (250 cm^3) was added, and then 1.5 M aqueous NaOH (180 cm^3, 0.27 mol) was added dropwise over 30 min to the stirred mixture. Finally solid $NaHSO_3$ (69.9 g, 0.673 mol) was added in portions (to react with the released CH_2O). The two-phase mixture was then stirred vigorously for 54 h, after which the ^{31}P NMR spectrum showed complete conversion to *s*-PhobPH. The pentane layer was separated and the aqueous layer extracted with pentane (4 × 50 cm^3). The combined organic phase was dried over Na_2SO_4 and then the solvent removed under reduced pressure to give colorless, solid *s*-PhobPH (17.4 g, 0.123 mol, 91% yield, >99.9% pure). ESI mass spectrum: *m*/*z* 142 (M^+). ^{31}P NMR ($CDCl_3$): δ −54.1 (d, J_{PH} = 192 Hz). ^1H NMR ($CDCl_3$): 3.20 (1H, d, J_{PH} = 192.1 Hz), 1.55−2.55 (14H, br m). ^{13}C NMR ($CDCl_3$): 33.9 (d, J_{PC} = 6.1 Hz), 30.0 (d, J_{PC} = 9.2 Hz), 22.6 (s), 22.4 (d, J_{PC} = 42.7 Hz), 22.1 (s).

(49) There was also ca. 3.5% of an unidentified primary phosphine impurity having δ_P−125 (probably (5-cyclooctenyl)PH_2 or (cycloctyl)PH_2) which was present in the commercial phobane. This caused no problems with the purity of the derivatives.

To the pentane phase (D) was added deoxygenated water (170 cm^3), 1 M aqueous NaOH solution (100 cm^3), and solid $NaHSO_3$ (104 g, 1.00 mol) and the mixture was vigorously stirred at ambient temperature for 4.5 days. The pentane layer was separated and the aqueous phase extracted with pentane (3 × 40 cm^3). The combined organic phase was dried over Na_2SO_4 and then the solvent removed under reduced pressure to give colorless, solid *a*-PhobPH (9.36 g, 0.066 mol, 69% yield, >99.9% pure). ESI mass spectrum: *m*/*z* 142 (M^+).^{31}P NMR ($CDCl_3$): −48.4 (d, J_{PH} = 188.1 Hz). ^1H NMR ($CDCl_3$): 2.70 (1H, d, J_{PH} = 188.1 Hz), 2.59 (br s, 2H), 2.06 (2H, m), 1.35−1.82 (m, 10H). ^{13}C NMR ($CDCl_3$): 37.1 (d, J_{PC} = 7.6 Hz), 35.5 (d, J_{PC} = 7.6 Hz), 35.3 (d, J_{PC} = 15.3 Hz), 25.8 (d, J_{PC} = 7.6 Hz).

Preparation of [*s*-PhobPH$_2$]Cl. *s*-PhobPH (0.68 g, 4.80 mmol) was dissolved in diethyl ether, and 1 M HCl in diethyl ether (4.8 cm^3, 4.80 mmol) was added over 5 min to give a white precipitate immediately. The solid was filtered off, washed with diethyl ether (10 cm^3), and dried briefly in vacuo (0.47 g, 2.63 mmol, 55%). Anal. Found (calcd for $C_8H_{16}ClP$): C, 53.63 (53.79); H, 9.36 (9.03). ^{31}P NMR ($CDCl_3$): −17.0 ppm; ^1H NMR ($CDCl_3$): 7.47 (2H, br), 3.04 (2H, d, J_{PH} = 13.44), 2.45−2.25 (10H, br), 1.92−1.74 (2H, br). ^{13}C NMR ($CDCl_3$): 29.1 (d, J_{PC} = 1.54 Hz), 21.6 (d, J_{PC} = 33.82 Hz), 21.1 (d, J_{PC} = 7.69 Hz).

Attempted Preparation of [*a*-PhobPH$_2$]Cl. *a*-PhobPH (0.12 g, 0.84 mmol) was dissolved in diethyl ether, and 1 M HCl in diethyl ether (0.84 cm^3, 0.84 mmol) was added over 1 min to give a white precipitate immediately. Isolation of [*a*-PhobPH$_2$]Cl was difficult as it spontaneously loses significant amounts of HCl even upon brief drying in a stream of N_2. ^{31}P NMR ($CDCl_3$ to which ethereal HCl had been added to make it 0.2 M HCl): −2.0 ppm.

^{31}P NMR Study of Phobane Protonation. Solutions (0.050 M) of [*s*-PhobPH$_2$]Cl (0.1395 g, 0.7809 mmol) in methanol/C_6D_6 (14.06/1.56 cm^3) and *s*-PhobPH (0.1243 g, 0.8724 mmol) in methanol/C_6D_6 (15.0/1.75 cm^3) were prepared. In an NMR tube, the amounts of these two solutions were varied from 0 to 1.00 cm^3 with the total volume maintained at 1.00 cm^3 and therefore total P-concentration was 0.05 M. The δ_P was measured in each case and the values plotted (see Figure 1). To a methanolic solution of [*s*-PhobPH$_2$]Cl (1.0 cm^3, 0.050M, 0.10 mmol), 1 and then 2 equiv of *a*-PhobPH (0.0071 g, 0.0142 g) were added, and the δ_P value for the *s*-PhobP signal measured. Using the plot in Figure 1, the *s*-PhobPH/*s*-PhobPH$_2^+$ was estimated from the values of δ_P (−34.51, −35.19 ppm) and used to calculate the relative acidities.

