General Routes to Alkyl Phosphatrioxaadamantane Ligands

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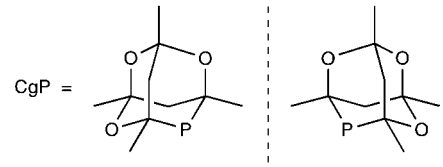
The secondary phosphine CgPH (CgP = 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamantyl group) is made in 50% yield by a modification of the literature method (avoiding high pressures of PH_3) by bubbling PH_3 through an acidified solution of 2,4-pentanedione at 0 °C. Under similar conditions the ethyl analogue ^{Et}CgPH is formed from 3,5-heptanedione in 75% yield. The halophosphines CgPCl and CgPBr are made by treatment of CgPH with *N*-halosuccinimide. CgPBr is also made by treatment of CgPH with Br_2. Three methods are described for the synthesis of CgPR, where R = alkyl: (a) the previously reported acid-catalyzed condensation reaction of RPH_2 with 2,4-pentanedione, which has been extended to R = ^{i}Pr; (b) treatment of CgP(BH_3)Li with RX followed by borane deprotection with Et_2NH, which has been used for R = ^{i}Pr, benzyl, *n*-$C_{20}H_{41}$; (c) treatment of CgPBr with RMgX, which has been used for R = ^{i}Pr, Me. The complexes [$PtCl_2$(CgPH)$_2$] (**1**), [$PdCl_2$(CgPH)$_2$] (**2**), [$PdCl_2$(CgPR)$_2$] (where R = ^{i}Pr (**3a**), Cy (**3b**)), and [$PtCl_2$(CgPR)$_2$] (where R = ^{i}Pr (**4a**), Cy (**4b**), *n*-$C_{20}H_{41}$ (**4c**)) are described. The crystal structures of CgPH, CgPCl, [CgP(CH_2Ph)$_2$]Br, CgP(*n*-$C_{20}H_{41}$), and complexes **1**, **3b**, and **4c** are reported. From the ν(CO) values for *trans*-[RhCl(CO)(CgPX)$_2$], the σ-donor/π-acceptor properties of CgPX are in the order X = ^{i}Pr > Me > Ph > H > Cl.

Introduction

The first metal complexes of ligands containing the 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamantyl group (denoted CgP throughout; see Chart 1) were reported in the late 1990s,[1] and since then, several examples have emerged of the applications of CgP ligands in metal complex catalyzed hydroformylation,[2,3] alkene carbonylation,[4] C−C coupling,[5,6] and hydrogenation.[7] We have shown previously that the rigid CgP substituent is at least as bulky as ^{t}Bu$_2$P and resembles (PhO)$_2$P in terms of σ/π-bonding characteristics.[2] It is this unusual combination of stereoelectronic characteristics which might be at the root of the remarkable catalytic performance of ligands containing CgP. The C_1 symmetry of the CgP group means that enantiomers of its derivatives, labeled α and β in Chart 1, are formed.

Chart 1. Enantiomeric Structures of the CgP Moiety



Previously, CgPR species (R = alkyl, aryl) have been synthesized by the reaction of RPH_2 with acetylacetone,[2,8] by metal-catalyzed RBr substitutions using CgPH,[6] or by radical-initiated P−H addition of CgPH to alkene.[6,9] We report here general methods for the synthesis of monodentate ligands of the type CgPR (R = alkyl) from the secondary phosphine CgPH or bromophosphine CgPBr. The stereoelectronic properties of these ligands are assessed from the structural and spectroscopic properties of some coordination complexes of CgPH and CgPR.

Results and Discussion

Cage Phosphine Synthesis. The parent cage phosphine CgPH was originally made by Epstein and Buckler[8] in 81% yield in

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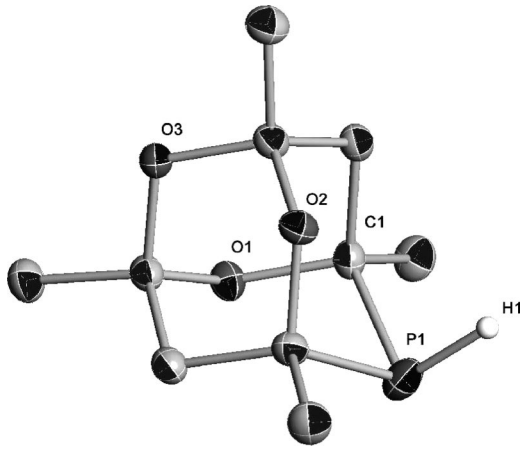
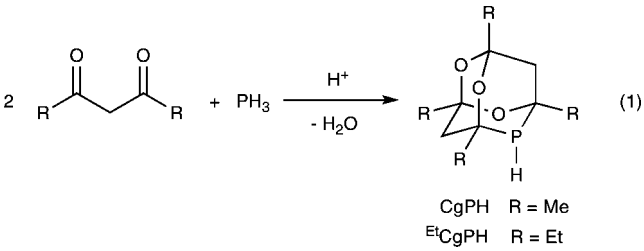


Figure 1. Crystal structure of CgPH showing 50% probability ellipsoids. All hydrogen atoms except H1 are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C4 = 1.865(2), P1−C1 = 1.872(2), P1−H1 = 1.30(4); C4−P1−C1 = 93.54(9), C4−P1−H1 = 95.0(17), C1−P1−H1 = 101.8(17).

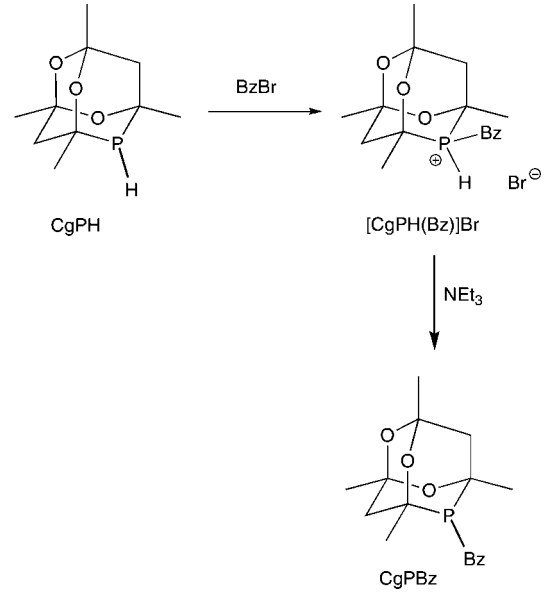
less than 1 h from the acid-catalyzed condensation reaction of acetylacetone with PH_3 under 2−3 atm pressure (eq 1). We found that CgPH was precipitated in 15% yield when PH_3 was bubbled through an acidified aqueous solution of acetylacetone at atmospheric pressure for 7 h at 25 °C. In an attempt to improve this yield, the PH_3 addition was carried out at higher temperatures, but this led to lower yields, and at 80 °C, no CgPH precipitate was observed. Instead, a complicated mixture of products was formed, as evidenced by the 10 significant ^{31}P resonances across the range −40 to +20 ppm, none of which corresponded to CgPH. Under atmospheric pressure, the best yields of CgPH (50%) were obtained when the reaction was conducted at 0 °C (see Experimental). Under similar conditions we have also obtained the previously reported[8] cage phosphine ^{Et}CgPH (eq 1) in 75% yield (see the Experimental Section). The air sensitivity of the ^{Et}CgPH oil contrasts with the air stability of the crystalline CgPH.



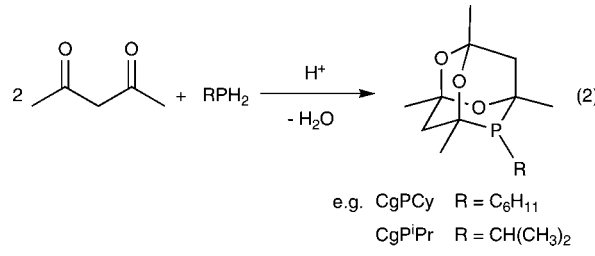
The complicated mechanism of the cage formation reaction has been discussed previously,[1,8,10] with many intermediates purported to be involved in a series of equilibria. The formation of CgPH is probably driven by its precipitation, and the improved yields in ice cold aqueous media are likely a consequence of the higher solubility of the gaseous PH_3 and the lower solubility of CgPH at lower temperatures.

