Coordination Chemistry of Isomeric Mixtures of Linked Di(phosphaguanidine) Compounds: A Spectroscopic and Crystallographic Study

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Multinuclear NMR spectroscopy and X-ray diffraction techniques have been used to identify diastereomeric mixtures of *rac*- and *meso*-di(phosphaguanidine) compounds. A brief survey of their coordination chemistry has demonstrated the formation of *N*,*N*′-bound bimetallic aluminum species and monometallic platinum complexes in which the ligand chelates to the metal through the two phosphorus donor atoms.

Phosphines remain a fundamentally important ligand in coordination chemistry and are routinely used as ancillary groups in many transition-metal-mediated catalytic processes.[1] During the course of their development, the steric and electronic properties have been extensively modified, facilitated by the ease with which substituents possessing different physical and chemical properties can be incorporated at the phosphorus atom. We have recently developed a novel class of phosphine compound with general formula $Ph_2PC\{NR\}\{NHR\}$ (R = ^{i}Pr, Cy) (we refer to this class of compound as phospha(III)-guanidines, by reference to its relationship to conventional tetrasubstituted guanidines of general formula $R'_2NC\{NR\}\{NHR\}$), featuring a *C*-bound amidine unit,[2] and reported different coordination behavior including anionic $[N,N']^-$ and $[N,P]^-$ and neutral *P*- and *N*,*P*-coordination and a bridging mode between different metal centers.[3]

During analysis of the phosphaguanidines, different arrangements of the *N*-substituents were noted, depending on the orientation of the imine bond and the relative position of the N*H* hydrogen atom (Figure 1).[4] For example, data for the noncomplexed species were consistent with an E_{syn} pattern in the solid and solution states, while the Z_{anti} conformation is enforced upon chelation to a "$M(CO)_4$" fragment.[2] More recently we have identified an equilibrium between the E_{syn} and Z_{syn} forms for the phospha(V)guanidines, $Ph_2P(E)C\{NR\}\{NHR\}$ (E = S, Se),[5] postulated as arising from attractive E···H−N nonbonded interactions. Given that chelating diphosphines frequently offer advantages over their monodentate counterparts (e.g., enhanced thermal stability, enforced *cis*-geometry about square planar metal centers), we were keen to explore the possibility of incorporating more than one phosphaguanidine moiety in the same molecule.

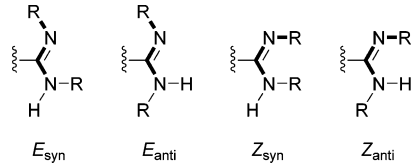

Figure 1. The four possible conformations of *N*-substituents about an amidine unit.

Reaction of $[PhP(Li\{THF\}_2)CH_2-]_2$[6] with RN═C═NR at low temperature and quenching the intermediate lithium species[7] with $[HNEt_3][Cl]$ afforded the ethylene-linked di(phosphaguanidine) compounds $[PhP(C\{NR\}\{NHR\})CH_2-]_2$ [**1a**, R = ^{i}Pr; **1b**, R = Cy]. $^{31}P\{^1H\}$ NMR spectroscopic analysis of analytically pure crystals of **1a** revealed two singlets (δ −29.3 and −29.5) and two widely spaced AB quartets at δ −14.7/−27.2 (J = 42 Hz) and δ −15.0/−26.0 (J = 33 Hz), consistent with two symmetric (**i** and **ii**) and two asymmetric (**iii** and **iv**) species in solution (Figure 2). The corresponding ^1H NMR spectrum is complex, reflecting the presence of these four species (**i**−**iv**) in addition to localized C−N single and C═N double bonds within each amidine unit, which render the nitrogen substituents inequivalent. Using a combination of selective decoupling, 2D-NMR experiments, and investigation of the NOE between key resonances, it has been determined that the major symmetric resonances (**i** and **ii**) have an E_{syn} arrangement of substituents about both amidine units, whereas the nonsymmetrical minor isomers (**iii** and **iv**) contain a combination of Z_{anti} and E_{syn} amidines, resulting in inequivalent phosphorus atoms. Given that the phosphorus atoms in **1** are chiral, the presence of *rac*- and *meso*-diastereoisomers accounts for the observed 1:1 ratio of $\{E_{syn}{:}E_{syn}\}$ (**i** and **ii**) and $\{Z_{anti}{:}E_{syn}\}$ (**iii** and **iv**) species. As may be expected, **i** and **ii** are in equillibrium with **iii** and **iv**, being related by isomerization of the C═N double bond and rotation of the C−N single bond. Monitoring the ratio of [(**i**) + (**ii**)]:[(**iii**) + (**iv**)] by ^{31}P NMR spectroscopy over the temperature range 303−348 K showed only a slight variation in the relative

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(7) Evidence for carbodiimide insertion has been obtained by trapping the lithium salt as the TMEDA adduct; the crystal structure of the resultant salt, $[PhP(C\{N^iPr\}_2Li\{TMEDA\})CH_2-]_2$, will be reported in a subsequent publication.

