Inorganic Chemistry
Article
Cite This: Inorg. Chem. XXXX, XXX, XXX–XXX
pubs.acs.org/IC

Ammonium and Potassium Salts of a Hexacoordinate Phosphorus(V) Anion Featuring P–O and P–C Bonds

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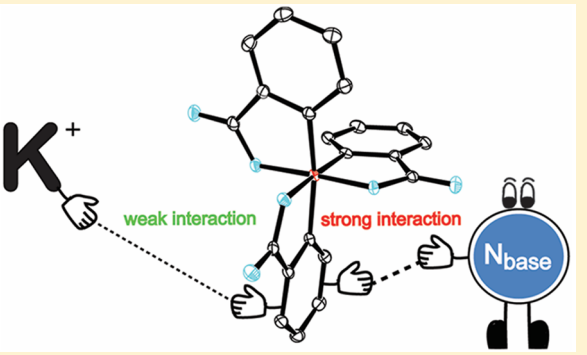
Supporting Information

ABSTRACT: Ammonium and potassium salts featuring the chiral *mer*-$[P(C_6H_4CO_2)_3]^-$, *mer*-$[\mathbf{1}]^-$, have been isolated. Specifically, treating phosphorane $P(C_6H_4CO_2)_2(C_6H_4CO_2H)$, **2**, with N-containing bases [N_{base} = $PhNMe_2$, $PhNH_2$, pyridine (py), isoquinoline, (−)-brucine, $N(n\text{-}C_8H_{17})_3$] afforded ammonium salts $[N_{base}H]^+$-*mer*-$[\mathbf{1}]^-$. Each compound was fully characterized spectroscopically, and four were subjected to X-ray crystallographic analysis. Salts were isolated with the racemic mixture of the *mer*-$[\mathbf{1}]^-$ anion except in the case of [(−)-brucineH]-Λ-*mer*-[**1**], for which the crystal analyzed was enantiomerically pure. The potassium salt, K-*mer*-[**1**], was synthesized by treating **2** with KH. The solid-state structure of K-*mer*-[**1**] is a coordination polymer consisting of seven- and eight-coordinate K^+ ions that are weakly bound by oxygen of either the racemic anion or the methanol solvent. Preliminary NMR and MS data for the formation of the Brønsted acid, $H(DMF)_n[\mathbf{1}]$, has also been obtained. An estimate of the basicity of anion *mer*-$[\mathbf{1}]^-$ was obtained from IR measurements of the N–H stretching frequency for $[(n\text{-}C_8H_{17})_3NH]$-*mer*-[**1**]. On the basis of these measurements, anion *mer*-$[\mathbf{1}]^-$ was ranked similar to the classical weakly coordinating anion, $[ClO_4]^-$, in terms of its coordinating ability.



INTRODUCTION

Phosphorus displays a tremendous diversity of coordination numbers in its compounds with the two extremes of one-coordinate (e.g., phosphaalkyne, phosphinidene) and six-coordinate (e.g., phosphate) systems being the rarest. Despite the fact that the simple anions $[PF_6]^-$ and $[PCl_6]^-$ are ubiquitous in inorganic chemistry, six-coordinate phosphorus(V) anions featuring organic substituents are rare (Figure 1). $[Et_3NH][P(1,2\text{-}(O_2C_6H_4)_3]$ was isolated in 1963 and represents the first salt featuring a hexacoordinate organophosphate anion (i.e., $[\mathbf{A}]^-$).[1] This catecholate system has evolved to the widely used chiral charge delocalized tris(tetrachlorobenzenediolato)phosphate, $[\mathbf{B}]^-$ (R = Cl), and the related binol-derivative, $[\mathbf{C}]^-$.[2] The tris(oxalato)phosphate anion, $[\mathbf{D}]^-$, has attracted attention as its lithium salt for potential application in lithium ion batteries.[3] The tris(pentafluoroethyl)trifluorophosphate anion, $[\mathbf{E}]^-$, has been widely used in ionic liquids.[4] Remarkably, the only known phosphorus(V) anion featuring P–C bonds, $[\mathbf{F}]^-$, was the first P(V) anion to be resolved into its optical isomers.[5]