Crystals of CgPH suitable for X-ray crystallography were obtained by slow cooling of its MeOH solution (Figure 1). CgPH crystallizes in the space group $P2_1/c$ with one molecule in the asymmetric unit; this crystal structure has previously been reported at a different temperature.[6]

Scheme 1



The literature route to CgPR (R = CH_2CHMe_2, n-C_8H_{17}, c-C_6H_{11})[8,11] is by the acid-catalyzed condensation reaction of primary phosphines RPH_2 with acetylacetone (eq 2), and this was used to make the new compound CgP^{i}Pr, though the reaction is slow (11 days) and the yield modest (41%). Another disadvantage of the route shown in eq 2 is that for each CgPR, the corresponding noxious primary phosphine RPH_2 has to be used. To avoid this, we have sought to use CgPH (which is now commercially available) as a starting material for general syntheses of CgPR.



Our first strategy was to attempt to make CgPR via quaternisation of CgPH (Scheme 1). Thus, a 1:1 mixture of CgPH and $PhCH_2Br$ (BzBr) was refluxed in MeCN but after 6 days, less than 10% quaternization to [CgPH(Bz)]Br was apparent from the ^{31}P NMR spectrum of the solution. Addition of NEt_3 to the NMR sample did give a ^{31}P NMR signal consistent with the desired product CgPBz (δ_P −24.4). However, since benzyl bromide is a particularly reactive electrophile, its slowness of reaction with CgPH led us to abandon this as a potentially general route.

A small amount (2% yield) of crystalline material separated from the MeCN solution of the quaternisation reaction mixture. The spectroscopic data (see the Experimental Section) and X-ray crystallography revealed that this product was [CgPBz$_2$]Br, presumably formed by quaternization of CgPBz with BzBr. [CgPBz$_2$]Br crystallizes in the space group $P\bar{1}$ with one molecule in the asymmetric unit, indicating that the crystal structure contains a racemic mixture of the α and β enantiomers of the cage phosphine (Figure 2). The phosphonium cage P−C bond lengths of 1.856(2) and 1.851(2) Å are slightly shorter than those (1.865−1.883 Å) found in the crystal structures of the uncom-

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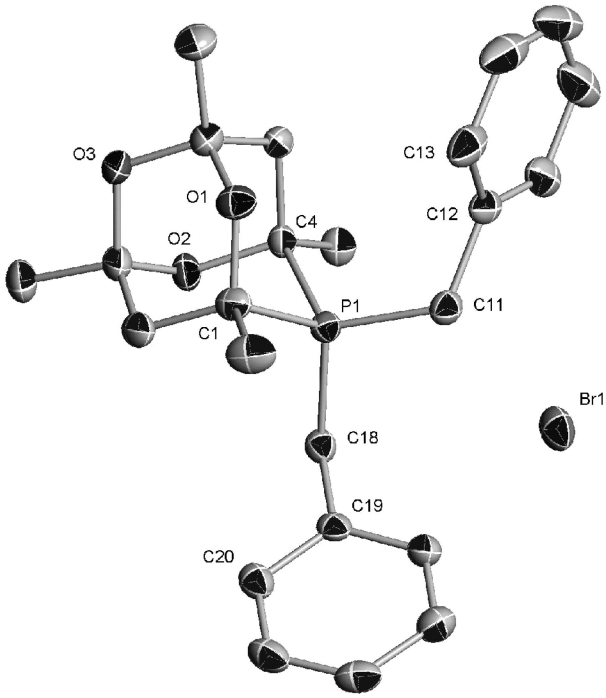
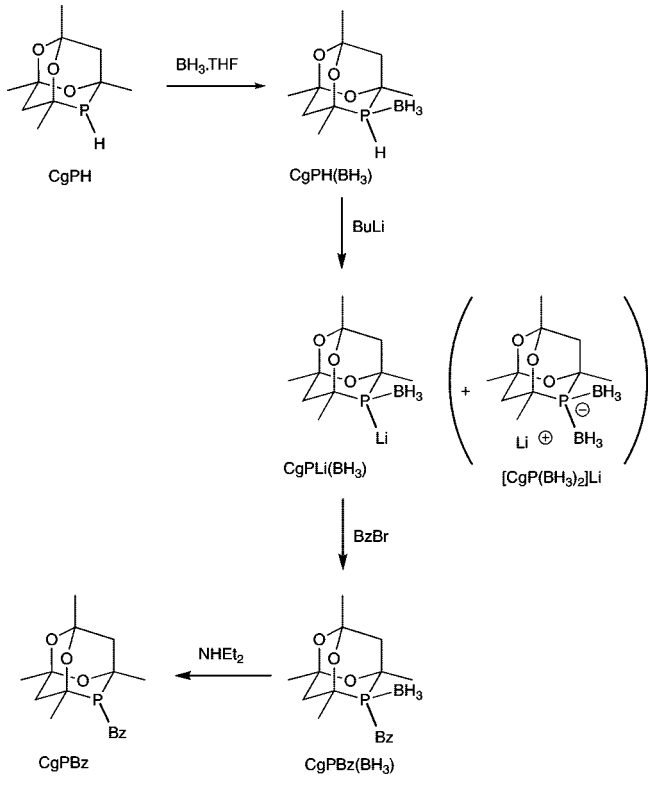


Figure 2. Crystal structure of [CgPBz$_2$]Br showing 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C18 = 1.8131(18), P1−C11 = 1.8169(19), P1−C2 = 1.851(2), P1−C9 = 1.856(2); C18−P1−C11 = 107.52(9), C18−P1−C2 = 113.70(9), C11−P1−C2 = 113.72(9), C18−P1−C9 = 108.49(8), C11−P1−C9 = 116.00(9), C2−P1−C9 = 97.28(9), P1−C11−C12−C13 = 84.1(2), P1−C18−C19−C20 = 104.8(2).

Scheme 2



plexed cage phosphines described here. The benzyl groups are orientated such that the torsion angles C18−P1−C11−C12 and C11−P1−C18−C19 are 151.1 and 66.1°, respectively.

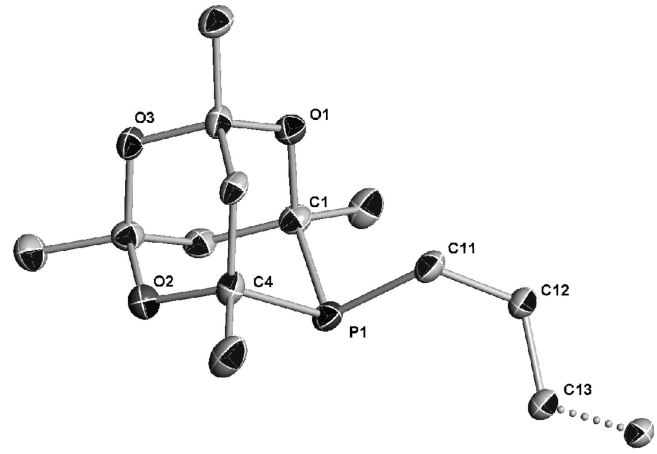
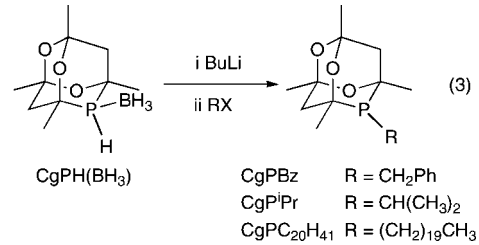


Figure 3. Crystal structure of CgP(n-$C_{20}H_{41}$) showing 50% probability ellipsoids. All hydrogens and all except the first four carbons of the $C_{20}H_{41}$ substituent are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C11 = 1.854(2), P1−C1 = 1.875(2), P1−C4 = 1.883(2); C11−P1−C1 = 101.66(10), C11−P1−C4 = 102.08(9), C1−P1−C4 = 92.59(10), C1−P1−C11−C12 = −101.10(16), C4−P1−C11−C12 = 163.66(15), P1−C11−C12−C13 = −70.1(2).

The low nucleophilicity of CgPH (evident from its slow reaction with BzBr) can be rationalized in terms of its bulk and the electron-withdrawing nature of the cage. Lithiation of its borane adduct CgPH(BH$_3$), prepared by treatment of CgPH with BH$_3$ in THF (Scheme 2), provided a versatile nucleophilic source of the CgP group. Thus, treatment of CgPH(BH$_3$) with n-BuLi gave CgPLi(BH$_3$) (δ_P −32.5, J(PB) = 31 Hz), which reacted smoothly with BzBr to give CgP(Bz)(BH$_3$), and upon borane deprotection with Et$_2$NH, the desired CgPBz was obtained in 62% overall yield. On occasion, after the lithiation step, the unreactive bis(borane) species [CgP(BH$_3$)$_2$]Li (broad signal at δ_P 3.1) was detected. [CgP(BH$_3$)$_2$]Li is formed upon treatment of CgPLi(BH$_3$) with BH$_3$ and therefore may arise from the presence of an excess of BH$_3$, but it was also observed to form slowly in solutions of CgPLi(BH$_3$), presumably by abstraction of BH$_3$ from another CgPLi(BH$_3$). Therefore, to minimize the formation of [CgP(BH$_3$)$_2$]Li, the presence of free BH$_3$ was avoided and CgPLi(BH$_3$) was generated in dilute solution and used immediately (see the Experimental Section).