Preparation of *a*-PhobPD. Pure *a*-PhobPH (0.58 g, 4.05 mmol) was dissolved in a 1:1 mixture of C_6D_6 and THF (2 cm^3) and then cooled to 0 °C. A solution of 1.6 M ^{n}BuLi in hexane (12.6 cm^3, 20.26 mmol) was added dropwise over 3 min. The solution was stirred for a further 2 min before a solution of 99.9% D_2O (25 cm^3, 1.38 mol) was added over 5 min. The resulting mixture was then stirred for a further 3 min before the organic layer was transferred to another flask. The solvent was removed under reduced pressure to give a colorless solid containing a 4:1 mixture of a_5-PhobPD and a_7-PhobPD (0.468 g, 3.27 mmol). Anal. Found (calcd for $C_8{}^1H_{14}{}^2HP$): C, 67.33 (67.11), H, 11.43 (11.26). Accurate mass spectrum: M_r = 144.1053 (calcd for $C_8{}^1H_{15}{}^2HP$, 144.1052). ^{31}P NMR (C_6D_6): −50.5 (t, J_{PD} = 28 Hz, a_5-PhobPD) −55.3 (t, J_{PD} = 28 Hz, a_7-PhobPD). ^1H NMR (C_6D_6): 2.48−2.34 (1H, br m), 2.05−1.15 (14H, br m). ^{13}C NMR (C_6D_6): 37.2 (d, J_{PC} = 7.6 Hz), 35.6 (d, J_{PC} = 8.65 Hz), 35.3 (d, J_{PC} = 15.0 Hz), 25.9 (d, J_{PC} = 7.5).

Preparation of *s*-PhobPCl. Pure *s*-PhobPH (2.21 g, 15.6 mmol) was dissolved in toluene (2 cm^3) and heated to 90 °C. A solution of C_2Cl_6 (3.84 g, 16.2 mmol) in toluene (8 cm^3) was then added dropwise over 30 min. The reaction mixture was then heated for 90 min at 115 °C before being allowed to cool to ambient temperature. The solvent was removed under reduced pressure and the residue sublimed (70 °C, 2 mmHg) to give *s*-PhobPCl as a colorless sticky solid (2.24 g, 12.7 mmol, 82%). Anal. Found (calcd for $C_8H_{14}ClP$): C, 54.66 (54.40), H, 7.98 (7.99). Accurate mass

spectrum: M_r = 176.0524 (calcd for $C_8H_{14}ClP$, 176.0522). ^{31}P NMR (202 MHz, C_6D_6): 89.12 ppm (^{35}Cl isotopomer), 89.09 ppm (^{37}Cl isotopomer). ^1H NMR (C_6D_6): 2.62−2.48 (2H, m), 1.97 (2H, br s), 1.94−1.45 (9H, m), 1.31−1.21 (1H, m). ^{13}C NMR (C_6D_6): 30.8 (s), 30.5 (d, J_{PC} = 16.5 Hz), 23.7 (d, J_{PC} = 3.7 Hz), 22.4 (d, J_{PC} = 3.7 Hz), 21.4 (d, J_{PC} = 1.8 Hz).

Preparation of *a*-PhobPCl. Pure *a*-PhobPH (0.67 g, 4.68 mmol) was dissolved in toluene (2 cm^3) and heated to 90 °C. A solution of C_2Cl_6 (1.11 g, 4.68 mmol) in toluene (6 cm^3) was then added dropwise over 20 min. The reaction mixture was heated for another 18 h at 115 °C. The reaction mixture was then allowed to cool and the solvent was removed under reduced pressure and the residue sublimed (70 °C, 2 mmHg) to give *a*-PhobPCl as a colorless sticky solid (0.40 g, 2.3 mmol, 49%). Anal. Found (calcd for $C_8H_{14}ClP$): C, 54.70 (54.40), H, 7.91 (7.99). Accurate mass spectrum: M_r = 176.0526 (calcd for $C_8H_{14}ClP$, 176.0522). ^{31}P NMR (202 MHz, C_6D_6): 135.58 ppm (^{35}Cl isotopomer), 135.55 ppm (^{37}Cl isotopomer). ^1H NMR (C_6D_6): 2.67−2.57 (2H, m), 2.55−2.39 (2H, m), 1.61−1.47 (2H, m) 1.45−1.29 (2H, m), 1.28−1.01 (2H, m). ^{13}C NMR (C_6D_6): 47.1 (d, J_{PC} = 27.6 Hz), 33.5 (d, J_{PC} = 4.9 Hz), 32.8 (d, J_{PC} = 20.6 Hz), 25.1 (d, J_{PC} = 8.4 Hz).

