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Low-Valent Chemistry: An Alternative Approach to Phosphorus-Containing Oligomers

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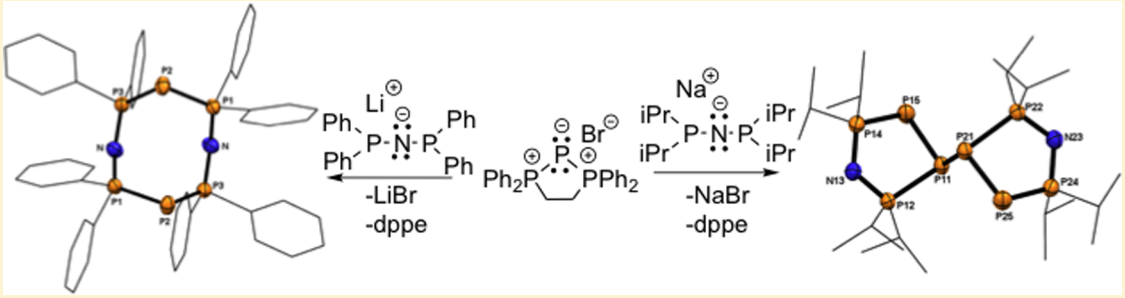
Supporting Information



ABSTRACT: A convenient preparative approach to low-valent phosphorus-rich oligomers is presented. Ligand substitution reactions involving anionic diphosphine ligands of the form $[(PR_2)_2N]^-$ and $[(PPh_2)_2C_5H_3]^-$ and a triphosphenium bromide P^I precursor result in the formation of phosphorus(I)-containing heterocycles, several of which are of types that have never been prepared before. The methodology described also allows for the preparation of the known heterocycle *cyclo*-$[P(PPh_2)N(PPh_2)]_2$ in better yields and purity than the synthetic approach reported previously. Preliminary reactivity studies demonstrate the viability of such zwitterionic oligomers as multidentate ligands for transition metals.

INTRODUCTION

Phosphorus-containing oligomers and macromolecules have been and continue to be materials of tremendous investigation, both from academic and industrial perspectives. The interest in such molecules stems primarily from the different properties that are engendered in these species by the presence of the phosphorus atoms in comparison to their "carbon copy" analogues. For example, the sometimes unique and often improved performance of phosphorus-containing polymers renders them useful for a very large number of applications, including: biomedical applications, catalysis, light-harvesting, sensing lubrication, flame-retardant materials, and much more.[1−5] In this context, the development of new or improved methods for the production of phosphorus-containing macromolecules is desirable.

Triphosphenium salts are a remarkable class of compounds first prepared by Schmidpeter and co-workers in the 1980s[6,7] that feature a dicoordinate and low-valent P^I atom but are unusually stable (Figure 1A,B). More recently, our development of a facile approach to cyclic triphosphenium iodide and bromide salts (cf. Figure 1C)[8] provided materials that are particularly amenable to anion-exchange metathesis reactions.[9] The availability of a convenient and high-purity route to such compounds is important because it has already been demonstrated that triphosphenium salts may be used as reagents for the preparation of other polyphosphorus compounds[9,10] or as convenient P^I sources.[7] In particular,

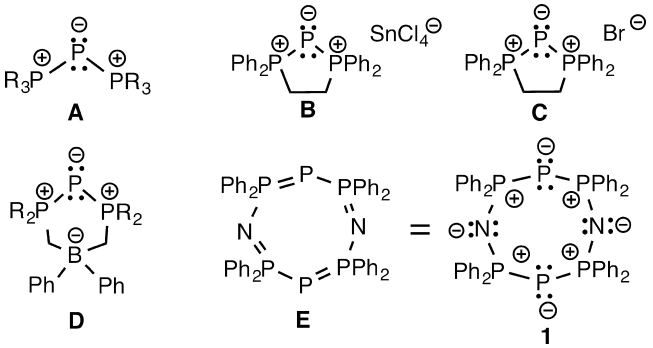


Figure 1. Triphosphenium species: a general depiction (A) and reported compounds (B, C), zwitterionic compounds (D, E, 1) featuring at least one P^I fragment.

access to other triphosphenium P^I salts is possible via ligand-exchange reactions[10] in which a relatively poor phosphine donor is replaced with a more strongly donating phosphine. The use of monodentate phosphine ligands to form acyclic P^I complexes has also been reported[7,11] (Figure 1A), although only a handful of these have been characterized comprehensively.

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Given the foregoing, anionic phosphinous ligands are particularly good ligands for generating P^I-containing compounds as they can readily displace neutral phosphine ligands. Importantly, the resultant zwitterionic products (e.g., Figure 1D)[12,13] are soluble in most organic solvents, and they can act as excellent ligands to various transition metals[13−15] with the capacity to bind one or two metal fragments simultaneously.[14]

In the context of larger molecules, we reasoned that the use of anionic, nonchelating linkers with P^I ions should lead to phosphorus-containing oligomers that are neutral overall. In fact, Schmidpeter and co-workers had previously reported compounds of this type (Figure 1E), which they had isolated from reactions of a phosphinous amide with P_4.[16] Notably, the heterocycle **E** is a phosphorus-rich isovalent analogue of phosphazenes, which are arguably the most useful class of phosphorus−nitrogen compounds and are precursors for polymers. Although phosphazenes are usually drawn with alternating single and double bonds to satisfy the rules of formal Lewis structures (Figure 2I), the more justifiable

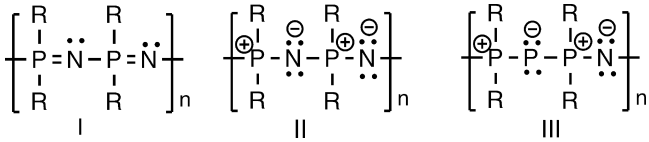


Figure 2. Lewis-type drawings structures of some phosphazene analogues. The typical depiction (I), a more justifiable depiction (II), and a related isolobal analogue in which one nitrogen fragment has been replaced by a P^I center.

zwitterionic Lewis-type description of the electron distribution (Figure 2II) highlights the electron-rich nature of the dicoordinate atom. In this canonical form, the dicoordinate nitrogen atom that bears two lone pairs of electrons is clearly isovalent with the univalent phosphorus centers in triphosphenium species. Given our experience in the development of methods for the preparation of triphosphenium ions[8] and our interest in the exploitation of the unique reactivity of this functional group, we reasoned that triphosphenium chemistry could provide a convenient route to make phosphorus-containing oligomers and perhaps polymers (Scheme 1).[17]

In this work, we demonstrate that the approach outlined in Scheme 1 can indeed be used to generate oligomers containing multiple P^I centers, we report the structural characterization of these heterocycles, and we demonstrate the utility of one of the macrocycles as a zwitterionic bisphosphanide-type ligand for noble metals.