The nucleophilic route to CgPBz (Scheme 2) has been generalized to make the CgPR compounds featuring the primary and secondary alkyl substituents shown in eq 3. This route (eq 3) avoids the need for RPH$_2$ used in the route shown in eq 2. The 71% yield of CgP^{i}Pr obtained after 24 h via the nucleophilic route (eq 3) is superior to the 41% yield of the same CgP^{i}Pr obtained after 11 days via the hydrophosphination/condensation route (eq 2).



(3)

Crystals of CgPC$_{20}$H$_{41}$ were grown from a saturated CDCl$_3$ solution have space group $P\bar{1}$ and contain a racemic mixture of α and β enantiomers (Figure 3). The first P−C−C−C torsion

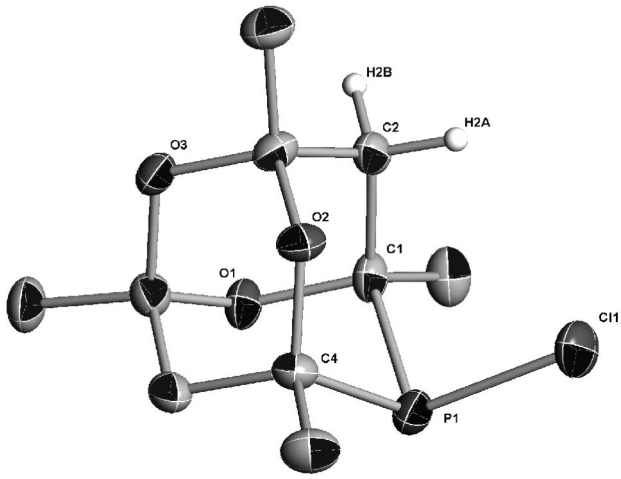
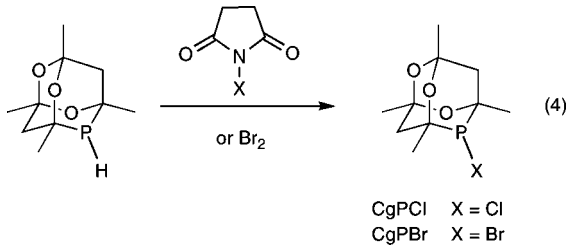


Figure 4. Crystal structure of CgPCl showing 50% probability ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 = 1.871(3), P1−C4 = 1.871(3), P1−Cl1 = 2.0754(11); C1−P1−C4 = 93.70(13), C1−P1−Cl1 = 101.42(10), C4−P1−Cl1 = 101.61(10).

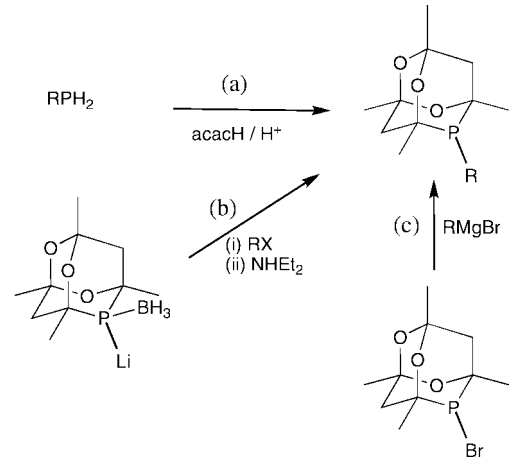
in the long C_{20} chain at C12−C13 is gauche at −70.1°, but all other C−C−C−C torsion angles which follow are anti. The carbon chains are packed such that the planes in which all the carbons in the long chains are packed are parallel.

Halophosphines are widely used precursors to tertiary phosphines. The chlorophosphine CgPCl was made in over 90% yield by treatment of CgPH with *N*-chlorosuccinimide in CCl_4 (eq 4). The conditions for this reaction need to be carefully controlled to avoid incomplete conversion or overoxidation with the formation of P(V) species (see the Experimental Section). The bromophosphine CgPBr can be made similarly, but a more convenient method is by treatment of CgPH with Br_2 (eq 4). The halophosphines CgPX have been fully characterized, including a crystal structure of CgPCl.

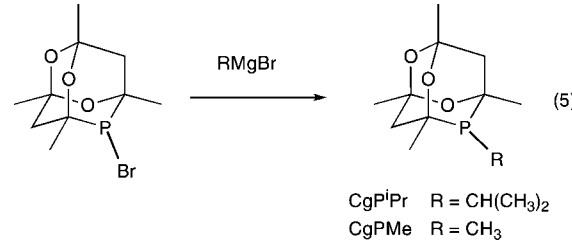


Crystals of CgPCl were grown by slow evaporation of its CCl_4 solution. The P−C bond lengths in CgPCl (see Figure 4) are similar to those in CgPH. The protons in the CH_2 groups in all the CgP ligands are diastereotopic, giving rise to four ^{1}H NMR signals, the multiplicity of which depends on the coupling constants ^2J(HH) and ^3J(PH). Often these signals overlap, but where they are resolved, they can be assigned by COSY NMR spectroscopy (see the Experimental Section). The ^{1}H NMR spectra of CgPX (X = H, Cl, Br) are similar, apart from one of the CH_2 signals which is significantly deshielded in the halophosphines, resonating at δ 2.25 in CgPCl and δ 2.41 in CgPBr compared to δ 1.73 in CgPH. The crystal structure of CgPCl shows that one of the CH_2 protons (H2A in Figure 4) is close to the chlorine (Cl···H = 2.73 Å), and since the rigidity of the cage precludes significant conformational change in solution, it is this proton that is assigned to the deshielded CH_2 resonance in the ^{1}H NMR spectra of CgPCl and CgPBr.

Scheme 3



The potential utility of CgPBr as an electrophilic precursor to CgPR was shown by treatment of CgPBr with RMgBr to give CgPR (R = Me, ^{i}Pr) in good yields (eq 5).



In summary, we have accessed CgP^{i}Pr by the three routes shown in Scheme 3 ((a) hydrophosphination/condensation, (b) nucleophilic, and (c) electrophilic) and established each to be general for CgPR.

Coordination Chemistry of CgPR. Addition of 2 equiv of secondary phosphine CgPH to $[PtCl_2(cod)]$ in CH_2Cl_2 gave the sparingly soluble *cis*-$[PtCl_2(CgPH)_2]$ (**1**). The ^{31}P{^{1}H} NMR spectrum showed 2 singlets (in 1:1 ratio) at 1.2 and 1.6 with ^1J(PtP) of 3292 and 3299 consistent with the *cis* geometry and the presence of *rac* ($\alpha\alpha/\beta\beta$) and *meso* ($\alpha\beta$) diastereoisomers. Similar diastereoisomerism is detected in the high field ^{31}P NMR spectra of many of the complexes reported here (see Experimental) and is associated with the C_1 symmetry of the CgPR ligands (see Chart 1). The proton-coupled ^{31}P NMR spectrum of **1** showed two *N* doublets for the AA'XX' spin system with $|^1J(PH) + {}^3J(PH)|$ of 405 Hz, significantly larger than the J(PH) of 190 Hz for free CgPH; similar increases in J(PH) have been reported in other secondary phosphine complexes.[12]

Crystals of **1** were grown by slow diffusion of a CH_2Cl_2 solution of $[PtCl_2(cod)]$ into a solution of CgPH in CH_2Cl_2 (Figure 5). Complex **1** crystallizes in space group *Cc* as the cis and meso isomer and has approximate mirror symmetry with the hydrogen substituents on the phosphorus atoms almost perfectly eclipsed and pointing toward each other. This is likely a consequence of the minimization of steric interactions between the CgP moieties.