Preparation of *s*-PhobPH(BH_3). Pure *s*-PhobPH (0.14 g, 0.99 mmol) was dissolved in THF (4 cm^3) and then cooled to 0 °C. A THF solution of BH_3·THF (1.0 cm^3, 1M, 1.0 mmol) was then added dropwise over 1 min. The solution was stirred for 30 min and then the solvent was removed under reduced pressure to give the white solid product (0.14 g, 0.90 mmol, 91%). EI mass spectrum: *m*/*z* 154 (M^+ − H). $^{31}P\{^1H\}$ NMR (C_6D_6): 0.0 (q, J_{PB} 44.7 Hz). ^{31}P NMR (C_6D_6): 0.0 (br d, J_{PH} = 352 Hz). ^{11}B NMR (C_6D_6): −41.8 (d, J_{PB} = 44.7 Hz). ^1H NMR (C_6D_6): 2.25−2.17 (3H, br m), 1.42−1.05 (15H, br m). ^{13}C NMR (C_6D_6): 31.3 (d, J_{PC} = 6.9 Hz), 25.3 (s), 21.6 (d, J_{PC} = 11.53 Hz), 21.5 (s).

Preparation of a_5-PhobPH(BH_3). Pure a_5-PhobPH (0.11 g, 0.77 mmol) was dissolved in THF (4 cm^3) and then cooled to 0 °C. A THF solution of BH_3·THF in THF (0.8 cm^3, 1M, 0.8 mmol) was then added dropwise over 1 min. The solution was stirred for 16 h, and then the solvent was removed under reduced pressure to give the white solid product (0.10 g, 0.64 mmol, 83%). EI mass spectrum: *m*/*z* 155 (M^+ − H). $^{31}P\{^1H\}$ NMR (C_6D_6): 16.1 (q, J_{PB} = 35.7 Hz). ^{31}P NMR (C_6D_6): 16.1 (br d, J_{PH} = 334 Hz). ^{11}B NMR (C_6D_6): −42.0 (d, J_{PB} = 35.7 Hz). ^1H NMR (C_6D_6): 1.99−1.97 (3H, br m), 1.86−1.63 (5H, br m), 1.22−1.05 (10H, br m). ^{13}C NMR (C_6D_6): 32.0 (d, J_{PC} = 28.4 Hz), 31.7 (s), 30.7 (d, J_{PC} = 3.1 Hz), 24.5 (d, J_{PC} = 3.1 Hz).

Isomerization Studies of *s*- and *a*-PhobPH(BH_3). Solutions (0.10M) of *s*- and a_5-PhobPH (0.058 g, 4.10 mmol) in THF (4.1 cm^3) and *s*- and a_5-PhobPH(BH_3) (0.17 g, 1.10 mmol) in THF (11 cm^3) were prepared and then used in the following experiments. (1) A solution of 0.10 M of *s*-PhobPH (0.50 cm^3, 0.050 mmol) and a_5-PhobPH(BH_3) (0.50 cm^3, 0.050 mmol) were added in an NMR tube and the tube shaken to mix the reactants. The proportions of *s*-, a_5-, and a_7-PhobPH(BH_3) was monitored daily by ^{31}P NMR until equilibrium was attained (6 days). (2) A similar procedure was carried out for a_5-PhobPH and *s*-PhobPH(BH_3). (3) A solution of 0.10 M pure a_5-PhobPH(BH_3) (1.0 cm^3, 0.10 mmol) was added to an NMR tube. The proportions of a_5- and a_7-PhobPH(BH_3) were monitored daily by ^{31}P NMR until equilibrium was attained (6 days). Data for a_7-PhobPH(BH_3): $^{31}P\{^1H\}$ NMR (THF): 11.8 (q, J_{PB} = 45 Hz). ^{31}P NMR (C_6D_6): 11.8 (dq, J_{PH} = 356 Hz, J_{PB} = 45 Hz). ^{11}B NMR (THF): −41.0 (d, J_{PB} = 45 Hz).

Preparation of *s*-PhobPBu via Quaternization. *s*-PhobPH (0.50 g, 3.5 mmol) was dissolved in acetonitrile (10 cm^3) and to this solution *n*-butylbromide was added. The solution was refluxed for 20 h, after which the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (10 cm^3), NEt_3 was added dropwise over 2 min, and the mixture stirred overnight. The resulting solution was filtered through Celite and solvent was then removed at reduced pressure to give the colorless liquid product (0.38 g, 1.9 mmol, 55%).

Preparation of *s*-PhobPBu via *s*-PhobPLi. *s*-PhobPH (3.00 g, 21.1 mmol) was dissolved in THF (20 cm^3) and then cooled to 0 °C. A solution 1.6 M ^{n}BuLi in hexane (14.5 cm^3, 23.25 mmol) was added dropwise over 15 min. The solution was stirred for a further 20 min and then cooled to −78 °C before 1-bromobutane (2.27 cm^3, 2.90 g, 21.13 mmol,) was added dropwise over 3 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 20 h before the solvent was removed under reduced pressure. The resulting residue was suspended in water (10 cm^3) and then extracted with hexane (4 × 15 cm^3). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was distilled (100−102 °C at 1.3 mmHg) to give a colorless liquid (2.50 g, 12.6 mmol, 60%). Accurate mass spectrum: M_r 198.1542 (calcd for $C_{12}H_{23}P$ 198.1537). ^{31}P NMR (C_6D_6): −36.1 ppm. ^1H NMR (C_6D_6): 2.25−1.12 (2H, m), 2.01−1.80 (6H, m), 1.70−1.48 (6H, m), 1.47−1.33 (6H, m), 0.89 (3H, t). ^{13}C NMR (C_6D_6): 32.4 (d, J_{PC} = 12.5 Hz), 28.1 (d, J_{PC} = 18.2 Hz), 24.6 (d, J_{PC} = 11.9 Hz), 24.5 (d, J_{PC} = 4.1 Hz), 24.3 (d, J_{PC} = 11.4 Hz), 23.7 (d, J_{PC} = 5.2 Hz), 22.4 (d, J_{PC} = 21.3 Hz), 21.9 (d, J_{PC} = 2.0 Hz), 13.9 (s).