RESULTS AND DISCUSSION

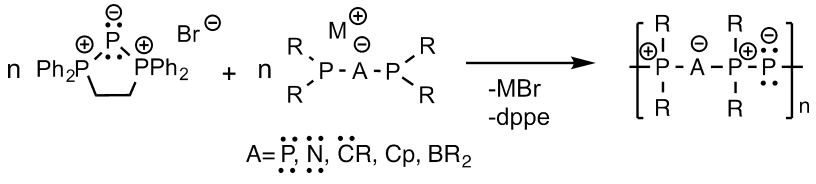
In the 1980s, Schmidpeter and co-workers were able to isolate the neutral, eight-membered ring compound **E** through the reaction of a phosphinous amide with elemental phosphorus.[16] However, the material was isolated in low yield (20%), and the reaction is complicated by the use of the highly toxic and pyrophoric P_4 reagent and by the formation of several polyphosphorus byproducts. Our experience with triphosphenium salts led us to posit that ligand exchange using a readily prepared, air-stable P^I precursor might provide a more convenient and generalizable route to such species.

To prove that hypothesis, we investigated the reaction of our easily prepared P^I source [dppeP][Br] (dppe = 1,2-bis(diphenylphosphino)ethane) with [Li][$N(PPh_2)_2$] in tetrahydrofuran (THF) in an effort to make **1**. Note that metalated phosphinous amide is notoriously difficult to isolate, so the lithiated amide was prepared and used in situ by adding excess butyl lithium to the amine precursor at −78 °C. The resultant mixture was allowed to stir for an hour and was then added to a solution of [dppeP][Br] in THF at −78 °C to produce compound **1** in very good isolated yield (79%). We have found that [dppeP][Br] is stable in the presence of many strong bases—at least for brief periods—so the reaction can also be done in one pot.

Surprisingly, the ^{31}P NMR spectrum of the compound we obtained is not consistent with the values reported originally for **1** by Schmidpeter and co-workers: they had noted that the spectrum of heterocycle **E** is indicative of an AA′A″A‴BB′ spin system using a spectrometer with a ^{31}P NMR frequency of 40.48 MHz (35.0 ppm, −141.5 ppm, $^1J_{P\text{-}P}$ = 429 Hz). In contrast, we observe a spectrum consistent with an $(A_2X)_2$ spin system with signals at 35.5 (d, $^1J_{P\text{-}P}$ = 423 Hz) and −140.2 (t, $^1J_{P\text{-}P}$ = 422 Hz) using a spectrometer with a ^{31}P NMR frequency of 121.5 MHz (Supporting Information, S-2). Thus, to confirm that we had indeed produced the same compound given the differences in the spectral data, we crystallized our compound from a concentrated dichloromethane solution and performed X-ray diffraction (XRD) experiments on the resultant material. The single-crystal structure (Figure 3) is indistinguishable from that reported previously and confirms the identity of the product and validates our synthetic approach. Powder XRD experiments on the bulk recrystallized material indicate that the only crystalline material is consistent with the single-crystal structure, and the reason for the difference in appearance of the ^{31}P NMR spectra remains unanswered. We had postulated that Schmidpeter and co-workers may have unintentionally collected the spectrum with ^1H coupling, but when we conducted our own ^1H-coupled ^{31}P NMR experiments to test this hypothesis, we were unable to obtain a spectrum similar to the reported one (Figures S-2 and S-3, Supporting Information).

The convenient and clean preparation of **1** (and analogous P-rich phosphazenes) allows for the investigation and development of such species as polydentate ligands or supramolecular building blocks. In fact, Schmidpeter had shown that **1** could form bidentate *P,P′*-complexes to Pd and Pt, but further

Scheme 1. Some Examples of Anion-Bridged Diphosphine Species That Could Undergo Ligand Exchange with a Triphosphenium P^I Salt (M = Li, Na, K, etc.)



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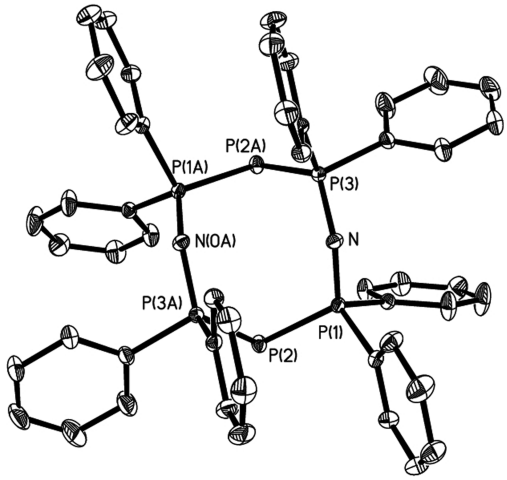

Figure 3. Thermal ellipsoid plot (30% probability surface) of the molecular structure of **1**. The hydrogen atoms and dichloromethane solvent of crystallization were removed for clarity. Selected metrical parameters are listed in Table 1.

investigations do not appear to have been pursued.[16] Thus, to probe the utility of **1** for other catalytically relevant species, we treated the zwitterion with some univalent group 11 halides.

NMR investigations indicate that the reaction of **1** with 1 equiv of CuBr results in the immediate formation of a complex featuring a different AX_2 spin system with chemical shifts at 28.6 (d, $^1J_{P-P}$ = 371.1 Hz) and −162.6 (t, $^1J_{P-P}$ = 369.0 Hz), which are consistent with the formation of a bidentate *P,P′*-complex. For the compound **1·CuBr**, we were able to grow crystals suitable for single-crystal X-ray diffraction from a concentrated solution in dichloromethane. The complex crystallizes in the space group C_2 with half a molecule and one disordered CH_2Cl_2 solvent molecule in the asymmetric unit. The molecular structure of the compound is illustrated in Figure 4 and confirms the formation of a κ^2-*P,P′* bidentate complex of **1** with CuBr. The Cu−Br distance of 2.3427(8) Å is consistent with those reported in the Cambridge Structural Database (CSD)[18] for compounds containing copper(I) bromide coordinated by two phosphorus atoms. Perhaps expectedly given the zwitterionic nature and geometrical constraints of the ligand, the unique P−Cu distance of 2.2953(10) Å is at the long end of the range of distances reported for phosphanido P−Cu bonds and is most comparable to the 2.286(2) Å phosphanido P−Cu distance observed in *cyclo*-$(P_5{}^tBu_4)Cu(PPh_3)_2$.[19] The P−Cu−P angle of 120.17(5)° is much wider than those observed in most other complexes of chelating diphosphine donors; however, it is on the smaller side of trans-spanning diphosphines and wide-bite angle diphosphines.[20−22] This is almost certainly a consequence of the geometrical constraints of the heterocyclic donor. It is perhaps worth noting that the $P^I\cdots P^I$ distance of 3.979(3) Å in **1·CuBr** is shorter than the corresponding value of 4.1101(7) Å in **1**. Consequently, the N···N distance of 3.449(1) in **1·CuBr** is longer than the N···N distance of 3.3018(6) Å in **1**. The molecules of **1·CuBr** pack in a manner reminiscent to the packing of badminton shuttlecocks: the Cu−Br fragment of one molecule is "cupped" by the aromatic substituents on an adjacent molecule (featuring six C_{aryl}−H···Br contacts under 3.3 Å with a closest pair being 3.1421(2) Å).