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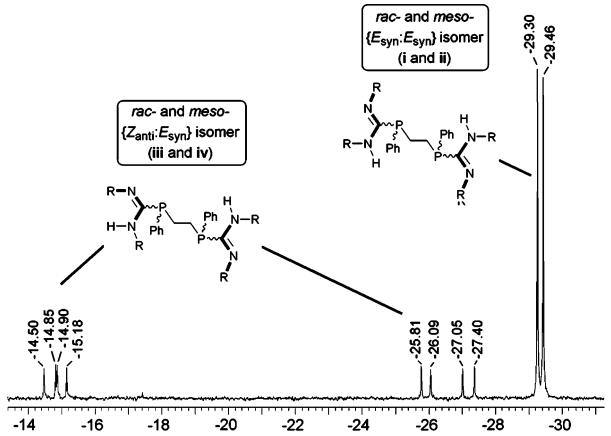


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **1a**, showing the presence of *rac*-/*meso*-{E_{syn}:E_{syn}} (**i** and **ii**) and *rac*-/*meso*-{E_{syn}:Z_{anti}} (**iii** and **iv**) diasteroisomers.

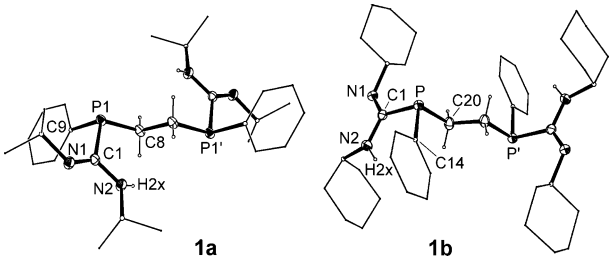


Figure 3. Molecular structure of *meso*-**1a** (′ $-x, -y+1, -z+1$; ″ $-x, -y+1, -z$) and *meso*-**1b** ($-x+1, -y+1, -z+1$); ellipsoids drawn at the 30% probability level; hydrogens omitted except N*H* and bridging carbon positions. *meso*-**1a**: C(1)−N(1) 1.283(3), C(1)−N(2) 1.375(3), P(1)−C(1) 1.870(2), P(1)−C(8) 1.850(2), P(1)−C(9) 1.836(2); N(1)−C(1)−N(2) 119.8(2), N(1)−C(1)−P(1) 124.09(19), N(2)−C(1)−P(1) 115.77(18), C(1)−P(1)−C(8) 103.97(11), C(1)−P(1)−C(9) 101.49(11), C(8)−P(1)−C(9) 99.94(11). *meso*-**1b**: C(1)−N(1) 1.273(4), C(1)−N(2) 1.376(4), P−C(1) 1.880(3), P−C(20) 1.849(3), P−C(14) 1.828(3). N(1)−C(1)−N(2) 120.0(3), N(1)−C(1)−P 124.5(2), N(2)−C(2)−P 115.6(2), C(1)−P−C(20) 96.55(14), C(1)−P−C(14) 101.67(15), C(14)−P−C(20) 102.64(15).

amounts of {E_{syn}:E_{syn}} and {Z_{anti}:E_{syn}} (303 K, 2.6:1; 348 K, 2.2:1), with the thermodynamically more stable symmetric form predominating in solution.

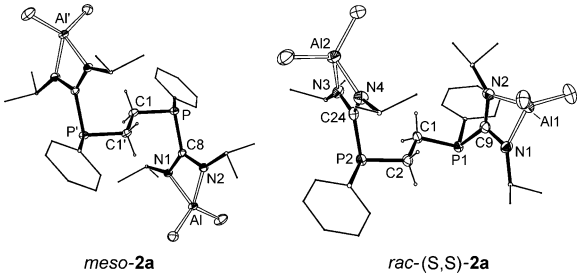
We are unable to definitively assign either of the pairs of isomers as *rac* or *meso* using spectroscopy alone, and recrystallization of the crude mixture afforded an intimately mixed 1:1 combination of these two forms that could not be separated. Prolonged heating of a $[^2H]_8$-toluene solution of **1a** (80 °C, 5 days) showed no change in the ratio of *rac*:*meso*, consistent with the expected high barrier to inversion at phosphorus. However, varying the reaction conditions (temperature, rate of addition, concentrations) has allowed *meso*-enriched mixtures to be isolated (as verified by X-ray diffraction data, vide infra), enabling full ^1H NMR spectroscopic assignments to be made for all four isomers of **1a**.

X-ray data[8] collected on representative crystals of **1a** and **1b** are consistent with the *meso*-form in each case (Figure 3), in which the two ends of the molecule are related by crystallographic symmetry. Both derivatives exhibit similar gross structural features, although two molecules are noted in the unit cell of **1a**, which differ slightly in their molecular geometry. The monomeric compounds contain the expected ethylene bridge between the two phosphine units, with a *C*-bound amidine unit and phenyl substituent completing the coordination environment about the pyramidal phosphorus. In accordance with solution NMR data, localized bonding is present in the amidine unit with Δ_{CN} values of 0.100 Å (av) and 0.103 Å for **1a** and **1b**, respectively [$\Delta_{CN} = d(C-N) - d(C{=}N)$].[4]

Upon *N*,*N*′-chelation of an anionic amidinate unit to a metal center and formation of the four-membered metallacycle, the configuration of nitrogen substituents is restricted to the {E_{anti}:E_{anti}} arrangement, reducing the possible number of species to two symmetrical isomers. Accordingly, the product of the reaction between **1a** and **1b** with 2 equiv of $AlMe_3$ displayed NMR spectra that were consistent with the bimetallic *rac*- and *meso*-compounds [PhP(C{NR}$_2$AlMe$_2$)CH$_2$−]$_2$ [**2a**, R = ^{i}Pr; **2b**, R = Cy]. The $^{31}P\{^1H\}$ NMR spectra of the crude material display two singlet resonances of equal intensity [**2a**, δ −27.6/−29.1; **2b**, δ −28.1 and δ −30.5], indicative of a 1:1 mixture of the *rac*- and *meso*-diastereoisomers. The corresponding ^1H NMR data are simplified further as both *N*-substituents also become equivalent, signifying symmetric delocalization of the π-electron density within the NCN moiety. In contrast to the observed cocrystallization of *rac*- and *meso*-**1**, successive recrystallizations of **2** has allowed separation of the two diastereoisomers, with the *meso*-compound proving less soluble. It has therefore been possible to obtain X-ray diffraction data for both *rac*- and *meso*-**2a** (Figure 4).[8]