Preparation of *s*-PhobPBu via *s*-PhobPCl. *s*-PhobPCl (0.50 g, 2.8 mmol) was dissolved in THF (10 cm^3) and the solution cooled to 0 °C. A solution of 1.6 M ^{n}BuLi in hexane (1.9 cm^3, 3.1 mmol) was added dropwise over 2 min. The solution was then stirred for a further 2 h after which the solvent was removed under reduced pressure. To the residue was added hexane (10 cm^3) and deoxygenated water (10 cm^3), and the mixture vigorously stirred. The organic phase was then separated and the aqueous phase washed with hexane (3 × 10 cm^3). The combined organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure to give the product as a colorless liquid (0.32 g, 1.6 mmol, 57%).

Preparation of a_7-PhobPBu. a_5-PhobPH (2.00 g, 14.1 mmol) and 1-bromobutane (3.2 cm^3, 30 mmol) were dissolved in acetonitrile (25 cm^3) and the mixture was heated to reflux for 48 h. The solvent was then removed under reduced pressure and the resulting colorless precipitate was suspended in diethyl ether (20 cm^3) and 1 M aqueous NaOH (15.5 cm^3, 15.5 mmol) added. The reaction mixture was stirred for 30 min after which the two phases were separated. The aqueous phase was extracted with diethyl ether (3 × 20 cm^3). The combined organic phase was dried over $MgSO_4$, and the solvent removed under reduced pressure. The product was distilled (100−102 °C at 1.3 mmHg) to give 94% pure a_7-PhobPBu as a colorless liquid (1.30 g, 6.60 mmol, 46%); the product was contaminated with 6% of the isomeric a_5-PhobPBu. Accurate mass spectrum: M_r 198.1528 (calcd for $C_{12}H_{23}P$ 198.1537). ^{31}P NMR (C_6D_6): −0.6 ppm. ^1H NMR (C_6D_6): 2.43−2.34 (2H, m), 2.12−2.08 (2H, m), 1.76−1.65 (4H, m), 1.64−1.56 (2H, m), 1.56−1.33 (10H, m), 0.89 (3H, t). ^{13}C NMR (C_6D_6): 34.4 (d, J_{PC} = 20.0 Hz), 34.4 (d, J_{PC} = 3.1 Hz), 33.2 (d, J_{PC} = 5.4 Hz), 30.9 (d, J_{PC} 18.4 = Hz), 25.9 (s), 24.4 (d, J_{PC} = 12.3 Hz), 19.8 (d, J_{PC} = 25.4 Hz), 13.9 (d, J_{PC} = 8.5 Hz).

Preparation of a_5-PhobPBu via *a*-PhobPLi. *a*-PhobPH (1.7 g, 12.0 mmol) was dissolved in THF (15 cm^3) and then cooled to 0 °C. A solution 1.6 M ^{n}BuLi in hexane (8.2 cm^3, 13.2 mmol) was added dropwise over 10 min. The solution was stirred for a further 20 min and then cooled to −78 °C before 1-bromobutane (1.28 cm^3, 1.60 g, 12.0 mmol) was added dropwise over 3 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 20 h before the solvent was removed under reduced pressure. The resulting residue was suspended in water (10 cm^3) and then extracted with hexane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was distilled (100−102 °C at 1.3 mmHg) to give the colorless liquid product (1.80 g, 9.10 mmol, 75%).

Preparation of a_5-PhobPBu via *a*-PhobP(BH_3)Li. *a*-PhobPH (2.00 g, 14.0 mmol) was dissolved in THF (14 cm^3) and then cooled to 0 °C. A solution of 1 M BH_3·THF in THF (15.5 cm^3, 15.5 mmol) was added dropwise over 5 min. The solution was stirred for 16 h,

Table 3. Crystal Data

compound	[*a*-PhobP(CH_2OH)$_2$]-[*s*-PhobP(CH_2OH)$_2$]Cl_2	[$PtCl_2${a_5-PhobP(CH_2OH)}$_2$]	**5s**	**5a$_7$**
empirical formula	$C_{20}H_{40}Cl_2O_4P_2$	$C_{18}H_{34}Cl_2P_2Pt$	$C_{24}H_{46}Cl_2P_2Pt$	$C_{24}H_{46}Cl_2P_2Pt$
formula weight	477.36	607.4	662.54	662.54
T/K	173(2)	293(2)	173(2)	173(2)
crystal system	orthorhombic	triclinic	triclinic	monoclinic
space group (No.)	$Pca2_1$ (29)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a (Å)	25.078(3)	11.2515(6)	7.7585(16)	19.0791(10)
b (Å)	7.7656(12)	14.1812(4)	7.8401(16)	8.1201(3)
c (Å)	11.962(2)	14.6186(5)	11.023(2)	19.1417(10)
α (deg)	90	82.687(26)	96.88(3)	90
β (deg)	90	70.963(35)	102.46(3)	116.866(2)
γ (deg)	90	76.951(34)	97.12(3)	90
V/Å^3	2329.5(7)	2144.4(15)	642.2(2)	2645.4(2)
Z	4	4	1	4
ρ/Mg m^{-3}	1.361	1.881	1.713	1.664
absorption coefficient (mm^{-1})	0.440	6.951	5.806	5.637
crystal size (mm)	0.30 × 0.20 × 0 × 10^3	0.5 × 0.5 × 0.4	0.302 × 0.288 × 0.243	0.11 × 0.1 × 0.03
reflections collected	18 722	7399	8247	23 275
independent reflections [R_{int}]	4087 [0.0552]	6981 [0.0663]	2942 [0.0231]	6020 [0.0663]
max./min. transmission	−	0.103/0.043	0.240/0.173	1.0/0.695751
data/restraints/parameters	4087/1/270	6981/0/207	2941/0/144	6020/0/262
R_1 ($I > 2\sigma$)	0.0464	0.0347	0.0148	0.0683
absolute structure parameter	−0.15(10)	N/A	N/A	N/A
largest diff. peak and hole (e Å^{-3})	0.76, −0.33	0.95, −1.46	1.08, −0.82	2.6, −2.1