The related compound **1·AgBr** is generated upon the treatment of **1** with a suspension of silver(I) bromide in dichloromethane as evidenced by the signals at 30.5 (d, $^1J_{P-P}$ = 376), −157.3 (dt, $^1J_{P-P}$ = 383 Hz, $^1J_{Ag-P} \approx$ 113 Hz) in the ^{31}P NMR spectrum. Crystals of the complex **1·AgBr** were obtained from acetonitrile solution, and the material crystallizes in the space group C_2; there is no solvent of crystallization, but the structure of the metal complex is roughly isomorphous with that of **1·CuBr** (Figure 4). Both the Ag−Br distance (2.5000(12) Å) and P−Ag distance (2.4907(12) Å) are within, but toward the short end of, the range of bond lengths for reported compounds in the CSD containing a phosphine ligand coordinated to a terminal Ag−Br fragment. The P−Ag−P bond angle of **1·AgBr** (114.26(6)°) is considerably narrower than that of the lighter copper analogue (120.17(5)°); this is almost certainly a consequence of the larger size of the Ag^I ion, and it results in a much larger $P^I\cdots P^I$ separation (4.1837(2) Å) within the ligand. The N···N separation in **1·AgBr** (3.3699(1) Å) is also more similar to the value in the free ligand **1** rather than that seen in **1·CuBr**, so it appears as if the binding to silver(I) requires considerably less distortion of the ligand. However, it is worth noting that both coordination compounds **1·AgBr** and **1·CuBr** feature longer $P-P^I$ bond lengths and wider $P-P^I-P$

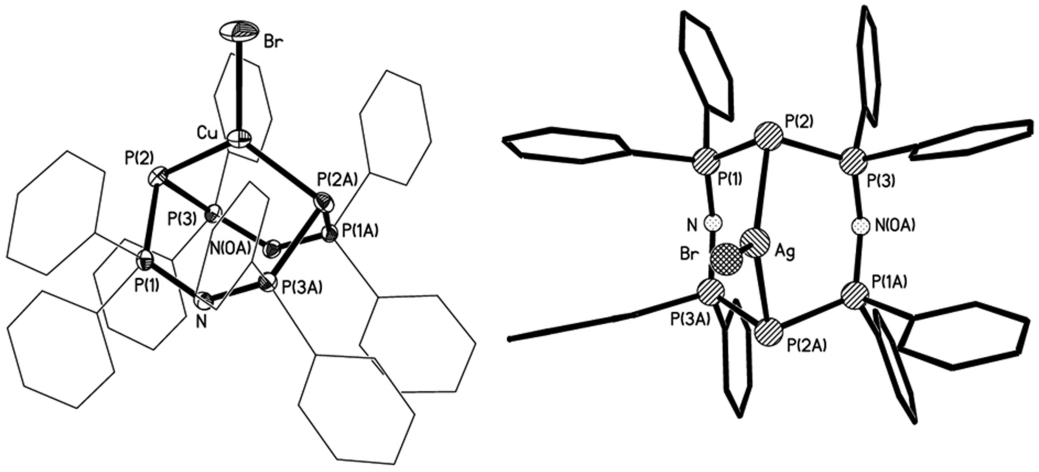

Figure 4. Thermal ellipsoid (30% probability) and ball-and-stick plots of **1·CuBr** and **1·AgBr**. Hydrogen atoms and the CH_2Cl_2 of crystallization for **1·CuBr** were removed; the phenyl substituents are presented in wire frame for clarity. Selected metrical parameters are listed in Table 1.

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Table 1. Selected Bond Lengths (Å), Angles (deg), and ^{31}P NMR Data for Structurally-Characterized Molecules in This Work

molecule	1	1·CuBr	1·AgBr	3	6
P–P^{I} (Å)	2.1390(6)	2.1654(12)	2.1625(16)	2.1635(7)	2.1259(11)
	2.1310(6)	2.1672(12)	2.1546(16)	2.2097(7)	2.1259(11)
P–P^{I}–P (deg)	95.44(2)	98.15(5)	98.50(6)	95.72(3)	100.82(4)
P–A[a] (Å)	1.5957(14)	1.595(3)	1.596(4)	1.6009(16)	1.746(3)
	1.6019(14)	1.600(3)	1.596(4)	1.6629(16)	1.758(3)
P–M (Å)		2.2952(10)	2.4906(12)		
		2.2953(10)	2.4907(12)		
δ ^{31}P (ppm)	35, d	28, d	31, d	123*, d	19, d
	−140, t	−162, t	−157, t	104**, d	−148, t
				−23, m	
				−150, m	
$^{1}J_{P-P}$ (Hz)	423	373	376	510*, 332**	459

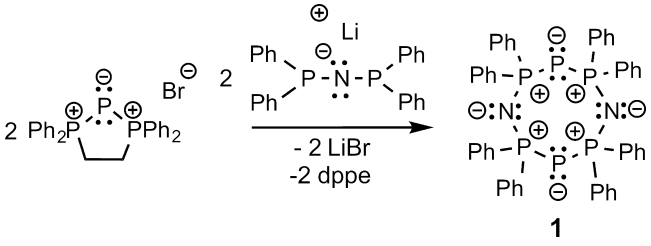
[a]Where A represents the bridging functionality: nitrogen for compounds **1**, **1·CuBr**, **1·AgBr**, and **3**; and carbon for compound **6**.

angles than proligand **1** (Table 1) as one would anticipate in light of the necessary decrease in negative hyperconjugation (i.e., $P^{I} \rightarrow PR_2$ backbonding) upon metal binding.