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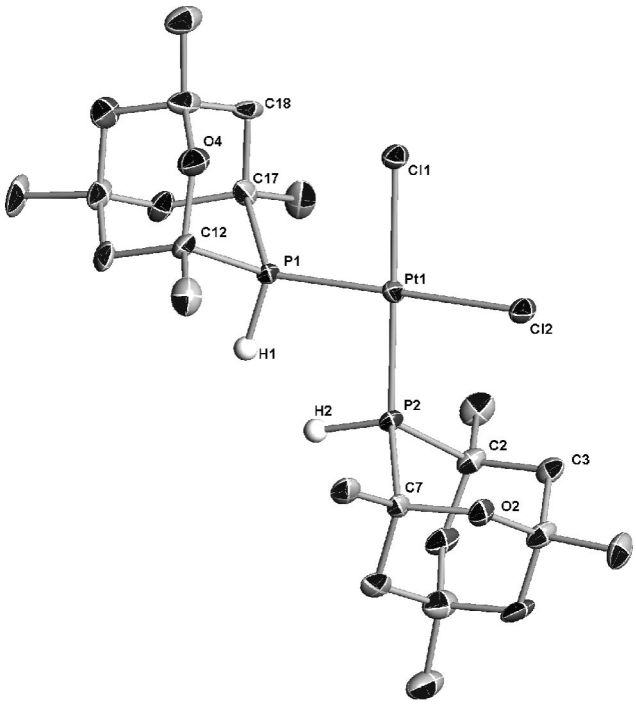
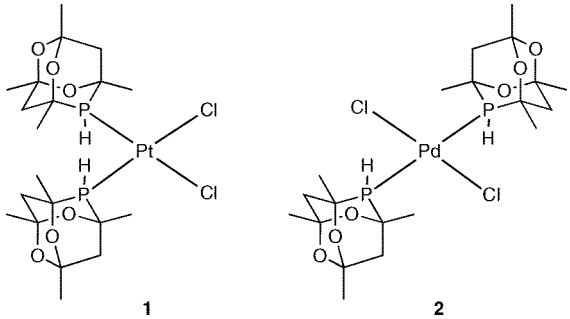


Figure 5. Crystal structure of **1** showing 50% probability ellipsoids. All hydrogen atoms are omitted for clarity, apart from the P−H hydrogens. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.2282(11), Pt1−P2 = 2.2439(12), Pt1−Cl1 = 2.3430(11), Pt1−Cl2 = 2.3605(11), P1−C17 = 1.856(4), P1−C12 = 1.869(4), P2−C2 = 1.866(4), P2−C7 = 1.864(4); P1−Pt1−P2 = 88.65(4), P1−Pt1−Cl1 = 91.07(4), P2−Pt1−Cl2 = 92.42(4), Cl1−Pt1−Cl2 = 87.85(4).

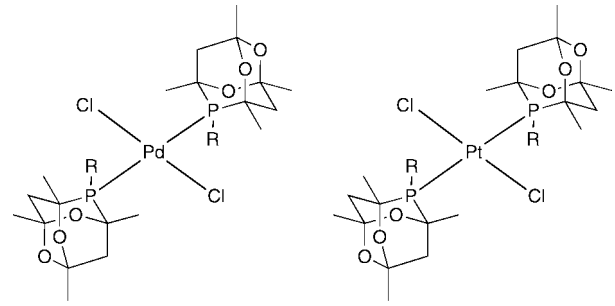
Addition of 2 equiv of CgPH to $[PdCl_2(cod)]$ in CH_2Cl_2 gave *trans*-$[PdCl_2(CgPH)_2]$ (**2**), as shown by the virtual triplets[13] observed for several of the resonances in its ^{13}C NMR spectrum (see the Experimental Section for the characterization data).



1 **2**

The palladium(II) complexes **3a**,**b** and platinum(II) complexes **4a**−**c** were made by addition of the tertiary phosphines CgPR to the appropriate dichlorometal precursor (see the Experimental Section for the characterization data).

Crystals of **3b** suitable for X-ray crystallography were grown from CH_2Cl_2/hexane. Complex **3b** crystallizes in space group $P\bar{1}$ with half a molecule in the asymmetric unit; the other half of the molecule is related by inversion symmetry and thus the complex is the trans and meso (α/β) isomer (see Figure 6). The cyclohexyl groups are anti to each other; thus, the improper torsion C11−P1···P1A−C11A is 180°.



3a R = ^{i}Pr
3b R = Cy

4a R = ^{i}Pr
4b R = Cy
4c R = $C_{20}H_{41}$

Crystals of **4c** suitable for X-ray crystallography were grown from CH_2Cl_2 (Figure 7). Complex **4c** crystallizes as the trans and meso ($\alpha\beta$) isomer in the space group $P\bar{1}$ with two independent molecules in the asymmetric unit and, hence, four independent C_{20} chains. The P−C−C−C and first C−C−C−C conformations vary among the four chains, but all adopt extended conformations so that the second and subsequent C−C−C−C torsion angles are close to 180°. The C_{20} chains pack so the planes formed by the carbons in three of the chains lie roughly parallel to each other, whereas the fourth chain is rotated at 90° to this. The alkyl groups are syn to each other: i.e., the improper torsion C−P1···P2−C is close to 0° in both of the independent molecules.

In order to assess the bonding characteristics of CgPX, the ν(CO) values (in CH_2Cl_2) for the carbonylrhodium complexes **5a**−**e** were measured (see Chart 2). The order of increasing ν(CO) is X = ^{i}Pr > Me > Ph > H > Cl, which is as expected in terms of an increase in the electronegativity of the substituent, leading to a decrease in the σ-donor and an increase in the π-acceptor capacity of the ligand. The values also confirm the relatively electron withdrawing nature of the CgP group compared with other R_2P groups;[2] under the same conditions,

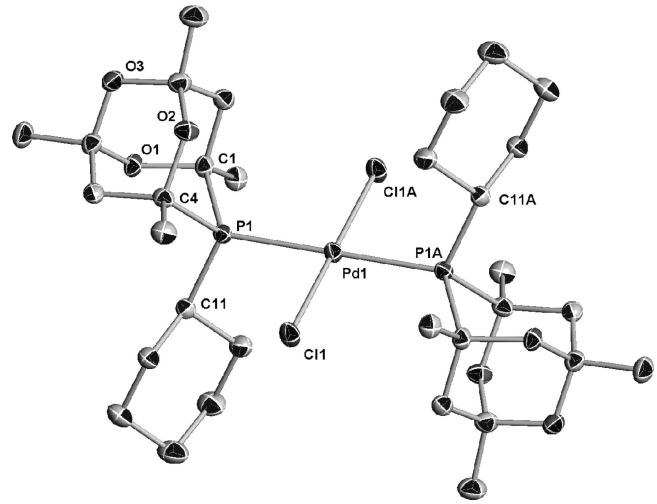


Figure 6. Crystal structure of *trans*-$[PdCl_2(CgPCy)_2]$ (**3b**) showing 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−Cl1 = 2.2934(7), Pd1−P1 = 2.3641(6), P1−C11 = 1.858(2), P1−C4 = 1.890(2), P1−C1 = 1.895(2); C11−P1−C4 = 110.66(8), C11−P1−C1 = 102.30(8), C4−P1−C1 = 93.38(8).

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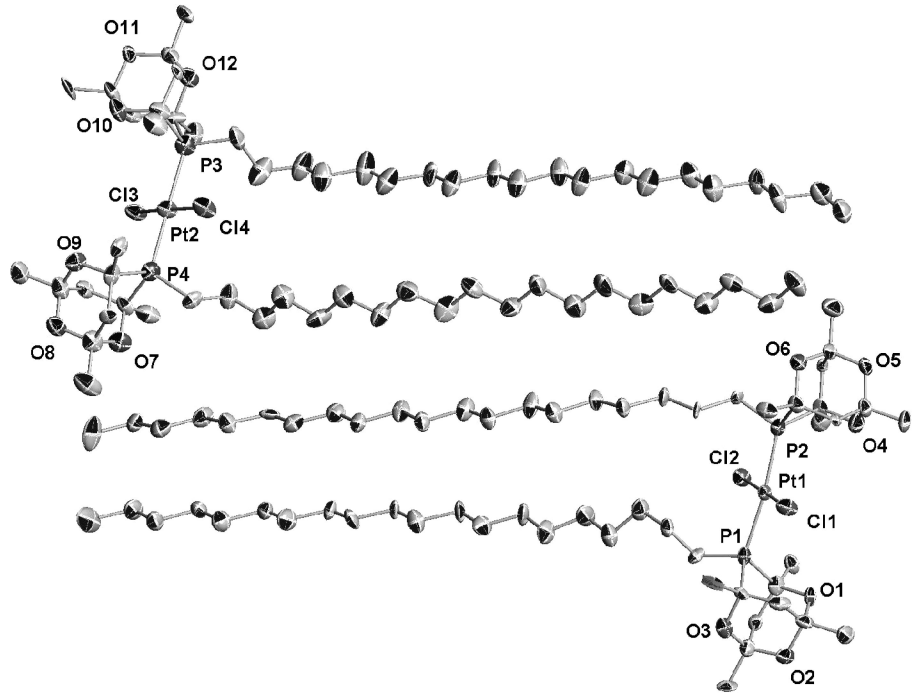
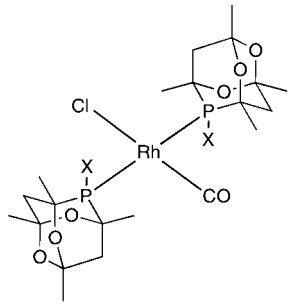