and then the solvent was removed under reduced pressure. The resulting solid was redissolved in THF (14 cm^3) and the solution cooled to −78 °C before 1.6 M ^{n}BuLi (10.0 cm^3, 16.0 mmol) was added dropwise over 10 min. The solution was stirred for a further 30 min and then allowed to warm to room temperature before being cooled again to −78 °C. ^{n}BuBr (1.5 cm^3, 14.0 mmol) was then added slowly dropwise over 3 min. The reaction mixture was slowly warmed to room temperature and stirred for a further 20 h. The solvent was removed under reduced pressure, and then pyrrolidine (10 cm^3) was added and the mixture was stirred for 20 h. The solvent was removed under reduced pressure and the liquid product was distilled (58−60 °C at 0.68 mmHg) to give pure a_5-PhobPBu as a colorless liquid (1.80 g, 9.10 mmol, 65%). Accurate mass spectrum: M_r 198.1532 (calcd for $C_{12}H_{23}P$ 198.1537). ^{31}P NMR (C_6D_6): 0.8 ppm. ^{1}H NMR (C_6D_6): 2.25−2.17 (2H, m), 2.16−2.07 (2H, m), 1.82−1.72 (2H, m), 1.67−1.59 (2H, m), 1.55−1.26 (10H, m), 1.13−1.06 (2H, m), 0.86−0.82 (3H, t). ^{13}C NMR (C_6D_6): 39.4 (d, J_{PC} = 12.3 Hz), 35.4 (d, J_{PC} =15.4 Hz), 33.9 (d, J_{PC} = 6.1 Hz), 29.4 (d, J_{PC} = 16.9 Hz), 25.7 (d, J_{PC} =7.7 Hz), 24.4 (d, J_{PC} = 12.3 Hz), 24.0 (d, J_{PC} = 16.9 Hz), 13.9 (s).

Isomerization Studies of *a*$_7$-PhobPBu. a_7-PhobPBu (0.060 g) was heated to 220, 210, 200, 190, or 170 °C in Ph_2O (2.1 g). Aliquots of the solutions were taken at different times and analyzed by ^{31}P NMR spectroscopy. The first order rate constants were calculated from the slope ($-k_{obs}/2.303$) obtained from the plots of log[a_7-PhobPBu] vs time (in s). The calculated values of k_{obs} (in s^{-1}) were 54.1 × 10^{-6} (493 K), 28.7 × 10^{-6} (483 K), 8.29 × 10^{-6} (473 K), 5.30 × 10^{-6} (463 K), 0.96 × 10^{-6} (443 K). The rate constants were fitted to the Eyring equation, $\ln(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(k_B/h)$ where k_B is Boltzmann's constant and h is Planck's constant. The Gibbs free energy of activation, $\Delta G^{\ddagger}$, was then calculated to be 38.1 kcal mol^{-1} (160 kJ mol^{-1}) from the standard free energy expression, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ using the calculated enthalpy (143 kJ mol^{-1}) and entropy (−41 J K^{-1} mol^{-1}) terms from the Eyring analysis.

Preparation of the Isomers of PhobP(Se)Bu (1). Pure *s*-, a_5-, or a_7-isomer of PhobPBu (0.049 g, 0.25 mmol) was placed in an NMR tube under N_2 and then KSeCN (0.07 g, 0.50 mmol) in MeOH (0.7 cm^3) was added and the tube shaken a few times. The reactions were complete after 10 min (as shown by ^{31}P NMR spectroscopy). The solvent was removed under reduced pressure, and the solid residue was extracted with chloroform (2 × 0.5 cm^3). Evaporation of the chloroform gave the desired compounds as white solids or colorless oils. The products were characterized by ^{31}P NMR spectroscopy only. ^{31}P NMR (MeOH): **1s**, 37.2 ppm (J_{PSe} = 671 Hz); **1*a*$_7$**, 60.7 ppm (J_{PSe} = 649 Hz); **1*a*$_5$**, 60.7 ppm (J_{PSe} = 696 Hz). In order to compare our data with those of others,[3] the spectra were also measured in $CDCl_3$. ^{31}P NMR ($CDCl_3$): **1s**, 35.4 ppm (J_{PSe} = 684 Hz); **1*a*$_7$**, 58.8 ppm (J_{PSe} = 662 Hz); **1*a*$_5$**, 59.4 ppm (J_{PSe} = 707 Hz).