The molecular structure of the aluminum complexes is in agreement with the spectroscopic data, revealing a chelating [*N*,*N*′]-coordination of the amidinate at each metal. In the case of *rac*-**2a**, four molecules are present in the unit cell, corresponding to a 1:1 mixture of the *R*,*R* and *S*,*S* diastereoisomers. In all cases, the resultant geometry at aluminum is distorted tetrahedral within which the bite angle of the phosphaguanidinate ligand represents the smallest angle [*meso*-**2a**, 68.83(11)°; *rac*-**2a** 68.8(2)° av; **2b**, 69.07(9)°]. Symmetrical bonding to the

(8) Crystallographic data for **1a**: $C_{28}H_{44}N_4P_2$, M = 498.61, T = 173(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 11.5200(7) Å, b = 11.9380(7) Å, c = 12.5195(10) Å, α = 83.491(3)°, β = 90.327(3)°, γ = 63.088(3)°, U = 1522.2(2) Å^3, Z = 2, D_c = 1.09 Mg m^{-3}, μ(Mo Kα) = 0.16 mm^{-1}, independent reflections = 5248 (R_{int} = 0.061), R1 [for 3962 reflections with $I > 2\sigma(I)$] = 0.054, wR2 (all data) = 0.126. Crystallographic data for **1b**: $C_{40}H_{60}N_4P_2$, M = 658.86, T = 173(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 9.2204(7) Å, b = 10.0638(8) Å, c = 11.1221(9) Å, α = 110.804(5)°, β = 97.381(5)°, γ = 94.342(4)°, U = 948.53(13) Å^3, Z = 1, D_c = 1.15 Mg m^{-3}, μ(Mo Kα) = 0.15 mm^{-1}, independent reflections = 2502 (R_{int} = 0.072), R1 [for 1910 reflections with $I > 2\sigma(I)$] = 0.058, wR2 (all data) = 0.135. Crystallographic data for *meso*-**2a** [*Note*: atoms C(13) and C(14) are disordered and were left isotropic]: $C_{32}H_{54}Al_2N_4P_2$, M = 610.69, T = 173(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 8.0203(3) Å, b = 9.6862(5) Å, c = 13.3190(6) Å, α = 107.397(2)°, β = 93.777(3)°, γ = 102.148(3)°, U = 956.02(7) Å^3, Z = 1, D_c = 1.06 Mg m^{-3}, μ(Mo Kα) = 0.18 mm^{-1}, independent reflections = 3707 (R_{int} = 0.070), R1 [for 2723 reflections with $I > 2\sigma(I)$] = 0.058, wR2 (all data) = 0.194. Crystallographic data for *rac*-**2a** [*Note*: four independent molecules present]: $C_{32}H_{54}Al_2N_4P_2$, M = 610.69, T = 173(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 13.0307(4) Å, b = 13.0404(4) Å, c = 45.5588(15) Å, α = 83.446(1)°, β = 82.619(2)°, γ = 85.102(2)°, U = 7607.6(4) Å^3, Z = 8, D_c = 1.07 Mg m^{-3}, μ(Mo Kα) = 0.19 mm^{-1}, independent reflections = 21 836 (R_{int} = 0.085), R1 [for 15 142 reflections with $I > 2\sigma(I)$] = 0.096, wR2 (all data) = 0.238. Crystallographic data for **2b** [*Note*: the cyclohexyl group on N(2) is disordered with resolved orientations included with isotropic C atoms and SADI restraints]: $C_{44}H_{70}Al_2N_4P_2$, M = 770.94, T = 173(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 9.2687(3) Å, b = 11.2746(3) Å, c = 12.3529(4) Å, α = 107.300(2)°, β = 92.690(2)°, γ = 103.330(2)°, U = 1189.98(6) Å^3, Z = 1, D_c = 1.08 Mg m^{-3}, μ(Mo Kα) = 0.16 mm^{-1}, independent reflections = 4672 (R_{int} = 0.050), R1 [for 3803 reflections with $I > 2\sigma(I)$] = 0.061, *wR*2 (all data) = 0.172. Crystallographic data for **3b**′ [*Note*: the toluene solvate molecules were included with isotropic C atoms; for the solvate disordered across an inversion center, SADI restraints were applied and H atoms omitted]: $C_{40}H_{60}I_2N_4P_2Pt{\cdot}1.5(C_7H_8)$, M = 1245.95, T = 173(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 16.8514(8) Å, b = 12.2242(4) Å, c = 25.0259(11) Å, β = 98.138(2)°, U = 5103.3(4) Å^3, Z = 4, D_c = 1.62 Mg m^{-3}, μ(Mo Kα) = 4.06 mm^{-1}, independent reflections = 7044 (R_{int} = 0.094), R1 [for 4934 reflections with $I > 2\sigma(I)$] = 0.052, wR2 (all data) = 0.104.