Figure 7. Crystal structure of *trans*-[$PtCl_2(CgPC_{20}H_{41})_2$] (**4c**) showing 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt1−Cl1 = 2.298(3), Pt1−P2 = 2.300(3), Pt1−Cl2 = 2.317(3), Pt1−P1 = 2.328(3), Pt2−P4 = 2.291(4), Pt2−P3 = 2.300(4), Pt2−Cl3 = 2.302(3), Pt2−Cl4 = 2.332(3).

for *trans*-[$RhCl(CO)\{PPh_n(C_6F_5)_{3-n}\}_2$], ν(CO)/cm^{-1} is 1965 (n = 3), 1983 (n = 2), 1996 (n = 1), and 2005 (n = 0).[14]

Chart 2



	X	ν(CO)/cm^{-1}
5a	^{i}Pr	1984
5b	Me	1987
5c	Ph	1988
5d	H	1989
5e	Cl	2006

Conclusion

The large bulk, robustness, and unusual electronic properties of CgPR have already been exploited in several applications in homogeneous catalysis. The three general routes to the monodentate cage tertiary phosphines CgPR described here should make accessible a great variety of CgPR ligands and stimulate further investigations of their chemistry. The routes described have been applied to the synthesis of chelating diphosphines containing CgP substituents, and this will be the subject of a future publication.

Experimental Section

Unless otherwise stated, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk line techniques. Dry N_2-saturated solvents were collected from a Grubbs solvent system[15] in flame- and vacuum-dried glassware. MeOH was dried over 3 Å molecular sieves and deoxygenated by N_2 saturation. Commercial reagents were used as supplied unless otherwise stated. All phosphines were stored under nitrogen at room temperature. The secondary phosphine CgPH can be obtained from Cytec but, in this work, was made by the route described below. Most complexes were stable to air in the solid state and were stored in air at room temperature. The starting materials [$PtCl_2$(cod)],[16] [$PdCl_2$(cod)],[17] [$PdCl_2(NCPh)_2$],[18] and [$RhCl(CO)_2]_2$[19] were prepared by literature methods. Elemental analyses were carried out by The Microanalytical Laboratory of the School of Chemistry, University of Bristol. Electron impact and fast atom bombardment mass spectra were recorded by The Mass Spectrometry Service, University of Bristol, on MD800 and Autospec instruments. Infrared spectroscopy was carried out on a Perkin-Elmer 1600 Series FTIR spectrometer. NMR spectra were measured on a JEOL GX 300, JEOL Eclipse 400, or JEOL GX 400 spectrometer. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded at the ambient temperature of the probe at 300, 100, and 121 MHz, respectively, using deuterated solvent to provide the field/frequency lock.

1,3,5,7-Tetramethyl-4,6,8-trioxa-2-phosphaadamantane (CgPH). A three-necked 1 L flask was equipped with a large magnetic stirrer bar, a thermometer, a gas inlet fitted to a mineral oil bubbler and then a gas manifold to allow for N_2/PH_3 admission (fine gas bubbles were obtained using a sintered-glass bulb attached to the bottom of a standard glass inlet), a gas outlet fitted to a mineral oil bubbler followed by a bleach trap,[20] and then another mineral oil bubbler. The flask was charged with acetylacetone (150 cm^3, 1.46 mol) and aqueous HCl (300 cm^3, 5 M), and then N_2 was passed through the

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solution for 18 h to ensure the elimination of oxygen. The reaction vessel was cooled in an ice/water bath to 0 °C, and then gaseous PH_3 was passed through the solution for 7 h at such a rate that it was absorbed by the reaction mixture (monitored by observation of the oil bubblers). *Caution! PH_3 gas is highly toxic and an explosion hazard. It should be handled with extreme care*. Nitrogen was again bubbled through the mixture for 16 h to ensure the elimination of any PH_3 before workup. A very sensitive test for the presence of PH_3 is to use filter paper which has been dipped in a solution of $AgNO_3$—it turns black in the presence of minute quantities of PH_3 gas. The white crystalline solid was then filtered off in air, washed with water (3 × 200 cm^3), and dried under reduced pressure to give CgPH (78.5 g, 50% yield). Anal. Found (calcd for $C_{10}H_{17}O_3P$): C, 55.5 (55.6); H, 8.3 (7.9). ^{31}P NMR ($CDCl_3$): δ_P −49.5 (d × mult J(PH) = 190 Hz). ^{13}C NMR ($CDCl_3$): δ_C 96.6 (s), 96.3 (s), 71.9 (d, J(PC) = 18 Hz), 70.3 (s), 45.1 (s), 45.6 (d, J(PC) = 14 Hz), 29.7 (d, J(PC) = 23 Hz), 29.0 (d, J(PC) = 12 Hz), 27.9 (s), 27.7 (s). ^1H NMR ($CDCl_3$, assignment by COSY and spectral simulation): δ_H 3.08 (dm, 1H, J(PH) = 190 Hz, J(HH) = 1.6, 3.2, 0.6 Hz), 1.91 (ddd, 1H, CH_2, J(PH) = 2.6 Hz, J(HH) = 12.8, 0.6 Hz), 1.81 (ddd, 1H, CH_2, J(PH) = 6.6 Hz, J(HH) = 1.6, 13.1 Hz) 1.79 (ddd, 1H, CH_2, J(PH) = 21.4 Hz, J(HH) = 3.2, 13.1 Hz), 1.73 (d, 1H, CH_2, J(HH) = 12.8 Hz), 1.48 (d, 3H, CH_3, J(PH) = 14 Hz), 1.46 (d, 3H, CH_3, J(PH) = 14 Hz), 1.39 (s, 3H, CH_3), 1.38 (s, 3H, CH_3).

1,3,5,7-Tetraethyl-4,6,8-trioxa-2-phosphaadamantane (^{Et}CgPH). A three-necked 250 cm^3 flask was equipped as in the preparation of CgPH above. The flask was charged with 3,5-heptanedione (10 cm^3, 0.073 mol) and aqueous HCl (100 cm^3, 8 M), and then N_2 was passed through the solution for 18 h to ensure the elimination of oxygen. The reaction vessel was cooled in a dry ice/ethylene glycol bath to −12 °C, and then gaseous PH_3 was then passed through the solution for 7 h at such a rate that it was absorbed by the reaction mixture (monitored by observation of the oil bubblers). *Caution! PH_3 gas is highly toxic and an explosion hazard. It should be handled with extreme care*. Nitrogen was again bubbled through the mixture for 16 h to ensure the elimination of any PH_3 before workup. A very sensitive test for the presence of PH_3 is to use filter paper which has been dipped in a solution of $AgNO_3$—it turns black in the presence of minute quantities of PH_3 gas. The solution was then cooled in a salt/ice bath and neutralized by the slow addition of N_2-saturated NaOH solution (160 cm^3, 5 M) until pH 7. N_2-saturated diethyl ether (200 cm^3) was then added and stirred. The ethereal layer was separated and the aqueous layer washed with diethyl ether (3 × 20 cm^3). The organic extracts were combined and dried over $MgSO_4$, and then the solvent was removed under reduced pressure to give ^{Et}CgPH as a viscous air-sensitive oil (7.42 g, 75% yield). Anal. Found (calcd for $C_{14}H_{25}O_3P$): C, 61.31 (61.73); H, 8.90 (9.26). FAB mass spectrum: m/z 272 (M^+). ^{31}P NMR ($CDCl_3$): δ_P −57.9 (d × mult J(PH) = 190 Hz). ^{13}C NMR ($CDCl_3$): δ_C 97.4 (s), 97.1 (s), 74.8 (d, J(PC) = 22 Hz), 73.5 (d, J(PC) = 8 Hz), 41.6 (d, J(PC) = 13 Hz), 39.0 (d, J(PC) = 14 Hz), 35.7 (s), 35.5 (s), 35.2 (s), 35.0 (s), 33.7 (s), 33.3(s). ^1H NMR ($CDCl_3$): δ_H 1.40−2.20 (m, 18H), 0.80−1.34 (m, 12H).