Our group has been interested in the development of Brønsted acids featuring hexacoordinate phosphorus(V) anions as potential initiators for the cationic polymerization of olefins. For instance, we have reported a series of protic acids, $HL_2[\mathbf{B}]$ (L = Et_2O, THF, CH_3CN, DMF; R = Cl), and have shown that they are effective initiators for the polymerization of *n*-butyl vinyl ether, styrene, α-methylstyrene, *p*-methoxystyrene, and isoprene.[6,7] These weighable, solid initiators are particularly attractive due to their convenient one-pot synthesis from PCl_5 and $C_6Cl_4(OH)_2$ in the presence of a donor solvent L. In addition, these initiators are active for olefin polymerization at temperatures well above the industrial polymerization temperature of −100 °C used in butyl rubber production. The degree of ion-pairing during propagation plays a major role in the relative rates of propagation and chain transfer/termination. Therefore, optimizing the coordinating properties of the anion by varying the substituents within a hexacoordinate phosphorus(V) anion may permit polymerization activity at even higher temperatures. In this regard, we were drawn to the phosphorus(V) anion, *mer*-$[\mathbf{1}]^-$,[8] which features both P–O and P–C moieties (Figure 2).

Herein, we report the syntheses and crystallographic characterization of a series of ammonium $[N_{base}H]^+$ salts featuring anion *mer*-$[\mathbf{1}]^-$. The general synthetic methodology developed involves treating phosphorane $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (**2**) with various amines [N_{base} = $PhNMe_2$, $PhNH_2$, pyridine (py), isoquinoline, (−)-brucine, $N(n\text{-}C_8H_{17})_3$]. In addition, the potassium salt, K-*mer*-[**1**], was prepared by treating **2** with KH, and its solid state polymeric structure is examined to provide insight into the weakly coordinating nature of the PO_3C_3 anion.

Received: August 1, 2018

DOI: 10.1021/acs.inorgchem.8b02174
Inorg. Chem. XXXX, XXX, XXX–XXX

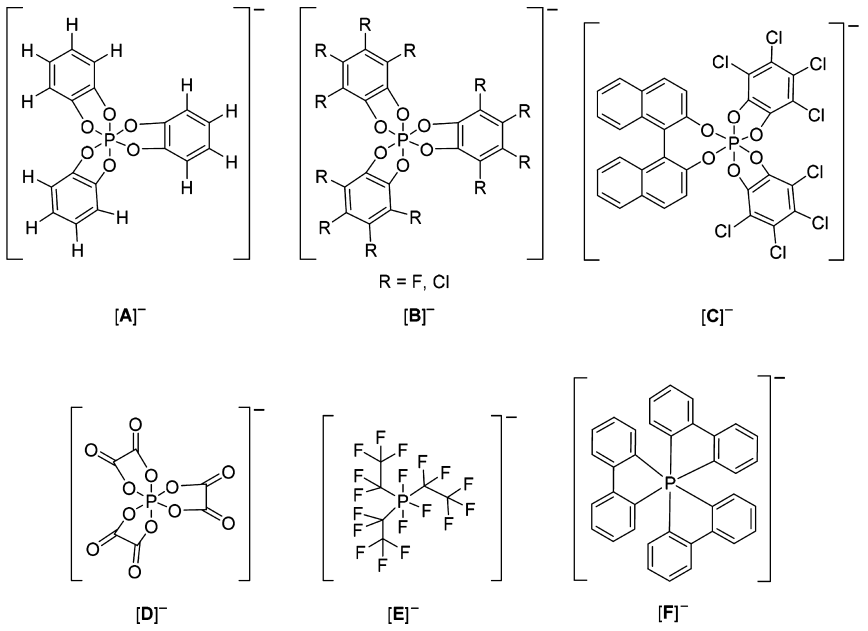


Figure 1. Examples of known hexacoordinate phosphorus(V) weakly coordinating anions.

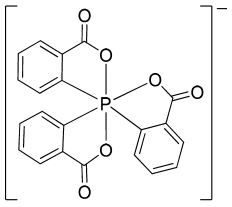


Figure 2. Hexacoordinate phosphorus(V) anion, $[P(C_6H_4CO_2)_3]^-$, *mer*-[**1**]$^-$.