meso-**2a** *rac*-(S,S)-**2a**

Figure 4. Molecular structure of *meso*-**2a** (′ $-x+1, -y+1, -z+1$) and *rac*-(*S*,*S*)-**2a**; ellipsoids drawn at the 30% probability level; hydrogens omitted except at bridging carbon positions. *meso*-**2a**: Al−N(1) 1.932(3), Al−N(2) 1.923(3), P−C(8) 1.872(3), C(8)−N(1) 1.333(4), C(8)−N(2) 1.325(4); N(1)−Al−N(2) 68.83(11), C(1)−P−C(2) 102.99(14), C(1)−P−C(8) 99.43(13), C(2)−P−C(8) 101.36(13). *rac*-**2a** [av value of all 4 molecules]: Al(1)−N(1) 1.929(6), Al(1)−N(2) 1.937(6), Al(2)−N(3) 1.923(6), Al(2)−N(4) 1.932(6), P(1)−C(9) 1.870(7), P(2)−C(24) 1.867(7), C(9)−N(1) 1.339(8), C(9)−N(2) 1.333(8), C(24)−N(3) 1.334(8), C(24)−N(4) 1.340(8); N(1)−Al(1)−N(2) 68.8(2), N(3)−Al(2)−N(4) 68.7(2), C(1)−P(1)−C(3) 105.5(3), C(1)−P(1)−C(9) 101.3(3), C(9)−P(1)−C(3) 101.3(3), C(2)−P(2)−C(18) 105.6(3), C(2)−P(2)−C(24) 100.6(3), C(18)−P(2)−C(24) 99.4(3).

aluminum atom is observed with full delocalization throughout the N−C−N moiety [$\Delta_{CN} \approx 0$]. All other parameters are unremarkable when compared with the growing library of related amidinate and phosphaguanidinate complexes incorporating the dialkyl and diaryl aluminum fragments.[3,9]

To demonstrate the ability of the di(phosphaguanidine) to also function as a chelating diphosphine ligand, compound **1a** was reacted with $PtCl_2$(COD), to afford the dichloride, $PtCl_2$([PhP(C{N^{i}Pr}{NH^{i}Pr})CH_2−]$_2$), **3a**. In this instance, the amidine unit is predicted to remain intact, and hence a mixture of isomeric products is expected. Indeed, the $^{31}P\{^1H\}$ NMR spectrum of the product shows four different phosphorus environments at δ 44.9, 43.2, 42.4, and 32.0, each of which displays platinum satellites indicating coordination to the metal center. In combination with results from ^1H and ^{195}Pt NMR experiments, it is deduced that these resonances originate from three species, the two low-frequency signals of which correspond to a symmetrical compound and the remaining peaks from an asymmetrical variant of **3a**. The predominant conformation for the amidine unit in **3a** is Z_{anti}, indicating a change in the energy profile of the different substituent positions compared with the proligand. However, the presence of a broad doublet centered at δ 5.32 in **3a** is characteristic of an N*H* resonance from an E_{syn} amidine,[2] suggesting that the asymmetric species corresponds to the {Z_{anti}:E_{syn}} isomer. This diastereoisomer is in exchange with one of the symmetrical species (but not the other), which we therefore assign as the corresponding {Z_{anti}:Z_{anti}}. Taking into account the 1:1 ratio of *rac*- and *meso*-**1a** used in the reaction and the high barrier to inversion at phosphorus, the mixture is therefore assigned as *rac*-{Z_{anti}:Z_{anti}} [δ 44.9], *meso*-{Z_{anti}:Z_{anti}} [δ 43.2], and *meso*-{Z_{anti}:E_{syn}} [δ 42.4 {Z_{anti}} and 32.0 {E_{syn}}], illustrated in Figure 5.

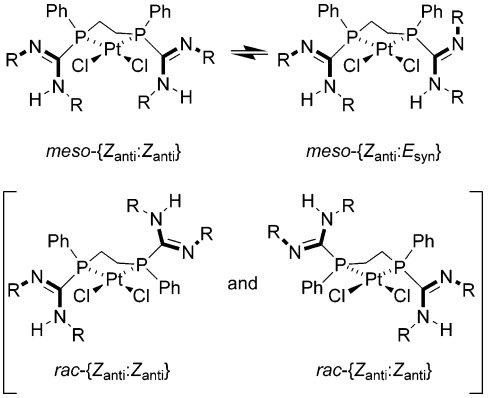


Figure 5. Different isomeric forms of **3a** identified in solution.