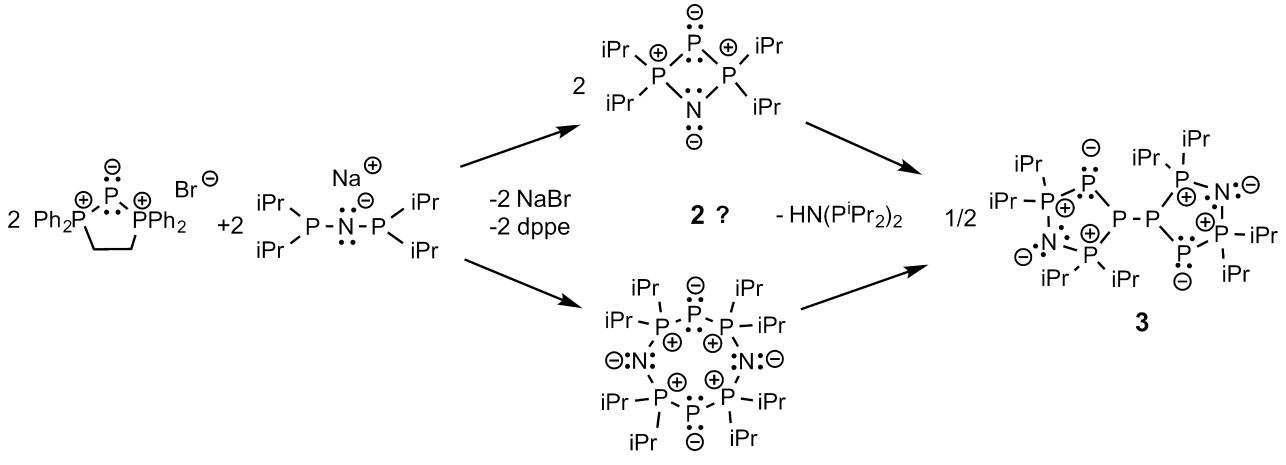
Although the ligand-exchange methodology outlined in Scheme 2 clearly works for **1**, we wish to emphasize that the stability of the resultant heterocycles is substituent-dependent, and this can affect the nature of the product obtained. For example, attempts to prepare the isopropyl-substituted analogue of **1** consistently produced the linked two-ring compound **3** (Scheme 3) rather than the analogous eight-membered ring. Even at low temperatures, ^{31}P NMR (Figure S-4, Supporting Information) experiments reveal the initial formation of a product (**2**) that exhibits a spectrum consistent with an AX_2 spin system with shifts at 78.9 (d, $^{1}J_{PP}$ = 271.7 Hz) and −162.6 (t, $^{1}J_{PP}$ = 271.7 Hz)—this could be either a four-membered triphosphenium zwitterion or the eight-membered ring analogue of **1**—but the compound rapidly transforms into a material that exhibits four chemically distinct phosphorus environments and generates byproducts including both the protonated proligand $(^{i}Pr_2P)_2NH$ and the anticipated dppe.

The identity of the product (**3**) was elucidated using single-crystal X-ray diffraction on a crystalline sample obtained at low temperature. The compound crystallizes in the space group $P2_1/n$ with one molecule in the asymmetric unit. The molecular structure of **3** (Figure 5) features two five-membered P_4N rings that are linked by a P–P bond to make an approximately centrosymmetric $[P_2(PC_2)_2N]_2$ dimer core. Although there are no examples of any P_4N rings in the CSD, the overall structure is clearly similar to that of the isolobal As_2P_2C dimer reported by Karsch and co-workers[23,24] and many other polyphosphorus compounds.[25] Each ring in **3** contains one dicoordinate P^{I} center featuring a short P–P bond distance (Table 1) to the adjacent tetracoordinate phosphorus atom (2.1435(7) Å and 2.1417 (7) Å) and a marginally longer bond to the tricoordinate phosphorus atom that links the two heterocycles (2.1635(7) Å and 2.1651(7) Å). Such short P–P bonds are

Scheme 2. Reaction of a Triphosphenium Bromide Reagent with a Salt Containing an Anionic, Nonchelating Bis(diphenylphosphino)amide Proligand to Produce 1



Scheme 3. Reaction of the Triphosphenium Bromide Precursor and Bis(isopropyl)phosphinoamide Ligand, Generating the Intermediate Molecule 2[a] and the Resulting Rearrangement Product 3



[a]Which may be either a four-membered or eight-membered ring.

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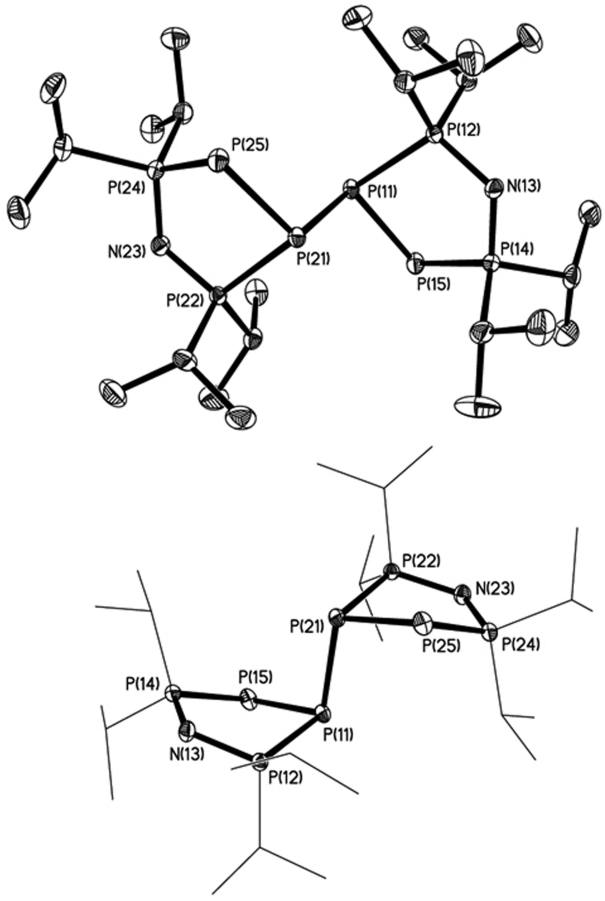


Figure 5. Thermal ellipsoid plots (30% probability) of **3**. Hydrogen atoms were removed for clarity. (upper) Ellipsoids for all atoms. (lower) Steplike dimeric arrangement. Selected metrical parameters are listed in Table 1.

consistent with those observed for other cyclic triphosphenium ions and related species.[9,26] In contrast, the 2.2647(7) Å P−P bond linking the two heterocycles lies at the long end of the range of P−P bonds reported in the CSD for tetraorganodiphosphines[18] and is considerably longer than the distances of 2.200 and 2.187 Å reported by Fritz and co-workers for two tetraphosphinodiphosphines.[27,28] The P−P−P angles for the dicoordinate phosphorus atoms of 95.72(3)° and 94.96(3)° are, as one would anticipate given the larger size of phosphorus, somewhat larger than those observed for five-membered ring triphosphenium cations of the type $[dppeP]^+$ and are more comparable to those observed in six-membered ring triphosphenium species.[9,10,12,26]