CgPH(BH_3). A solution of BH_3·THF (37.3 cm^3, 1 M in THF, 37.3 mmol) was added slowly over 30 min to a stirred, ice-cold solution of CgPH (8.00 g, 37.3 mmol) in THF (20 cm^3). The reaction mixture was then warmed to room temperature and the solvent removed under reduced pressure to give a white powder. The solid was dissolved in hot THF (6 cm^3) and the resulting solution cooled slowly to room temperature and then put in the freezer (−10 °C) to give the crystalline white solid CgPH(BH_3) (8.223 g, 96%). Anal. Found (calcd for for $C_{10}H_{20}BO_3P$): C, 52.2 (52.2); H, 8.8 (8.8). EI mass spectrum: m/z 230 (M^+). ^{31}P NMR ($CDCl_3$): δ_P 1.5 (br q, ^1J(PB) = 39 Hz). ^{13}C NMR ($CDCl_3$): δ_C 96.8 (s), 96.6 (s), 70.9 (d, J(PC) = 30 Hz), 68.7 (d, J(PC) = 37.5 Hz), 44.2 (s), 38.3 (d, J(PC) = 15.0 Hz), 27.7 (d, J(PC) = 22.5 Hz), 25.7 (d, J(PC) = 2.0 Hz), 25.5 (d, J(PC) = 7.5 Hz). ^1H NMR ($CDCl_3$): δ_H 4.40 (d, 1H, PH, ^1J(PH) = 180 Hz), 2.13 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.47 (m, 12H, CH_3), 1.08−0.18 (br, 3H, BH_3). ^{11}B NMR ($CDCl_3$): δ_B 45.6 (br).

CgPCl. To a solution of CgPH (4.32 g, 20.0 mmol) in CCl_4 (50 cm^3) cooled to between −5 and −10 °C was added *N*-chlorosuccinimide (4.42 g, 33.0 mmol) in ca. 0.5 g portions over 15 min. The reaction mixture was then cooled to −10 °C and the resulting white precipitate was filtered off and washed with CCl_4 (2 × 20 cm^3). The solvent was then reduced to dryness to give CgPCl as a yellow solid (4.96 g, 93%). Accurate mass spectrum: M_r = 250.0516 (calcd for $C_{10}H_{16}O_3PCl$ 250.0526). ^{31}P NMR ($CDCl_3$): δ_P 53.6.^{13}C NMR ($CDCl_3$): δ_C 96.6 (d, J(PC) = 1.5 Hz), 95.8 (s), 74.8 (d, J(PC) = 23.83 Hz), 74.2 (d, J(PC) = 39.21 Hz), 43.9 (d, J(PC) = 20.0 Hz, CH_2), 34.1 (s, CH_2), 27.7 (s, CH_3), 27.3 (d, J(PC) = 1.5 Hz, CH_3), 26.9 (d, J(PC) = 23.8 Hz, CH_3), 26.0 (d, J(PC) = 12.3 Hz, CH_3). ^1H NMR ($CDCl_3$): δ_H 2.25 (d, 1H, CH_2, J(HH) = 13.5 Hz), 1.99 (d, 1H, CH_2, J(PH) = 5.3 Hz), 1.93 (s, 1H, CH_2), 1.55 (dd, 1H, CH_2, J(HH) = 13.5 Hz, J(PH) = 5.0 Hz), 1.41 (d, 3H, CH_3, J(PH) = 1.3 Hz), 1.39 (s, 3H, CH_3), 1.36 (s, 6H, CH_3).

CgPBr. This could be made by a procedure similar to that for CgPCl, using *N*-bromosuccinimide. However, a more convenient procedure is as follows. A solution of Br_2 (1.83 mmol, 8.4 cm^{-3}, 0.218 M in CH_2Cl_2) was added dropwise over 10 min to a cooled (0 °C) solution of CgPH (0.368 g, 1.7 mmol) in CH_2Cl_2 (10 cm^{-3}). After 1 h the solvent was removed to give a yellow-orange solid. Toluene (10 cm^{-3}) was added to the solid and the suspension filtered. Removal of the toluene then yielded a white powder of CgPBr (0.393 g, 78%). Anal. Found (calcd for $C_{10}H_{16}BrO_3P$): C, 40.7 (40.7); H, 5.7 (5.5). EI mass spectrum: m/z 294, 296 (M^+). ^{31}P NMR ($CDCl_3$): δ_P 54.9. ^{13}C NMR ($CDCl_3$): δ_C 96.8 (d, J(PC) = 1.5 Hz), 95.9 (s), 74.0 (d, J(PC) = 26.9 Hz), 73.0 (d, J(PC) = 41.5 Hz), 43.8 (d, J(PC) = 19.2 Hz, CH_2), 34.8 (s, CH_2), 27.8 (s, CH_3), 27.3 (d, J(PC) = 2.4 Hz, CH_3), 27.06 (d, J(PC) = 23.1 Hz, CH_3), 27.03 (d, J(PC) = 12.5 Hz, CH_3). ^1H NMR ($CDCl_3$): δ_H 2.41 (d, 1H, CH_2, J(HH) = 13.5 Hz), 2.07 (s, 1H, CH_2), 2.00 (d, 1H, CH_2, J(PH) = 7.3 Hz), 1.62 (dd, 1H, CH_2, J(HH) = 13.5 Hz, J(PH) = 4.6 Hz), 1.43 (d, 3H, CH_3, J(PH) = 2.7 Hz), 1.40 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.36 (s, 3H, CH_3).

CgP^{i}Pr. Method a via P$H_2{}^i$Pr. Acetylacetone (7.1 cm^3, 69.1 mmol) was added to a mixture of P$H_2{}^i$Pr (1.0 cm^3, 11.5 mmol) and 10 M aqueous HCl (10 cm^3) and the resulting solution stirred at room temperature. After 6 days, a white precipitate had formed, and after a further 5 days, the precipitate was filtered off washed with water (3 × 20 cm^3). The filtrate then contained more precipitated product, and this too was filtered off and washed with water (2 × 20 cm^3). The combined yield of CgP^{i}Pr was 1.19 g (41%). Anal. Found (calcd for $C_{13}H_{23}O_3P$ + 0.25H_2O): C, 59.4 (59.5); H, 9.2 (9.0). EI mass spectrum: m/z 258 (M^+). ^{31}P NMR ($CDCl_3$): δ_P −7.4. ^{13}C NMR ($CDCl_3$): δ_C 96.3 (s), 95.8 (s), 73.4 (d, J(PC) = 25 Hz), 72.8 (d, J(PC) = 13 Hz), 45.7 (d, J(PC) = 15 Hz), 38.2 (s), 29.9 (d, J(PC) = 21 Hz), 28.6 (d, J(PC) = 12 Hz), 28.3 (s), 28.0 (s), 23.8 (d, J(PC) = 24 Hz), 21.3 (d, J(PC) = 21 Hz), 21.1 (d, J(PC) = 9 Hz). ^1H NMR ($CDCl_3$): δ_H 1.90−2.08 (m, 2H), 1.64−1.86 (m, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.24 (dd, 3H, ^2J(PH) = 17.1 Hz, ^3J(HH) = 7.6 Hz), 1.09 (dd, 3H, ^2J(PH) = 11.3 Hz, ^3J(HH) = 7.6 Hz).

Method b via CgPH(BH_3). A solution of BuLi (0.5 cm^3, 1.6 M in hexane, 0.80 mmol) was added dropwise over 5 min to a solution of CgPH(BH_3) (185 mg, 0.80 mmol) in THF (10 cm^2) at −78 °C. The resulting bright yellow solution was then warmed to room temperature and stirred for a further 15 min. The solution was then recooled to −78 °C, and a solution of 2-bromopropane (0.076 cm^3, 0.81 mmol) in THF (10 cm^3) was added dropwise over 15 min. The mixture was then warmed to room temperature and stirred for a further 24 h. The ^{31}P NMR spectrum of the solution showed a broad signal at δ_P 23.5 consistent with the formation of

$CgP^iPr(BH_3)$. An excess of distilled Et_2NH (2.0 cm^3, 19 mmol) was added, and the solution was stirred for a further 24 h. The ^{31}P NMR spectrum of this solution showed the borane adduct had been completely converted to CgP^iPr. The volatiles were removed under reduced pressure to leave a white solid. Pentane (40 cm^3) was added, and the colorless solution was filtered free of LiBr and Et_2NHBH_3 by cannula. The solvent was then removed under reduced pressure to give a white solid, which was recrystallized from hot methanol (10 cm^3) to give white solid CgP^iPr (147 mg, 71% yield).