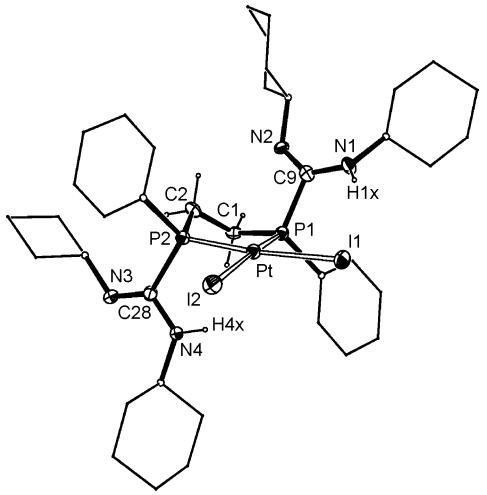


Figure 6. Molecular structure of *rac*-(R,R)-**3b′**; ellipsoids drawn at the 30% probability level; hydrogens omitted except at N*H* and bridging carbon positions. Pt−P(1) 2.234(2), Pt−P(2) 2.244(3), P(1)−C(9) 1.856(10), P(2)−C(28) 1.867(10), C(9)−N(1) 1.376(12), C(9)−N(2) 1.275(12), C(28)−N(3) 1.288(11), C(28)−N(4) 1.357(12); P(1)−Pt−P(2) 86.29(9), P(1)−Pt−I(1) 91.26(7), P(2)−Pt−I(2) 91.19(7), I(1)−Pt−I(2) 91.73(3), C(1)−P(1)−Pt 107.6(3), C(3)−P(1)−Pt 116.1(3), C(9)−P(1)−Pt 116.9(3), C(1)−P(1)−C(3) 105.1(5), C(1)−P(1)−C(9) 103.0(5), C(3)−P(1)−C(9) 106.9(4), C(2)−P(2)−Pt 108.2(3), C(22)−P(2)−Pt 115.1(3), C(28)−P(2)−Pt 114.6(3), C(2)−P(2)−C(22) 107.3(5), C(2)−P(2)−C(28) 102.4(5), C(22)−P(2)−C(28) 108.2(5).

In an effort to analyze the ligand bond parameters when coordinated to platinum, different combinations of ligand and platinum starting materials have been investigated. Recently we have successfully characterized the di-iodide PtI_2([PhP(C{NCy}{NHCy})CH_2−]$_2$) (**3b′**) by X-ray crystallography, confirming the chelation of the diphosphine ligand in the solid state (Figure 6). In this instance the structurally characterized isomer corresponds to the *rac*-(*R*,*R*)-{E_{syn}:Z_{syn}} form, indicating that other combinations of substituents are energetically accessible and may be present as low-concentration species in solution. The geometry about the *cis*-square planar metal is unremarkable compared with PtI_2(dppe),[10] with a notable twist of 7.5° present between the mean "P_2Pt" and "PtI_2" planes.

To conclude, we have synthesized the first examples of linked phosphaguanidine compounds, as a 1:1 ratio of *rac*- and *meso*-diastereoisomers. Different conformations of the amidine unit afford a mixture of symmetric and asymmetric species, and

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solid-state X-ray diffraction of the *meso*-{E_{syn}:E_{syn}} conformation has been performed. These compounds react via the amidine unit to afford bimetallic aluminum methyl complexes and through the phosphorus atoms in a chelating bonding mode to platinum. Further studies of the factors that influence the diastereomeric ratio during the synthesis of this class of compound are ongoing and will be reported in due course.

Experimental Section

General Procedures. All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. dppe (Aldrich), ^{n}BuLi (2.5 M solution in hexanes, Acros), ^{i}PrN═C═N^{i}Pr (Aldrich), CyN═C═NCy (Aldrich), and $AlMe_3$ (2.0 M solution in hexanes, Aldrich) were purchased from commercial sources and used without further purification. [$HNEt_3$][Cl] (Alrdich) was recrystallized from chloroform and stored under a dry nitrogen atmosphere. $PtCl_2$(COD) and PtI_2(COD) were made according to literature procedures.[11] Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^{1}H), 75 (^{13}C{^{1}H}), and 121 (^{31}P{^{1}H}) MHz, or a Bruker AMX 500 MHz spectrometer at 500 (^{1}H), 125 (^{13}C{^{1}H}) and 202 (^{31}P{^{1}H}) MHz. NMR were recorded in [$^2H]_6$-benzene at 298 K unless otherwise stated. Proton and carbon chemical shifts were referenced internally to residual solvent resonances; coupling constants, *J*, are quoted in Hz.