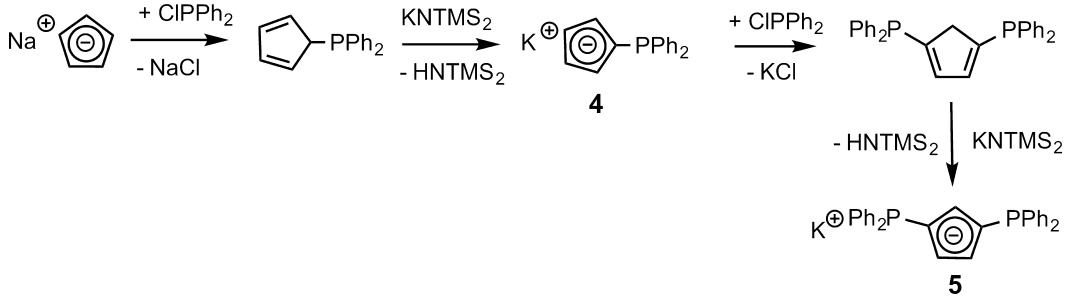
The formation of **3** from **2** involves the formal extrusion of one $(^iPr_2P)_2N$ fragment for each five-membered ring and the oxidative coupling of two P^I centers (Scheme 3). Although the mechanistic details of the process remain unclear, examination of putative models of the ^{i}Pr-substituted eight-membered ring (using the P_6N_2 core from **1**) suggest that the steric requirements of the isopropyl groups would engender considerable repulsion. Density functional theory geometry optimization (Supporting Information) suggests that the eight-membered ring is stable but only with a much more planar P_6N_2 core structure featuring a considerably longer $P^I\cdots P^I$ distance (4.90 vs 4.10 Å in **1**). Moreover, the nearly complete absence of bis(isopropyl)-substituted phosphazenes from the literature is noteworthy: in fact, there appears to be only one structurally characterized compound containing the repeat unit $[^iPr_2PN]_2$ in the CSD, and it is not a simple phosphazene.[29] Low-temperature ^{31}P NMR experiments only exhibit peaks attributable to **2** (Figure S-4, Supporting Information), and there is no indication of an anion of the form $[P((^iPr_2P)_2N)_2]^-$. Taken together, the evidence suggests that **3** is likely formed via the four-membered ring intermediate analogous to the compound $P(PPh_2)_2CSiMe_3$ reported by Karsch and co-workers,[24,30] rather than the eight-membered alternative.

We conducted a series of experiments in which the stoichiometry of the reagents was altered in an effort to optimize the yield of **3**. Interestingly, intermediate **2** is always observed regardless of the stoichiometric ratio of $[Na][(^iPr_2P)_2N]/[dppeP][Br]$ used, but compound **3** is formed only when the ratio is 1:1. We postulate that the extrusion of $HN(P(^iPr)_2)_2$ is essential in the formation of **3** and is not particularly surprising as this type of extrusion has been reported for compounds featuring similar ligands.[31] Unfortunately, efforts to characterize or identify intermediates other than **2** using NMR and EPR spectroscopy have not yet been successful.

In light of the successful generation of **1**, we wished to probe the applicability of the method to other diphosphines bridged by anionic linkers to produce larger neutral heterocycles containing multiple P^I centers. Toward this end we targeted the heterocycles derived from nonchelating 1,3-bis(diorganophosphine)cyclopentadienide ligands.

Although there are two reported syntheses of lithium 1,3-bis(diphenylphosphino)cyclopentadienide,[32,33] we were unable to isolate material of sufficient purity for further use with either of those methods, so we undertook the development of an improved approach to the preparation of such proligands. The method described by Brasse et al. had produced the most promising results in our hands, so we used this as a starting point.[32] Our modified synthesis (Scheme 4) is a stepwise

Scheme 4. Synthesis of Potassium 1,3-(Diphenylphosphino)cyclopentadienide, 5



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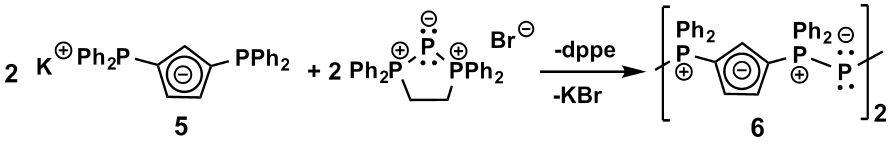
Scheme 5. Synthesis of the Heterocyclic Dimer 6 from 5 and the Triphosphenium Bromide P^I Precursor



approach that produces potassium 1,3-bis(diphenylphosphino)-cyclopentadienide (**5**) in excellent yield with no unanticipated byproducts.

With a pure salt of the anionic diphosphine ligand **5** in hand, the ligand-substitution reaction with [dppeP][Br] was investigated. ^{31}P NMR spectroscopy reveals that when a THF solution of **5** is mixed with a THF solution of [dppeP][Br], the heterocycle subsequently characterized as **6** is produced in quantitative yield (Scheme 5) with the concomitant generation of the anticipated dppe byproduct.

We discovered that is possible to precipitate the oligomeric product **6** selectively by exposing a diethyl ether solution of the crude product mixture (containing **6** and dppe) to sonication; the oligomer **6** may be collected as a pure product by filtration. It is worth noting, however, that the sonication of the mixture for a longer period (more than a few hours) results in the precipitation of mixtures containing some dppe in addition to **6**.

Crystals of **6** suitable for examination by single-crystal XRD were obtained by the slow vapor diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the heterocycle. The compound crystallizes in the space group $P\bar{1}$ with half of the molecule present in the asymmetric unit; the complete molecular structure is depicted in Figure 6. The P–P bond

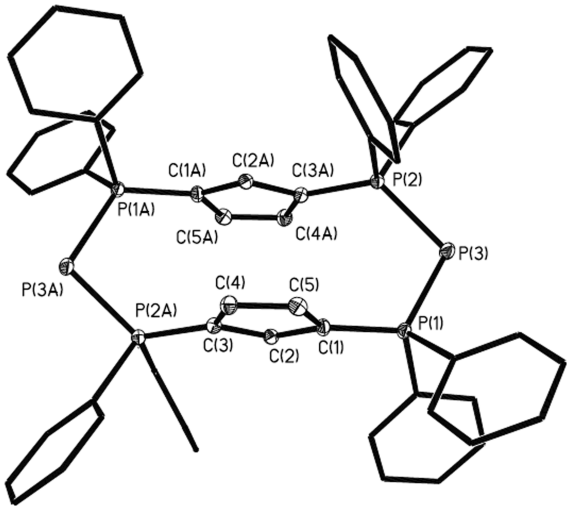


Figure 6. Thermal ellipsoid plot (30% probability plot) of the contents of the unit cell for **6**. Hydrogen atoms are removed and phenyl groups are in wire frame for clarity. Selected metrical parameters are listed in Table 1.