Method c via CgPBr. ^{i}PrMgCl (7.52 mmol, 3.76 cm^3, 2 M in THF) was added dropwise over 15 min to a solution of CgPBr (0.40 g, 1.36 mmol) in toluene (10 cm^3) at room temperature. The solution was then stirred for 1 h, quenched with water (5 cm^3), and extracted using hexane (3 × 10 cm^3). Removal of the solvent under reduced pressure gave white solid CgP^iPr (0.23 g, 66% yield).

CgPBz was made in 62% yield by method b. Anal Found (calcd for for $C_{17}H_{23}O_3P$): C, 66.7 (66.5); H, 7.5 (7.1). EI mass spectrum: *m*/*z* 306 (M^+). ^{31}P NMR ($CDCl_3$): δ_P −24.4. ^{13}C NMR ($CDCl_3$): δ_C 143.5 (d, 1*J*(PC) = 10.5 Hz), 140.3 (s), 130.2 (d, *J*(PC) = 7.0 Hz), 127.8 (s), 127.2 (d, *J*(PC) = 2.0 Hz), 96.6 (s), 95.4 (s), 76.1 (d, *J*(PC) = 26 Hz), 72.7 (d, *J*(PC) = 5 Hz), 44.7 (d, *J*(PC) = 14 Hz), 37.4 (s), 27.8 (d, *J*(PC) = 11 Hz), 27.3 (s), 26.9 (s), 26.7 (s), 25.6 (s). ^1H NMR ($CDCl_3$): δ_H 7.75−6.95 (m, 5H, Ph), 3.11 (dd, 2H, C*H*$_2$Ph, ^2J(PH) = 16 Hz, ^2J(HH) = 4 Hz), 2.59 (2H, C*H*$_2$, ^2J(PH) = 16 Hz, ^2J(HH) = 4 Hz), 1.98−1.05 (m, 16H, 2C*H*$_2$ and 4C*H*$_3$).

$CgPC_{20}H_{41}$ is a white solid which was made in 82% yield by method b. Anal. Found (calcd for $C_{30}H_{57}O_3P$), C, 72.7 (72.5); H, 11.6 (11.5). EI mass spectrum: *m*/*z* 497 ($M^+ + 1$). ^{31}P NMR ($CDCl_3$): δ_P −28.1. ^{13}C NMR ($CDCl_3$): δ_C 96.7 (s), 95.8 (s), 76.7 (d, *J*(PC) = 1.5 Hz), 72.3 (d, *J*(PC) = 19 Hz), 44.8 (d, *J*(PC) = 22 Hz), 37.3 (d, *J*(PC) = 4 Hz), 30−23 (alkyl C). ^1H NMR ($CDCl_3$): δ_H 2.81−0.78 (m).

CgPMe is an off-white solid which was made in 75% yield by method c. Accurate mass spectrum: M_r = 230.1070 (calcd for $C_{11}H_{19}O_3P$, 230.1072). ^{31}P NMR ($CDCl_3$): δ_P −41.5. ^{13}C NMR ($CDCl_3$): δ_C 96.8 (s), 95.8 (s), 72.2 (d, *J*(PC) = 6 Hz), 71.5 (d, *J*(PC) = 21 Hz), 44.4 (d, *J*(PC) = 16 Hz, CH_2), 36.2 (d, *J*(PC) = 1.5 Hz, CH_2), 28.0 (d, *J*(PC) = 13 Hz, CH_3), 27.5 (d, *J*(PC) = 23.0 Hz, C*H*$_3$), 26.2 (d, *J*(PC) = 13.0 Hz, C*H*$_3$) 4.0 (d, *J*(PC) = 25 Hz, C*H*$_3$), ^1H NMR ($CDCl_3$): δ_H 1.96−1.81 (m, 2H), 1.75 (d, 1H, *J*(HH) = 13.2 Hz), 1.53 (dd, 1H, *J*(HH) = 13.2, 4.0 Hz), 1.35 (s, 6H), 1.28 (d, 3H, *J*(PH) = 12.9 Hz), 1.25 (d, 3H, *J*(PH) = 12.5 Hz), 0.92 (d, 3H, *J*(PH) = 3.3 Hz).

***cis*-[$PtCl_2$(CgPH)$_2$] (1).** A solution of CgPH (0.800 g, 3.70 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of [$PtCl_2$(cod)] (0.690 g, 1.90 mmol) in CH_2Cl_2 (10 cm^3) and the mixture stirred for 4 h. The white solid product (0.820 g, 64% yield) that had precipitated was filtered off and washed with pentane. Anal. Found (calcd for $C_{20}H_{34}Cl_2O_6P_2Pt$): C, 34.4 (34.4); H, 5.2 (4.9). ^{31}P NMR ($CDCl_3$): δ_P 1.2 (^1J(PtP) = 3292 Hz) and 1.6 (^1J(PtP) = 3299 Hz), $|^1J(PH) + {}^3J(PH)|$ = 405 Hz. Complex **1** was very sparingly soluble, and no ^{13}C NMR spectrum was obtained. Crystals of **1** grew when a CH_2Cl_2 solution of CgPH was allowed to diffuse into a CH_2Cl_2 solution of [$PtCl_2$(cod)].

***cis*-[$PdCl_2$(CgPH)$_2$] (2).** A solution of CgPH (1.00 g, 4.60 mmol) in CH_2Cl_2 (15 cm^3) was added to a solution of [$PdCl_2$(cod)] (0.660 g, 2.30 mmol) in CH_2Cl_2 (15 cm^3) and the mixture stirred for 10 min. The cloudy solution was concentrated to 5 cm^3, and then pentane (15 cm^3) was added to precipitate the yellow solid product (1.07 g, 75% yield), which was filtered off and washed with pentane. Anal. Found (calcd for $C_{20}H_{34}Cl_2O_6P_2Pd$): C, 39.4 (39.4); H, 6.0 (5.6). ^{31}P NMR ($CDCl_3$): δ_P 3.0, 2.7 (d, $|^1J(PH) + {}^3J(PH)|$ = 368 Hz). ^{13}C NMR ($CDCl_3$): δ_C 96.8 (s), 96.7 (s), 73.6 (t, $|^1J(PC) + {}^3J(PC)|$ = 19.8 Hz), 73.4 (t, $|^1J(PC) + {}^3J(PC)|$ = 13.8 Hz), 72.2 (t, $|^1J(PC) + {}^3J(PC)|$ = 26.0 Hz), 46.65 (s), 46.60 (s), 39.9 (s), 39.7

Table 1. X-ray Crystallographic Data

	CgPH	CgPCl	CgP($C_{20}H_{41}$)	[$CgPBz_2$]Br	**1**	**3b**	**4c**
color, habit	colorless block	colorless block	colorless block	colorless block	colorless prism	yellow block	colorless stalk
size (mm)	0.28 × 0.24 × 0.20	0.30 × 0.24 × 0.20	0.25 × 0.10 × 0.05	0.2 × 0.2 × 0.1	0.30 × 0.21 × 0.18	0.28 × 0.24 × 0.20	0.38 × 0.10 × 0.06
empirical formula	$C_{10}H_{17}O_3P$	$C_{10}H_{16}ClO_3P$	$C_{30}H_{57}O_3P$	$C_{24}H_{30}BrO_3P$	$C_{21}H_{36}Cl_4O_6P_2Pt$	$C_{32}H_{54}Cl_2O_6P_2Pd$	$C_{60}H_{114}Cl_2O_6P_2Pt$
M_r	216.21	250.65	496.73	477.36	783.33	773.99	1259.44
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Cc	$P\bar{1}$	$P\bar{1}$
a (Å)	8.176(2)	9.656(3)	8.6589(13)	10.108(5)	12.0568(4)	8.3750(19)	14.959(3)
b (Å)	8.0969(13)	8.3144(18)	10.335(9)	10.339(4)	21.1776(6)	9.9901(14)	16.978(3)
c (Å)	16.669(3)	15.116(2)	17.863(2)	11.856(2)	12.7975(4)	11.0436(19)	26.764(5)
α (deg)	90	90	89.713(14)	71.83(2)	90.00	87.130(14)	85.08(3)
β (deg)	94.144(13)	100.463(12)	77.730(14)	88.97(3)	114.415(4)	85.581(16)	84.42(3)
γ (deg)	90	90	73.231(17)	73.25(3)	90.00	84.121(17)	76.65(3)
V (Å^3)	1100.7(4)	1193.4(5)	1493.0(13)	1123.7(8)	2975.43(16)	915.6(3)	6568(2)
Z	4	4	2	2	4	1	4
μ (mm^{-1})	0.23	0.439	1.008	1.923	5.215	0.779	2.31
T (K)	173	173	100	173	100	100	100
no. of rflns: total/indep (R_{int})	5082/1723 (0.0255)	6005/2090 (0.0510)	11 870/5119 (0.0369)	11 702/5059 (0.0257)	65 740/8380 (0.0494)	7939/3201 (0.0205)	75 284/30 029 (0.1530)
final R1 and wR2	0.0331, 0.0903	0.0418, 0.0980	0.0476, 0.1232	0.0284, 0.0643	0.0274, 0.0578	0.0195, 0.0508	0.1024, 0.2447
largest peak, hole (eA^{-3})	0.366, −0.240	0.323, −0.279	0.450, −0.220	0.355, −0.263	2.46, −1.57	0.275, −0.330	1.870, −2.977