[PhP(C{N^{i}Pr}{NH^{i}Pr})CH_2−]$_2$ (1a). A solution of ^{i}PrN═C═N^{i}Pr (0.290 mL, 1.83 mmol) in THF (∼10 mL) was added dropwise to a solution of [PhP(Li{THF}$_2$)CH_2−]$_2$ (0.500 g, 0.92 mmol) also in THF (∼15 mL) at −78 °C. The resultant yellow suspension was stirred for 2 h at low temperature, affording a paler yellow suspension, to which a slurry of [$HNEt_3$][Cl] (0.250 g, 1.83 mmol) in THF (∼10 mL) was added. The reaction mixture was allowed to warm slowly to ambient temperature over a period of 5 h, affording a clear colorless solution, which was stirred for a further 16 h. Removal of volatiles under reduced pressure yielded the product species as a crude white solid. Recrystallization from hexane at −30 °C afforded colorless crystals of the product species. Yield: 0.32 g, 69%. Anal. Calc for $C_{28}H_{44}N_4P_2$ (*498.30)*: C 67.45, H 8.89, N 11.24. Found: C 67.52, H 9.06, N 11.00. ^{1}H NMR (500 MHz): ***meso***-{***E*$_{syn}$:*E*$_{syn}$} δ 7.42 (m, 4H, *o*-C_6H_5), *, 4.59 (m, 2H, ═NC*H*), 4.25 (sept, *J* = 6.5, 2H, NHC*H*), 3.52 (d, *J* = 6.7, 2H, N*H*), 2.29 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 1.36 (d, *J* = 6.1, 6H, ═NCHMe_2), 1.29 (d, *J* = 6.1, 6H, ═NCHMe_2), 0.95 (d, *J* = 6.4, 6H, NHCHMe_2), 0.88 (d, *J* = 6.4, 6H, NHCHMe_2); ***meso***-{***E*$_{syn}$:***Z*$_{anti}$} δ 7.65 (m, 4H, *o*-C_6H_5), *, 4.58 (m, 1H, ═NC*H* {E_{syn}}), 4.25 (sept, *J* = 6.5, 1H, NHC*H* {E_{syn}}), 3.97 (m, 1H, NHC*H* {Z_{anti}}), 3.84 (m, 1H, N*H* {Z_{anti}}), 3.58 (d, *J* = 7.2, 1H, N*H* {E_{syn}}), 3.36 (sept, *J* = 6.1, 1H, ═NC*H* {Z_{anti}}), 2.74 (m, 1H, CH_2), 2.63 (m, 1H, CH_2), 2.21 (m, 1H, CH_2), 2.04 (m, 1H, CH_2), 1.36 (d, *J* = 6.1, 3H, ═NCHMe_2 {E_{syn}}), 1.34 (d, *J* = 6.3, 3H, ═NCHMe_2 {Z_{anti}}), 1.29 (d, *J* = 6.1, 3H, ═NCHMe_2 {E_{syn}}), 1.22 (d, *J* = 6.2, 3H, ═NCHMe_2 {Z_{anti}}), 0.95 (d, *J* = 6.4, 3H, NHCHMe_2 {E_{syn}}), 0.91 (d, *J* = 6.3, 3H, NHCHMe_2 {Z_{anti}}), 0.88 (d, *J* = 6.4, 3H, NHCHMe_2 {E_{syn}}), 0.44 (d, *J* = 6.3, 3H, NHCHMe_2 {Z_{anti}}); ***rac***-{***E*$_{syn}$:*E*$_{syn}$} δ 7.42 (m, 4H, *o*-C_6H_5), *, 4.59 (m, 2H, ═NC*H*), 4.25 (sept, *J* = 6.5, 2H, NHC*H*), 3.56 (d, *J* = 6.8, 2H, N*H*), 2.22 (m, 4H, CH_2), 1.38 (d, *J* = 6.1, 6H, ═NCHMe_2), 1.29 (d, *J* = 6.1, 6H, ═NCHMe_2), 0.98 (d, *J* = 6.5, 6H, NHCHMe_2), 0.90 (d, *J* = 6.5, 6H, NHCHMe_2). ***rac***-{E_{syn}:Z_{anti}} δ 7.71 (m, 2H, *o*-C_6H_5), 7.57 (m, 2H, *o*-C_6H_5), *, 4.58 (m, 1H, ═NC*H* {E_{syn}}), 4.25 (sept, *J* = 6.5, 1H, NHC*H* {E_{syn}}), 3.97 (m, 1H, NHC*H* {Z_{anti}}), 3.94 (m, 1H, N*H* {Z_{anti}}), 3.66 (d, *J* = 7.2, 1H, N*H* {E_{syn}}), 3.36 (sept, *J* = 6.1, 1H, ═NC*H* {Z_{anti}}), 2.74 (m, 1H, CH_2), 2.40 (m, 1H, CH_2), 2.22 (m, 1H, CH_2), 2.08 (m, 1H, CH_2), 1.40 (d, *J* = 6.1, 3H, ═NCHMe_2 {E_{syn}}), 1.33 (d, *J* = 5.9, 3H, ═NCHMe_2 {Z_{anti}}), 1.26 (d, *J* = 6.1, 3H, ═NCHMe_2 {E_{syn}}), 1.23 (d, *J* = 6.2, 3H, ═NCHMe_2 {Z_{anti}}), ‡, 0.45 (d, *J* = 6.3, 3H, NHCHMe_2 {Z_{anti}}) [* remaining aromatic resonances for all isomers overlap in the region δ 7.13−6.99; ‡ with the exception of one of the NHCHMe_2 {Z_{anti}} resonances, which appears at high field, the remaining doublets corresponding to the NH^{i}Pr substituents were overlapping with those of the other isomers and could not be deconvoluted]. ^{31}P NMR (121 MHz): ***meso***-{***E*$_{syn}$:*E*$_{syn}$} δ −29.5 (s); ***rac***-{***E*$_{syn}$:*E*$_{syn}$} δ −29.3 (s); ***meso***-{***E*$_{syn}$:*Z*$_{anti}$} δ −14.7 (d, *J* = 42.3 Hz), −27.2 (d, *J* = 42.3 Hz); ***rac***-{***E*$_{syn}$:*Z*$_{anti}$} δ −15.0 (d, *J* = 33.9 Hz), −26.0 (d, *J* = 33.9 Hz).