distances (Table 1) in macrocycle **6** fall within the ranges of distances (2.113(2)–2.184(2) Å) for cyclic triphosphenium complexes[6,8,10,34–36] reported in the CSD, but the P–P–P angle of 100.82(4)° is considerably larger and is more consistent with those of *acyclic* triphosphenium cations[35,37] The centroid-to-centroid distance between the two cyclopentadiene rings is 3.590 Å, and the interplanar spacing of the rings is 3.195 Å. Thus, it would appear as if the heterocycle should be capable of generating endocyclic sandwich-type complexes. The powder XRD pattern of the bulk material isolated by this recrystallization method is in excellent agreement with the pattern simulated on the basis of the single-crystal structure and confirms that sample contains only a single crystalline product (Figure S-9, Supporting Information). However, note that on one occasion we obtained a polymorph of this compound (also in the space group $P\bar{1}$; see the Supporting Information) in which the asymmetric unit contains an entire heterocycle and more than one diethyl ether molecule; data are of low quality, but the nonparallel arrangement of the cyclopentadienyl (Cp) fragments in the molecule suggests that macrocycle **6** can exhibit considerable conformational flexibility.

■ CONCLUSION

We have demonstrated that ligand exchange using stable P^I reagents is a viable synthetic approach for the preparation of electron-rich phosphorus-rich oligomers. The use of this protocol for the generation of such heterocycles appears only to be constrained by the preparation of suitable diphosphine ligands. We are currently evaluating a variety of methods for the reliable production of larger oligomers and the related polymeric species. Furthermore, the macrocycles presented herein are also being studied to assess their abilities to serve as multifunctional donors using both the dicoordinate P atoms and the bridging functionality (i.e., N or Cp).

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) bromide, sodium cyclopentadienide, and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) bromide was distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs'-type columns and were degassed prior to use. Deuterated THF (THF-d_8) was dried over sodium and benzophenone. The precursors $HN[P(^iPr_2)]_2$ and $NaN[P(^iPr_2)]_2$ were synthesized based on modified literature procedures,[38] and Cu(I)Cl was purified by a literature procedure.[39] NMR spectra were recorded at room temperature in THF-d_8 or CD_2Cl_2 solutions on a Bruker Advance 300-MHz spectrometer or Bruker Advance III 500 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards ($SiMe_4$ for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P). Coupling constant magnitudes, $|J|$, are given in Hz. The high-resolution mass spectra (HRMS) were obtained using electrospray ionization of acetonitrile solutions of species either by The McMaster Regional Centre for Mass Spectrometry, Hamilton, Canada or in house; calculated and reported mass/charge ratios are reported for the most intense signal of the isotopic pattern. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an Electrothermal Melting Point Apparatus. Elemental analysis was performed by Atlantic Microlabs, Norcross, Georgia, USA.

Specific Procedures. *[–N–PPh_2–P–PPh_2]$_2$–, (1).* To a flask containing $NH(PPh_2)_2$ (1.000 g, 2.59 mmol) in THF (50 mL) was added 1.3 equiv of *n*-BuLi (1.62 mL, 3.37 mmol) via syringe at −78 °C. The reaction mixture was stirred for 2 h and was then added to a −78 °C solution of [dppeP][Br] (1.321 g, 2.59 mmol) in THF (20 mL). The reaction was allowed to stir overnight before the resulting

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Table 2. Summary of X-ray Diffraction Collection and Refinement Details for the Feature Compounds Reported in This Work

	1	1·CuBr	1·AgBr	3	6
formula	$C_{49}H_{42}Cl_2N_2P_6$	$C_{49}H_{42}BrCl_2CuN_2P_6$	$C_{48}H_{40}N_2P_6AgBr$	$C_{24}H_{56}N_2P_8$	$C_{58}H_{46}P_6$
FW (g/mol)	915.56	1059.01	1018.42	620.46	928.77
T (K)	173(2)	173(2)	173(2)	150(2)	173(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2/n$	$C2$	$C2$	$P2_1/n$	$P\bar{1}$
a (Å)	12.153(2)	21.2636(18)	20.9310(9)	15.4287(13)	8.8331(7)
b (Å)	9.3574(16)	10.1246(7)	10.3138(4)	13.3702(12)	11.4721(10)
c (Å)	20.114(3)	15.1840(12)	12.3702(5)	17.2421(15)	12.3802(10)
α (deg)	90	90	90	90	74.9880(10)
β (deg)	90.115(2)	133.915(5)	124.1150(10)	109.4820(10)	72.7380(10)
γ (deg)	90	90	90	90	80.5270(10)
V (Å^3)	2287.3(7)	2354.8(3)	2210.91(16)	3353.1(5)	1151.90(16)
Z	2	2	2	4	1
ρ (Mg/m^3)	1.329	1.494	1.530	1.229	1.339
absorption coeff.	0.389 mm^{-1}	1.667 mm^{-1}	1.613 mm^{-1}	0.433 mm^{-1}	0.274 mm^{-1}
F(000)	948	1076	1028	1336	484
crystal size (mm^3)	0.9 × 0.7 × 0.7	0.4 × 0.35 × 0.25	0.19 × 0.10 × 0.02	0.5 × 0.5 × 0.4	0.1 × 0.1 × 0.1
θ data collection (deg)	2.401 to 27.498	3.567 to 30.00	3.296 to 26.383	1.536 to 27.498	1.767 to 27.492
index ranges	$-15 \le h \le 15$, $-12 \le k \le 12$, $-26 \le l \le 25$	$-27 \le h \le 29$, $-21 \le l \le 21$ $14 \le k \le 14$	$-24 \le h \le 26$, $-12 \le k \le 12$, $-15 \le l \le 15$	$-20 \le h \le 20$, $-17 \le k \le 17$, $-22 \le l \le 21$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-15 \le l \le 16$
reflections collected	24 924	31 572	26 616	37 787	13 098
indep. reflect.	5192	6779	4464	7654	5142
R(int)	0.0265	0.0806	0.0722	0.0412	0.0395
max., min. trans.	0.762, 0.618	0.659, 0.537	0.973, 0.836	0.841, 0.790	0.973, 0.916
refinement method			full-matrix least-squares on F^2		
data/restraints/parameters	5192/0/267	6779/14/282	4464/1/264	7654/0/323	5142/0/289
GOF[a], F^2	1.083	1.032	1.031	1.103	1.210
R_1, wR_2 $[I > 2\sigma(I)]$[a]	0.0392, 0.0950	0.0472, 0.1270	0.0323, 0.0669	0.0399, 0.0903	0.0565, 0.1433
R_1, wR_2 (all data)[a]	0.0434, 0.0978	0.0503, 0.1302	0.0392, 0.0697	0.0499, 0.0966	0.0749, 0.1764
diff. peak and hole (e·Å^{-3})	0.518, −0.226	1.194, −1.243	0.387, −0.698	0.551, −0.249	0.484, −0.488