Preparation of the Isomers of [RhCl(CO)(PhobPBu)$_2$] (2). Pure *s*-, a_5-, or a_7-isomer of PhobPBu (0.018 g, 0.091 mmol) and [$Rh_2Cl_2(CO)_4$] (0.009 g, 0.023 mmol) were placed in an NMR tube. Upon dropwise addition of CH_2Cl_2 (0.5 cm^3), effervescence was observed. The products were characterized by ^{31}P NMR and IR spectroscopy only. ^{31}P NMR (CD_2Cl_2): **2s**, 14.8 ppm (d, J_{PRh} = 119 Hz); **2a$_7$**, 44.0 ppm (d, J_{PRh} = 113 Hz); **2a$_5$**, 52.0 ppm (d, J_{PRh} = 115 Hz). IR (CH_2Cl_2): **2s**, ν_{CO} = 1950 cm^{-1}; **2a$_7$**, ν_{CO} = 1947 cm^{-1}; **2a$_5$**, ν_{CO} = 1954 cm^{-1}.

Preparation of the Isomers of [PtCl$_2$(PEt$_3$)(PhobPBu)] (3). Pure *s*-, a_5-, or a_7-isomer of PhobPBu (0.021 g, 0.10 mmol) and [$Pt_2Cl_4(PEt_3)_2$] (0.039 g, 0.050 mmol) were placed in an NMR tube and CD_2Cl_2 (0.5 cm^3) was added. ^{31}P NMR (CD_2Cl_2): **3s**, 3.7 ppm (*s*-PhobPBu, J_{PPt} = 2413 Hz, J_{PP} = 457 Hz), 13.1 ppm (PEt_3, J_{PPt} = 2423 Hz); **3*a*$_7$**, 13.3 ppm (PEt_3, J_{PPt} = 2406 Hz), 34.4 ppm (a_7-PhobPBu, J_{PPt} = 2306 Hz, J_{PP} = 441 Hz); **3a$_5$** 11.7 ppm (PEt_3, J_{PPt} = 2456 Hz), 42.1 ppm (a_5-PhobPBu, J_{PPt} = 2352 Hz, J_{PP} = 457 Hz).

Preparation of the Isomers of [PtMe(dppe)(PhobPBu)]BPh$_4$ (4). A solution of pure *s*-, a_5-, or a_7-isomer of PhobPBu (0.035 g, 0.17 mmol) in MeOH (3 cm^3) was added to [PtMeCl(dppe)] (0.114 g, 0.17 mmol). The solution was stirred for 20 min, after which $NaBPh_4$ (0.064 g, 0.19 mmol) was added. The colorless precipitate was filtered off and dried under vacuum. Data for **4s**: Yield, 0.163 g, 0.14 mmol, 85%. Anal. Found (calcd for $C_{63}H_{70}BP_3Pt$): C 67.55 (67.20), H 6.30 (6.27). ^{31}P NMR (CD_2Cl_2): 8.0 ppm (dd, J_{PP} = 365 and 19 Hz, J_{PPt} = 2689 Hz, *s*-PhobPBu), 46.3 ppm (dd, J_{PP} = 19 and 6 Hz, J_{PPt} = 1783, PPh_2 cis to *s*-PhobPBu), 52.2 ppm (dd, J_{PP} = 365 and 6 Hz, J_{PPt} = 2573 Hz, PPh_2 trans to *s*-PhobPBu). ^{11}B NMR (CD_2Cl_2): −7.5 ppm. ^{1}H NMR (CD_2Cl_2): 7.96−7.46 (20H, m), 7.38−7.33 (8H, br), 7.04 (8H, t), 6.90 (4H, t), 2.76−1.22 (24H, m), 1.03 (3H, t), 0.66 (3H, m). ^{13}C NMR (CD_2Cl_2): 164.0 (q, J_{CB} = 49 Hz), 135.9 (s), 134.6 (q, J_{CB} = 30 Hz), 134.0 (q, J_{CB} = 37 Hz), 132.8 (s), 132.6 (d, J_{PC} =11 Hz), 132.5 (s), 131.8 (s), 129.5 (m), 129.2 (d, J_{PC} = 10 Hz), 125.6 (m), 121.7 (s), 31.6 (ddd, J_{PC} = 4, 12, 34 Hz), 29.8 (d, J_{PC} = 54 Hz), 27.0 (m), 26.7 (dd, J_{PC} = 3, 13 Hz), 26.2 (d, J_{PC} = 29 Hz), 24.5