[PhP(C{NCy}{NHCy})CH_2−]$_2$ (1b). Compound **1b** was synthesized using a procedure analogous to that described for **1a**, using [PhP(Li{THF}$_2$)CH_2−]$_2$ (0.500 g, 0.92 mmol), CyN═C═NCy (0.380 g, 1.83 mmol), and [$HNEt_3$][Cl] (0.250 g, 1.83 mmol). Recrystallization of the crude white product from hexane at −30 °C afforded pure **1b**. Yield: 0.280 g, 61%. Anal. Calc for $C_{40}H_{60}N_4P_2$ *(658.43)*: C 72.92, H 9.18, N 8.50. Found: C 73.02, H 9.16, N 8.53. ^{1}H NMR (300 MHz): **mixture of *meso*-{*E*$_{syn}$:*E*$_{syn}$} and *meso*-{*E*$_{syn}$:*Z*$_{anti}$}** δ 7.72 (m, *o*-C_6H_5), 7.50 (m, *o*-C_6H_5), 7.12−7.00 (m, *m*- and *p*-C_6H_5), 4.27 (m, NC*H*), 4.16 (m, N*H*), 4.06 (m, NC*H*), 3.75 (d, *J* = 7.2, N*H*), 3.68 (d, *J* = 7.2, N*H*), 3.28 (m, NC*H*), 3.23 (m, NC*H*), 2.82 (m, CH_2), 2.69 (m, CH_2), 2.40 (m, NC*H*), 2.30 (m), 2.20 (m, NC*H*), 2.03−0.71 (m, Cy-CH_2); **mixture of *rac*-{*E*$_{syn}$:*E*$_{syn}$} and *rac*-{*E*$_{syn}$:*Z*$_{anti}$}** δ 7.78 (m, *o*-C_6H_5), 7.63 (m, *o*-C_6H_5), 7.08−6.99 (m, *m*- and *p*-C_6H_5), 4.25 (m, NC*H*), 4.15 (m, N*H*), 4.08 (m, NC*H*), 3.79 (d, *J* = 7.0, N*H*), 3.72 (d, *J* = 7.2, N*H*), 3.29 (m), 3.11 (m, NC*H*), 2.83 (m), 2.44 (m), 2.31 (m), 2.21 (m), 1.97−0.82 (m, Cy-CH_2). ^{31}P NMR (121 MHz): ***meso***-{***E*$_{syn}$:*E*$_{syn}$} δ −28.7 (s); ***rac***-{***E*$_{syn}$:*E*$_{syn}$} δ −29.0 (s); ***meso***-{***E*$_{syn}$:*Z*$_{anti}$} δ −14.5 (d, *J* = 41.0 Hz), −26.9 (d, *J* = 41.0 Hz); ***rac***-{***E*$_{syn}$:*Z*$_{anti}$} δ −14.9 (d, *J* = 33.5 Hz), −26.1 (d, *J* = 33.5 Hz).

[PhP(C{N^{i}Pr}$_2$$AlMe_2$)$CH_2$−]$_2$ (2a). A 0.20 mL portion of a solution of $AlMe_3$ (2.0 M in hexanes, 0.40 mmol) was added dropwise via syringe to a solution of [PhP(C{N^{i}Pr}{NH^{i}Pr})CH_2−]$_2$ (0.100 g, 0.20 mmol) in hexane (∼15 mL). The resultant clear, colorless solution was stirred at ambient temperature for 15 h. The volatiles were removed in vacuo to afford a crude white solid. Analytically pure samples were obtained by crystallization from hexane at −30 °C. Yield: 0.084 g, 76%. Anal. Calc for $C_{32}H_{54}N_4Al_2P_2$ *(610.34)*: C 62.93, H 8.91, N 9.17. Found: C 62.91, H 8.84, N 8.99. ^{1}H NMR (300 MHz): ***meso*** δ 7.36 (m, 2H, *o*-C_6H_5), 7.03 (t, *J* = 7.4, 2H, *m*-C_6H_5), 6.92 (d, *J* = 7.5, 1H, *p*-C_6H_5), 3.95 (sept, *J* = 6.2, 2H, C*H*Me$_2$), 2.56 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 1.08 (d, *J* = 6.3, 6H, CHMe_2), 0.91 (d, *J* = 6.0, 6H, CHMe_2), −0.20 (s, 6H, AlMe_2); ***rac*** δ 7.34 (m, 2H, *o*-C_6H_5), 7.05−6.89 (m, 3H, *m*-, *p*-C_6H_5), 3.95 (br sept, 2H, C*H*Me$_2$), 2.52 (m, 2H, CH_2), 1.10 (d, *J* = 6.9, 6H, CHMe_2), 0.90 (d, *J* = 6.0, 6H, CHMe_2), −0.22 (s, 6H, AlMe_2). ^{31}P NMR (121 MHz): ***meso*** δ −27.6 (s); ***rac*** δ −29.0 (s).

[PhP(C{NCy}$_2$$AlMe_2$)$CH_2$−]$_2$ (2b). Compound **2b** was synthesized using a procedure analogous to that described for **2a**, using [PhP(C{NCy}{NHCy})CH_2−]$_2$ (0.100 g, 0.15 mmol) and $AlMe_3$ (0.15 mL of a 2.0 M solution in hexane, 0.30 mmol). Recrystallization of the crude white product from hexane at −30 °C afforded pure **2b**. Yield: 0.070 g, 58%. Anal. Calc for $C_{44}H_{70}N_4Al_2P_2$ *(770.47)*: C 68.55, H 9.15, N 7.27. Found: C 68.67, H 9.21, N 7.18. ^{1}H NMR (300 MHz): ***meso*** δ 7.41 (m, 2H, *o*-C_6H_5), 7.03 (t, *J* = 7.3, 2H, *m*-C_6H_5), 6.94 (d, *J* = 7.3, 1H, *p*-C_6H_5), 3.61 (m, 2H, NC*H*), 2.63 (m, 2H, CH_2), 1.93−0.91 (m, 20H, Cy-CH_2), −0.14 (s, 6H, AlMe_2). ^{31}P NMR (121 MHz): ***meso*** δ −28.1 (s); ***rac*** δ −30.5 (s).