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$, $wR_2 = [\ \Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)\ ]$. GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

solid was filtered and the solution was collected. Solvent was removed under reduced pressure and washed with hexane, which yielded a yellow solution containing dppe. The solvent was removed under reduced pressure, and the subsequent paste was then sonicated for 1 h in hexane and was filtered and washed with hot hexane (100 mL) to give the pale yellow solid **1**, 79% (0.850 g). Note: Although this is a known compound, the NMR data are not consistent with those previously reported, so these data are presented here: $^{31}P\{^1H\}$ NMR (THF-d_8): δ 35.5 (d, $^1J_{PP}$ = 423 Hz), −140.2 (t, $^1J_{PP}$ = 422 Hz); ^1H NMR (THF-d_8): δ 7.66−7.59 (m, 2H, Ph-*meta*); 7.12−7.09 (m, 1H, Ph-*para*); 7.10−6.98 (m, 2H, Ph-*ortho*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135.3 (d, J_{PC} = 93.98 Hz, Ph-*ipso*); 131.3 (s, Ph-*meta*); 129.7 (s, Ph-*para*); 129.7 (m, J_{PC} = 5.9 Hz, Ph-*ortho*).

*[−N−PPh$_2$−P−Ph$_2$−]$_2$CuBr, (**1·CuBr**).* To an orange solution of **1** (0.085g, 0.102 mmol) in dichloromethane was slowly added a suspension of white Cu(I)Br (0.0146g, 0.102 mmol) in dichloromethane, over the course of 5 min. The mixture was allowed to stir for 2 h, yielding a dark red mixture. The solution was centrifuged, and the resulting yellow-orange precipitate was collected. The solid was washed with cold dichloromethane twice to yield a golden-orange powder. Gold-colored crystals were obtained from dichloromethane. Yield: 60% (0.061g) $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.6 (d, $^1J_{PP}$ = 373 Hz), −162.5 (t, $^1J_{PP}$ = 373 Hz) ^1H NMR (deuterated dimethyl sulfoxide (DMSO-d_6)): δ 7.43 (m, 2H, Ph-*meta*); δ 7.56−7.59 (m, 1H, Ph-*para*); δ 7.71 (m, 2H, Ph-*ortho*). Anal. Calcd for $C_{48}H_{40}BrCuP_6N_2\cdot(CH_2Cl_2)$: C, 55.57; H, 4.00; N, 2.65; found: C, 53.57; H, 4.23; N, 2.04%.

*[−N−PPh$_2$−P−Ph$_2$−]$_2$AgBr, (**1·AgBr**).* As AgBr is light-sensitive, the reaction was performed in a dark room to avoid any degradation of the starting material. A suspension of AgBr (0.0137g, 0.734 mmol) in dichloromethane was added to a stirring orange solution of **1** (0.061g, 0.734 mmol) in dichloromethane over 10 min. The mixture was stirred for 30 min thereafter, yielding a light orange suspension. Solvent was removed under reduced pressure, the resulting powder was washed with THF, and the orange powder was collected using a frit. The product does not appear to be light-sensitive. Yield: 81% (0.061g) $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.5 (d, $^1J_{P\text{-}P}$ = 376), −157.3 (dt, $^1J_{P-P}$ = 383 Hz, $^1J_{Ag-P} \approx$ 113 Hz; due to a broadening of the triplet peaks, individual coupling to ^{107}Ag and ^{109}Ag could not be resolved). ^1H NMR (DMSO-d_6): δ 6.97 (m, Ph-*meta*, 1H), 7.04 (m, Ph-*meta*, 1H), 7.15 (m, Ph-*para*, 1H), 7.36 (m, Ph-*ortho*, 1H), 7.56 (m, Ph-*ortho*, 1H)

*Reaction of NaN(P(^{i}Pr)$_2$)$_2$ and [dppeP][Br] (**2**, **3**).* The white solids [Na][N(P(^{i}Pr)$_2$)$_2$] (0.184 g, 0.677 mmol) and [dppeP][Br] (0.379 g, 0.745 mmol) were added to a Schlenk flask and cooled to −78 °C in a dry ice−acetone bath. Approximately 40 mL of cold dichloromethane was added to the flask. The solution turned yellow immediately and was allowed to stir for 6 h at −78 °C. $^{31}P\{^1H\}$ NMR spectroscopy was performed on an aliquot of this stirring solution, showing evidence of the formation of **2** [$^{31}P\{^1H\}$ NMR: δ 82.0 (d, $^1J_{PP}$ = 273 Hz), δ −142.5 (t, $^1J_{PP}$ = 267 Hz)]; see Supporting Information, Figure S-4. The dichloromethane was removed from the resulting yellow-orange solution under reduced pressure, while maintaining a temperature of approximately 0 °C. To the resulting precipitate was added cold pentane, yielding a pale yellow solution. The solution was decanted

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and stored in a Schlenk flask under reduced pressure at −10 °C, yielding pale yellow crystals. Because of similarities in solubility, the isolated product, **3**, and the byproduct, $HN[P(^iPr)_2]_2$, were not able to be separated in our hands. $^{31}P\{^1H\}$ NMR of the product mixture (CD_2Cl_2): 67.7 (s, $HN[\mathbf{P}(^iPr)_2]_2$), −11.2 (s, dppe), 123.8 (d, $^1J_{PP}$ = 510 Hz, $(^iPr)_2P-N-\mathbf{P}(^iPr)_2-P^I-P$), 104.77 (d, $^1J_{PP}$ = 332.7 Hz), $(^iPr)_2\mathbf{P}-N-P(^iPr)_2-^I-P$), −23.3 (m, $(^iPr)_2P-N-P(^iPr)_2-P-\mathbf{P}$), −150.6 (m, $(^iPr)_2P-N-P(^iPr)_2-\mathbf{P}^1-P$).