(d, J_{PC} = 14 Hz), 22.6 (m), 22.3 (d, J_{PC} = 28 Hz), 21.7 (s), 21.4 (d, J_{PC} = 6 Hz), 20.2 (d, J_{PC} = 5 Hz), 13.7 (s). Data for **4a$_7$**: Yield, 0.174 g, 0.15 mmol, 91%. Anal. Found (calcd for $C_{63}H_{70}BP_3Pt$): C 67.24 (67.20), H 6.23 (6.27). ^{31}P NMR (CD_2Cl_2): 32.5 ppm (dd, J_{PP} = 355 and 21 Hz, J_{PPt} = 2551 Hz, a_7-PhobPBu), 48.0 ppm (dd, J_{PP} = 21 and 6 Hz, J_{PPt} = 1740, PPh_2 cis to a_7-PhobPBu), 52.1 ppm (dd, J_{PP} = 355 and 6 Hz, J_{PPt} = 2549 Hz PPh_2 trans to a_7-PhobPBu). ^{11}B NMR (CD_2Cl_2): −7.5 ppm. ^{1}H NMR (CD_2Cl_2): 7.86−7.50 (20H, m), 7.88−7.46 (8H, br), 7.08 (8H, t), 6.89 (4H, t), 3.24−1.23 (24H, brm), 0.97 (3H, t), 0.66 (3H, m) ^{13}C NMR (CD_2Cl_2, −60 °C): 164.0 (q, J_{CB} 49 Hz), 135.8 (s), 135.0 (d, J_{CP} 13 Hz), 133.5 (s), 133.1 (s), 132.3 (d, J_{CP} 10 Hz), 131.8 (d, J_{CP} 14 Hz), 131.2 (d, J_{CP} 9 Hz), 130.2−129.6 (m), 129.3 (d, J_{CP} 13 Hz), 126.1 (q, J_{CB} 2 Hz), 122.1 (s), 34.3−33.6 (m), 33.3 (d, J_{CP} 12 Hz), 33.0 (s), 32.8 (t, J_{CP} 16 Hz), 32.4−31.5 (m), 30.1 (ddd, J_{CP} 2, 14, 35 Hz), 27.7−27.0 (m), 26.9 (d, J_{CP} 14 Hz), 23.0 (d, J_{CP} = 22 Hz), 16.5 (s). Data for **4a$_5$**: Yield, 0.167 g, 0.14 mmol, 87%. Anal. Found (calcd for $C_{63}H_{70}BP_3Pt$): C 67.03 (67.20), H 6.02 (6.27). ^{31}P NMR (CD_2Cl_2): 41.2 ppm (dd, J_{PP} = 361 and 19 Hz, J_{PPt} = 2601 Hz, a_5-PhobPBu), 44.6 ppm (dd, J_{PP} = 19 and 6 Hz, J_{PPt} = 1730, PPh_2 cis to a_5-PhobPBu), 50.2 ppm (dd, J_{PP} = 361 and 6 Hz, J_{PPt} = 2612 Hz PPh_2 trans to a_5-PhobPBu). ^{11}B NMR (CD_2Cl_2): −7.5 ppm.^{1}H NMR (CD_2Cl_2): 7.86−7.50 (20H, m), 7.36−7.31 (8H, br), 7.03 (8H, t), 6.89 (4H, t), 2.69−1.04 (24H, brm), 0.96 (3H, t), 0.81 (3H, m) ^{13}C NMR (CD_2Cl_2): 164.0 (q, J_{CB} = 50 Hz), 135.9 (s), 134.5 (d, J_{CP} = 29 Hz), 133.7 (d, J_{CP} = 37 Hz), 132.8 (s), 132.3 (s), 131.9 (d, J_{CP} = 12 Hz), 131.6 (d, J_{CP} = 11 Hz), 129.5−129.2 (m), 125.5 (q, J_{CB} = 9 Hz), 121.7 (s), 34.3 (d, J_{CP} = 26 Hz), 33.3 (d, J_{CP} = 25 Hz), 32.2 (d, J_{CP} = 10 Hz), 31.6 (m), 30.2 (m), 28.0 (t, J_{CP} = 11 Hz), 26.9 (ddd, J_{CP} = 4, 13, 37 Hz), 25.8 (d, J_{CP} = 6 Hz), 25.6 (d, J_{CP} = 29 Hz), 24.7 (d, J_{CP} = 3 Hz), 24.5 (d, J_{CP} = 13 Hz), 13.6 (s).