(s), 29.0 (s), 28.8 (s), 27.7 (s), 27.6 (s), 27.4 (s), 27.3 (s). ^{1}H NMR ($CDCl_3$): δ_H 4.28 (m, 2H, P*H*, $|^1J(PH) + {}^3J(PH)| = 363$ Hz), 2.80 (m, 4H, CH_2), 1.97 (m, 4H, CH_2), 1.68 (m, 12H, CH_3), 1.43 (m, 6H, CH_3), 1.39 (m, 6H, CH_3).

***trans*-[PdCl$_2$(CgP^{i}Pr)$_2$] (3a).** A solution of CgP^{i}Pr (44 mg, 0.17 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of [$PdCl_2$(NCPh)$_2$] (30 mg, 0.078 mmol) in CH_2Cl_2 (1 cm^3). The pale yellow solution was stirred for 30 min at room temperature, after which time a yellow precipitate had formed, which was filtered off, washed with CH_2Cl_2 (2 cm^3), and dried. The yellow solid product was sparingly soluble (33 mg, 62% yield). Anal. Found (calcd for $C_{26}H_{46}Cl_2O_6P_2Pd$): C, 44.8 (45.0); H, 6.8 (6.7). FAB mass spectrum: *m*/*z* 658 ($M^+ - Cl$). ^{31}P NMR ($CDCl_3$): δ_P 13.1, 13.3. Complex **3b** as an orange solid was made similarly from CgPCy in 72% yield. Satisfactory elemental analyses were not obtained, but a crystal structure was determined (see the Results and Discussion). FAB mass spectrum: *m*/*z* 739 ($M^+ - Cl$). ^{31}P NMR ($CDCl_3$): δ_P 9.2, 9.4.

***trans*-[PtCl$_2$(CgP^{i}Pr)$_2$] (4a).** A solution of CgP^{i}Pr (44 mg, 0.17 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of [$PtCl_2$(cod)] (30 mg, 0.080 mmol) in CH_2Cl_2 (1 cm^3). The pale yellow solution was stirred for 2 h at room temperature, and then all the volatiles were removed under reduced pressure. The yellow residue was recrystallized from diethyl ether/pentane to give the off-white solid product (32 mg, 51% yield). Anal. Found (calcd for **4a**·2CH_2Cl_2, $C_{28}H_{50}Cl_6O_6P_2Pt$): C, 35.0 (35.3); H, 5.0 (5.3). FAB mass spectrum: *m*/*z* 783 (M^+). ^{31}P NMR ($CDCl_3$): δ_P 3.08 (J(PtP) = 2600 Hz), 3.16 (J(PtP) = 2610 Hz). ^{195}Pt NMR ($CDCl_3$): δ_{Pt} 868 (J(PtP) = 2600 Hz), 871 (J(PtP) = 2610 Hz). Complex **4b** was made similarly from CgPCy in 68% yield. FAB mass spectrum: *m*/*z* 862 (M^+). ^{31}P NMR ($CDCl_3$): δ_P −0.0 (J(PtP) = 2599 Hz), 0.1 (J(PtP) = 2599 Hz).

***trans*-[PtCl$_2$(CgPC$_{20}$H$_{41}$)$_2$] (4c).** A solution of $CgPC_{20}H_{41}$ (380 mg, 0.76 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of [$PtCl_2$(cod)] (130 mg, 0.35 mmol) in CH_2Cl_2 (5 cm^3). The pale yellow solution was stirred for 1 h at room temperature, and then the volatiles were removed under reduced pressure. The yellow residue was triturated with diethyl ether (50 cm^3) to give the pale yellow solid, which was filtered off, washed with diethyl ether (20 cm^3), and dried to give **4c** (430 mg, 98% yield). An analytically pure sample of **4c** was crystallized by slow evaporation of a CH_2Cl_2 solution. Anal. Found (calcd fofor $C_{60}H_{114}Cl_2O_6P_2Pt$): C, 56.9 (57.2); H, 8.8 (9.1). FAB mass spectrum: *m*/*z* 1188 ($M^+ - 2Cl$). ^{31}P NMR ($CDCl_3$): δ_P 1.22 (J(PtP) = 2594 Hz), 1.41 (J(PtP) = 2602 Hz). ^{1}H NMR ($CDCl_3$): δ_H 2.13−0.75.

***trans*-[RhCl(CO)(CgPH)$_2$] (5d).** A solution of CgPH (144 mg, 0.67 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of [$Rh_2Cl_2(CO)_4$] (65 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3). The pale yellow solution was stirred for 10 min at room temperature, and then the solution was reduced to ca. 2 cm^3. Addition of pentane (10 cm^3) precipitated the yellow solid product (140 mg, 70%). Anal. Found (calcd for $C_{21}H_{34}ClO_7P_2Rh$): C, 42.3 (42.1); H, 6.0 (5.7). ^{31}P NMR (CD_2Cl_2): δ_P 14.4 (J(RhP) = 117 Hz). IR (CH_2Cl_2): ν(CO) 1989 cm^{-1}. The analogous complexes *trans*-[RhCl(CO)(CgPX)$_2$] (**5a**−**c**,**e**) were made in situ and characterized in solution by IR (see the Results and Discussion) and ^{31}P NMR (CD_2Cl_2): **5a**, δ_P 33.3 and 33.1 (J(RhP) = 130 and 128 Hz); **5b**, δ_P 15.1 and 14.6 (J(RhP) = 128 and 129 Hz); **5c**, δ_P 27.3 (J(RhP) = 134 Hz); **5e** (at −80 °C), δ_P 97.7 and 99.0 (J(RhP) = 145 and 145 Hz).

X-ray Experiments. X-ray diffraction experiments on **3b** and **4c** were carried out at 100 K on a Bruker SMART APEX diffractometer, experiments on [CgP(CH_2Ph)$_2$]Br, CgPH, and CgPCl were carried out at 173 K on a Bruker SMART diffractometer, using Mo Kα X-radiation (λ = 0.710 73 Å), the experiment on **1** was carried out at 100 K on an Oxford Diffraction Gemini R Ultra diffractometer, using Mo Kα X-radiation (λ = 0.710 73 Å), and the experiment on CgP(*n*-$C_{20}H_{41}$) was carried out at 100 K on a Bruker PROTEUM diffractometer using Cu Kα X-radiation (λ = 1.541 78 Å); all data collections were performed using a single crystal coated in paraffin oil mounted on a glass fiber. Intensities were integrated from several series of θ scan exposures. Absorption corrections were based on equivalent reflections,[21,22] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[23] Crystal and refinement data are given in Table 1. For **4c**, the residual electron density different maps showed some extra electron density in regions between the complex molecules which could not be identified. The data were refined using SQUEEZE,[24] which resulted in an improvement in the *R* factor of approximately 0.03. The SQUEEZE algorithm calculated an extra 154 electrons in a volume of 383 Å^3. This approximates to between three and four solvent molecules of CH_2Cl_2 per molecule of complex.

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Supporting Information Available: CIF files giving X-ray crystal data, atomic coordinates, bond lengths and angles, and thermal displacement parameters for the compounds CgPH, CgPCl, CgP($C_{20}H_{41}$), [$CgPBz_2$]Br, **1**, **3b**, and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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