*Potassium (Diphenylphosphino)cyclopentadienide, (**4**).* NaCp in diethyl ether (5.0 mL, 10.0 mmol) was added to a stirring solution of $ClPPh_2$ (2.251 g, 10.2 mmol) in diethyl ether (ca. 15 mL) at 30 °C. Upon addition, the reaction mixture turned red and gradually became orange after stirring for 2 h at which point the mixture was filtered through Celite© to remove NaCl. The filtrate was washed with diethyl ether, and volatiles were removed under reduced pressure. The resulting oil was dissolved in toluene and cooled to −78 °C, and a solution of $KN(SiMe_3)_2$ (2.074 g, 10.4 mmol) in toluene was added. A white precipitate that appeared upon the addition was isolated after stirring for 3 h and subsequently washed with diethyl ether yielding a white solid powder characterized as **4**. 97% (2.800 g, 0.97 mmol). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −17.6; ^1H NMR (THF-d_8): δ 7.33−7.29 (m, 4H, Ph-*ortho*); 7.14−7.07 (m, 8H, Ph- *meta/para*); 5.97−5.87 (m, 4H, C_5H_4); $^{13}C\{^1H\}$ NMR (THF-d_8): δ 147.26 (d, J_{PC} = 13.2 Hz, Ph-*ipso*); 133.72 (d, J_{PC} = 18.3 Hz, Ph-*ortho*); 127.98 (d, J_{PC} = 6.2 Hz, Ph-*meta*); 126.70 (s, Ph-*para*); 114.44 (d, J_{PC} = 22.7 Hz, C_5H_4P); 109.1 (d, J_{PC} = 10.1 Hz, C_5H_4P); 104.78 (d, J_{PC} = 4.2 Hz, C_5H_4P). HRMS: calcd for $C_{17}H_{14}P^-$ 249.0840, found 249.0833 (−2.8 ppm).

*Potassium 1,3-Bis(diphenylphosphino)cyclopentadienide, (**5**).* A solution of chlorodiphenylphosphine (2.306 g, 10.05 mmol) in toluene (ca. 80 mL) was added by cannula to a solution containing the previously prepared **4** (2.955 g, 10.2 mmol) in toluene (ca. 20 mL) at −78 °C. Upon addition, the solution underwent a color change to orange and gradually became yellow over time. The resulting solution was allowed to stir for 2 h and was then filtered through Celite© to remove the potassium chloride precipitate, which was subsequently washed with additional toluene (ca. 10 mL). The filtrate was cooled to −78 °C, and then a solution of $KN(SiMe_3)_2$ (2.125 g, 10.7 mmol) in toluene (ca. 30 mL) was slowly added. The resultant mixture immediately produced a white precipitate and was refluxed for 3 h. Diethyl ether (ca. 50 mL) was then added to the mixture, which was stirred for an additional hour. The resulting solid was collected by filtration and washed with diethyl ether (ca. 50 mL). Any remaining volatile components were removed from the solid under reduced pressure to afford a white powder characterized as **5**. 99% (4.800 g, 10.2 mmol). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −18.2; ^1H NMR (THF-d_8): δ 7.36−7.30 (m, 4H, Ph-*ortho*); 7.17−7.10 (m, 8H, Ph-*meta/para*); 7.36−7.30 (m, 1H, C5H3); 7.17−7.10 (m, 2H, C_5H_3); $^{13}C\{^1H\}$ NMR (THF-d_8): δ 146.0 (d, J_{PC} = 13.1 Hz, Ph-*ipso*); 133.8 (d, J_{PC} = 19.2 Hz, Ph-*ortho*); 128.2 (d, J_{PC} = 5.7 Hz, Ph-*meta*); 127.1 (s, Ph-*para*); 124.0 (t, J_{PC} = 20.1 Hz, C in $C_5H_3P_2$); 117.1 (dd, J_{PC} = 18.5 Hz, J_{PC} = 8.5 Hz, $C_5H_3P_2$); 110.4 (d, J_{PC} = 9.0 Hz, C in $C_5H_3P_2$). HRMS: calcd for $C_{29}H_{23}P_2^-$ 433.1283, found 433.1275 (−1.8 ppm). Anal. Calcd for $C_{29}H_{23}P_2K$: C, 73.7; H, 4.91; found: 71.2; H, 4.94%.

*[−C_5H_3−PPh$_2$−P−PPh$_2$−]$_2$, (**6**).* To a flask containing [dppeP][Br] (1.500 g, 2.95 mmol) in THF (20 mL) was added a solution of **5** (1.391 g, 2.95 mmol) in THF (30 mL) at −78 °C. The reaction mixture was stirred for 2 h before the resulting KBr was removed by filtration. The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in ether and subjected to ultrasonic agitation for 1 h. The product precipitated from the ether and was collected by filtration; removal of the volatile components provided a pale yellow solid characterized as **6**. 95% (1.300 g, 1.4 mmol). Crystals suitable for XRD were obtained by dissolving the powder in CH_2Cl_2 followed by vapor diffusion with Et_2O. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 19.71 (d, $^1J_{PP}$ = 459 Hz), −148.40 (t, $^1J_{PP}$ = 459 Hz); ^1H NMR (THF-d_8): δ 7.74−7.68 (m, 8H, Ph-*ortho*); 7.34−7.20 (m, 12H, Ph-*meta/para*); 6.21 (s, 1H, C_5H_3); 5.84 (s, 2H, C_5H_3); $^{13}C\{^1H\}$ NMR (THF-d_8): δ 134.9 (d, J_{PC} = 16.3 Hz, Ph-*ipso*); 133.6 (d, J_{PC} = 3.5 Hz, Ph-*ortho*); 131.2 (s, Ph-*meta*); 128.6 (s, Ph-*para*); 119.2 (broad singlet, $C_5H_3P_2$); 97.6 (broad singlet, $C_5H_3P_2$); (C_1 in $C_5H_3P_2$ not visible). Mp. 164−168 °C. Anal. Calcd for $C_{58}H_{46}P_6\cdot(C_4H_{10}O)$: C, 74.2; H, 5.63; found: 72.9; H, 5.02%.

X-ray Crystallography. Each crystal was covered in Nujol and placed rapidly into a cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using the SMART[40] software package on a Bruker APEX CCD diffractometer employing a graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) source or using the APEX2 software on a Bruker Photon 100 diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) source. Hemispheres of data were collected using counting times of 10−30 s per frame at −100 °C. The details of crystal data, data collection, and structure refinement are listed in Table 2. Data reductions were performed using the SAINT[41] implementations in the SMART or APEX2 software packages, and the data were corrected for absorption using SADABS.[42] The structures were solved by direct methods using SIR97[43] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2012[44] and the WinGX[45] software package; thermal ellipsoid plots were produced using SHELXTL.[46] Please note that for the metal complexes **1·CuBr** and **1·AgBr**, although only the predominant enantiomeric form within each experimental chiral crystal is depicted, both enantiomers should have an equal probability of formation. Powder XRD experiments were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using Cu Kα radiation (λ = 1.541 86 Å).

■ ASSOCIATED CONTENT

Supporting Information

$^{31}P\{^1H\}$ NMR spectra of compounds **1**−**6**. Crystal data and structure refinement for the polymorph of compound **6**. Crystallographic structural data in CIF format of studied compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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