Preparation of the isomers of [PtCl$_2$(PhobPBu)$_2$] (5). A solution of a pure *s*-, a_5-, or a_7-isomer of PhobPBu (0.046 g, 0.23 mmol) in CH_2Cl_2 (1.5 cm^3) was added to a solution of [$PtCl_2(NC^tBu)_2$] (0.050 g, 0.11 mmol) in CH_2Cl_2 (1.5 cm^3). The mixture was stirred for 2 h, after which the solvent was removed under reduced pressure. The product was recrystallized from pentane to give a pale yellow precipitate which was filtered off and dried under vacuum. Crystals were obtained by slow evaporation of CH_2Cl_2 solutions. Data for **5s**: Yield, 0.078 g (0.12 mmol, 98%). Anal. Found (calcd for $C_{24}H_{46}Cl_2P_2Pt$): C, 43.68 (43.51); H, 7.06 (7.00). ^{31}P NMR (CD_2Cl_2): 4.1 ppm (J_{PPt} = 2437 Hz). ^{1}H NMR (CD_2Cl_2): 2.69−2.55 (4H, bm), 2.49 (2H, bm), 2.12−1.75 (24H, m), 1.69−1.48 (8H, m), 1.00−0.93 (3H,t). ^{13}C NMR (CD_2Cl_2): 29.5 (s), 26.4 (s), 25.9 (s), 24.4 (t, J_{PC} = 12.3 Hz), 22.4 (t, J_{PC} = 6.1 Hz), 21.4 (t, J_{PC} = 3.8 Hz), 21.4 (s), 20.8 (t, J_{PC} = 30.0 Hz), 13.6 (s). Data for **5a$_7$**: Yield, 0.067 g (0.10 mmol, 85%). Anal. Found (calcd for $C_{24}H_{46}Cl_2P_2Pt$): C 43.44 (43.51), H 7.25 (7.00). ^{31}P NMR (CD_2Cl_2): 0.8 ppm (J_{PPt} = 2311 Hz). ^{1}H NMR (CD_2Cl_2): 3.13 (2H, s), 2.82−1.24 (38H, bm), 0.92 (6H, t). ^{13}C NMR (CD_2Cl_2): 36.5 (s), 31.0 (t, J_{PC} = 29.9 Hz), 29.4 (t, J_{PC} = 7.7 Hz), 28.5 (s), 25.2 (s), 24.0 (t, J_{PC} = 6.9 Hz), 19.7 (t, J_{PC} = 22.3 Hz), 13.7 (s). Data for **5a$_5$**: Yield, 0.073 g (0.11 mmol, 92%). Anal. Found (calcd for $C_{24}H_{46}Cl_2P_2Pt$): C 43.55 (43.51), H 6.84 (7.00). ^{31}P NMR (CD_2Cl_2): 40.7 ppm (J_{PPt} = 2411 Hz). ^{1}H NMR (CD_2Cl_2): 2.66−2.61 (2H, br), 2.33−2.24 (2H, br), 2.20−2.09 (4H, m), 1.81−1.1.54 (6H, m), 1.51−1.34 (6H, m), 0.86 (3H, t). ^{13}C NMR (CD_2Cl_2): 32.3 (t, J_{PC} = 30.4 Hz), 31.3 (s), 30.1 (t, J_{PC} = 7.0 Hz), 26.4 (s), 24.7 (t, J_{PC} = 4.7 Hz), 23.5 (t, J_{PC} = 12.5 Hz), 23.4 (s), 12.8 (s).

Crystal Structure Determinations. Data were collected using Mo Kα X-radiation (λ = 0.71073 Å) on single crystals mounted on a glass fibers with silicone grease or paraffin oil at temperatures listed in Table 3. Data for [*a*-PhobP($CH_2OH)_2$][*s*-PhobP($CH_2OH)_2$]Cl_2 were collected on a Siemens Smart CCD detector diffractometer. Data for [$PtCl_2$(*a*-PhobP$CH_2OH)_2$] were collected on a Siemens four circle point detector diffractometer. Data for *trans*-[$PtCl_2$(*s*-PhobPBu)$_2$] (**5s**) were collected on a Bruker Apex CCD detector diffractometer. Data for *trans*-[$PtCl_2$(a_7-PhobPBu)$_2$] (**5a$_7$**) were collected at the National Crystallography Service (NCS), Southampton, with an Bruker-Nonius APEX II CCD camera on a κ-goniostat diffractometer with a rotating anode source using 10 cm confocal mirrors. Structure solution and refinement was performed using SHELX-TL software.[50] All atoms were refined with anisotropic displacement parameters except the hydrogen atoms which were refined in constrained geometries with fixed isotropic displacement parameters. The structure of **5s** shows a small amount of whole molecule disorder (ca. 3%) modeled as a second low occupancy platinum atom location (see CIF in the Supporting Information). The structure of **5a$_7$** shows nonmerohedral twinning resulting from the pseudosymmetric shape of the unit cell ($a \approx c$) and refinement converged to twin component values (0.558 and 0.442) and for components related by twin law (0 0 −1 0 −1 0 −1 0 0).

Computational Details. All calculations used density functional theory as implemented in Schrödingers Jaguar 6 package[51] and the BP86 functional.[52] A standard 6-31G* basis set was applied on all atoms apart from Pd and Pt, where the LACV3P basis set was used. Test calculations with the B3LYP hybrid functional confirmed the structural and energetic trends, but binding energies were found systematically lower. Likewise, the effects of changing basis set size and including a continuum dielectric solvation model were explored but did not affect the trends discussed in this work and have thus not been reported in detail. Structures were optimized with loose structural convergence criteria (five times larger than default criteria[53]), ultrafine grids and tighter accuracy settings compared to Jaguar default settings; minima and the inversion transition state were confirmed by frequency calculations. Application of zero-point energy (ZPE) corrections was found to lower the energy differences between *sym*- and *asym*-PhobPH by 0.4 kcal mol^{-1} in the free ligand (no significant difference would be expected for the two *asym*-isomers) and to retain consistency with the LKB descriptors, these have not been included here unless stated otherwise. Calculation details for LKB descriptors have been described elsewhere.[43]

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Note Added after ASAP Publication. After ASAP publication on January 30, 2009, changes were made to cite the correct equation in the "Oxidation Studies of PhobPH Isomers" section, and to correct the order of affinity for platinum(II) in the discussion of Scheme 12. The corrected version was published February 4, 2009.

Supporting Information Available: CIF files and/or text files reporting crystal and refinement data) are provided for all crystal structures. Table 3 of crystal data for all the crystal structures. Plots of the kinetic data for the inversion of a_7-PhobPBu to a_5-PhobPBu in Ph_2O are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(53) Test calculations using the more stringent default convergence criteria did not lead to significant changes in energies, bond lengths, or angles but were much more time-consuming.