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$PtCl_2$([PhP(C{N^{i}Pr}{NH^{i}Pr})CH_2−]$_2$) (3a). A clear colorless solution of [PhP(C{N^{i}Pr}{NH^{i}Pr})CH_2−]$_2$ (**1a**, 0.100 g, 0.20 mmol) in toluene (∼10 mL) was added dropwise to a stirred suspension of $PtCl_2$(COD) (0.075 g, 0.20 mmol) in toluene (∼10 mL). Filtration from a small amount of particulate matter, followed by removal of the volatiles under reduced pressure, afforded **3a** as a crude white solid. Analytically pure samples were obtained by crystallization from THF at −30 °C. Yield: 0.11 g, 35%. Anal. Calc for $C_{28}H_{44}N_4Cl_2P_2Pt$ *(763.21)*: C 43.98, H 5.80, N 7.33. Found: C 44.06, H 5.87, N 7.39. ^{1}H NMR (500 MHz): ***meso***-{Z_{anti}:Z_{anti}} δ 8.21 (m, 4H, *o*-C_6H_5), 7.55 (m, 2H, N*H*), *, 3.81 (sept, J = 6.1, 2H, ═NC*H*), 3.48 (m, 2H, NHC*H*), 2.64 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.18 (d, J = 6.2, 6H, ═NCHMe_2), 1.16 (d, J = 6.1, 6H, ═NCHMe_2), 0.97 (d, J = 6.3, 6H, NHCHMe_2), 0.81 (d, J = 6.2, 6H, NHCHMe_2); ***meso***-{E_{syn}:Z_{anti}} δ 7.97 (m, 2H, *o*-C_6H_5 {Z_{anti}}), 7.88 (m, 2H, *o*-C_6H_5 {E_{syn}}), 7.12 (m, 1H, N*H* {Z_{anti}}), 5.31 (d br, 1H, N*H* {E_{syn}}), 4.29 (m br, 1H, ═NC*H* {E_{syn}}), 4.21 (m br, 1H, NHC*H* {E_{syn}}), 3.78 (sept, J = 6.1, 1H, ═NC*H* {Z_{anti}}), 3.55 (sept, J = 6.5, 1H, NHC*H* {Z_{anti}}), 2.64 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.37 (d br, 3H, ═NCHMe_2 {E_{syn}}), 1.09 (d br, 3H+3H, NHCHMe_2 {E_{syn}}), 1.05 (d, 3H+3H, ═NCHMe_2 {E_{syn}} + NHCHMe_2 {Z_{anti}}), 0.98 (d, J = 6.5, 6H, ═NCHMe_2 {Z_{anti}}), 0.85 (d, J = 6.3, 3H, NHCHMe_2 {Z_{anti}}); ***rac***-{$\boldsymbol{Z_{anti}}$:$\boldsymbol{Z_{anti}}$} δ 8.13 (m, 4H, *o*-C_6H_5), 7.34 (m, 2H, N*H*), *, 3.81 (sept, J = 6.1, 2H, ═NC*H*), 3.48 (sept, J = 6.8, 2H, NHC*H*), 2.65 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.18 (d, J = 6.1, 6H, ═NCHMe_2), 1.16 (d, J = 6.1, 6H, ═NCHMe_2), 0.97 (d, J = 6.3, 6H, NHCHMe_2), 0.81 (d, J = 6.3, 6H, NHCHMe_2) [* remaining aromatic resonances for both isomers overlap in the region δ 7.05−6.96]. ^{31}P NMR (202 MHz): ***rac***-{$\boldsymbol{Z_{anti}}$:$\boldsymbol{Z_{anti}}$} δ 44.9 (J = 3380); ***meso***-{$\boldsymbol{Z_{anti}}$:$\boldsymbol{Z_{anti}}$} δ 43.2 (J = 3382); ***meso***-{$\boldsymbol{E_{syn}}$:$\boldsymbol{Z_{anti}}$} δ 42.4 (J = 3372 {Z_{anti}}), 32.0 (J = 3479 {E_{syn}}). ^{195}Pt (107 MHz): ***meso***-{$\boldsymbol{E_{syn}}$:$\boldsymbol{Z_{anti}}$} δ − 4540 (dd, J = 3372, 3479); ***rac***-{$\boldsymbol{Z_{anti}}$:$\boldsymbol{Z_{anti}}$} δ −4594 (t, J = 3380); ***meso***-{$\boldsymbol{Z_{anti}}$:$\boldsymbol{Z_{anti}}$} δ −4608 (t, J = 3382).

PtI_2([PhP(C{NCy}{NHCy})CH_2−]$_2$) (3b′). Compound **3b′** was synthesized using a procedure analogous to that described for **3a**, using [PhP(C{NCy}{NHCy})CH_2−]$_2$ (0.10 g, 0.15 mmol) and PtI_2(COD) (0.08 g, 0.15 mmol). Recrystallization of the crude yellow product from toluene at −30 °C afforded pure **3b′**. Yield: 0.05 g, 29%. Anal. Calc for $C_{40}H_{60}N_4I_2P_2Pt$ *(1107.20)*: C 43.37, H 5.46, N 5.06. Found: C 43.43, H 5.56, N 4.94. ^{31}P NMR (121 MHz)†: δ 57.7 (J = 3154) 52.8 (J = 3157), 44.7 (J = 3209), 33.8 (J = 3198) († definitive assignment of isomers has not been possible due to the complexity of the ^{1}H NMR spectra arising from the presence of the cyclohexylsubstituents; however, the resonances at δ 52.8 and 44.7 are believed to represent two different phosphorus environments within an asymmetric molecule due to their similar intensities and the observation of an additional 7 Hz coupling of unknown origin in each case).

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Supporting Information Available: CIF files for **1a**, **1b**, *meso*-**2a**, *rac*-**2a**, **2b**, and **3b′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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