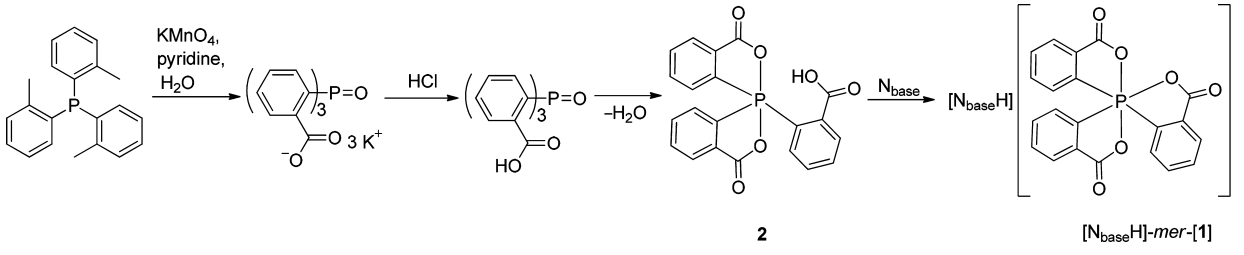
RESULTS AND DISCUSSION

Ammonium Salts of *mer*-[1]$^-$. Inspired by the single report of $[Et_2NH_2]^+$ and $[Et_3NH]^+$ salts of anion *mer*-[**1**]$^-$,[8] we prepared a series of ammonium salts as a starting point to explore the weakly coordinating anion (WCA) potential of *mer*-[**1**]$^-$. Initially, an acetone solution of acid P-$(C_6H_4CO_2)_2(C_6H_4COOH)$ (**2**) was treated with dimethylaniline ($PhNMe_2$) to afford $[PhNMe_2H]$-*mer*-[**1**] (Scheme 1). On the basis of these encouraging results, other bases were also explored [i.e., $PhNH_2$, pyridine (py), isoquinoline, (−)-brucine and tri(*n*-octyl)amine]. In some cases, excess base was needed to ensure quantitative conversion to the desired salt.

Each crude product purified by recrystallization (details given in the Experimental Section) and was subjected to detailed characterization to confirm its formulation. Colorless crystals suitable for X-ray crystallographic analysis were obtained for $[PhNMe_2H]$-*rac-mer*-[**1**], [pyH]-*rac-mer*-[**1**], [isoquinolineH]-*rac-mer*-[**1**], and [(−)-brucineH]-Λ-*mer*-[**1**]. The molecular structures of these ammonium salts are shown in Figure 4, and the metrical parameters will be discussed in detail below. Interestingly, the crystal that was selected for [(−)-brucineH]-*rac-mer*-[**1**] was revealed to be enantiomerically pure [(−)-brucineH]-Λ-*mer*-[**1**]. Spectroscopic analyses of the isolated complexes were performed in either acetone-d_6 or DMSO-d_6 due to their low solubility in other solvents. The $^{31}P\{^1H\}$ NMR spectra revealed dominant singlet resonances assigned to the desired anion *mer*-[**1**]$^-$ (range: −104.7 to −135.2 ppm, see Table 1) and are comparable to those previously reported for $[Et_2NH_2][1]$ and $[Et_3NH][1]$ (δ = −135.5 and −135.7 in DMF-d_7, respectively).[8]

In the case of $[PhNH_3]$-*mer*-[**1**], the $^{31}P\{^1H\}$ NMR spectrum in DMSO-d_6 was accompanied by a second signal at −55.7 ppm (ca. 5%). This downfield signal was assigned to **2**, which may be formed by the protonation of *mer*-[**1**]$^-$ with anilinium. This is not surprising since anilinium is the most acidic conjugate acid of the N_{bases} used in the present study. In contrast, regular monitoring of the $^{31}P\{^1H\}$ NMR spectra of solutions of all other salts in acetone-d_6 or DMSO-d_6 solutions showed only the signal attributed to *mer*-[**1**]$^-$, even after several weeks at ambient temperature. While the $^{31}P\{^1H\}$

Scheme 1. General Synthetic Route to $[N_{base}H]$-*mer*-[1] with N_{base} = $PhNMe_2$, $PhNH_2$, py, Isoquinoline, (−)-Brucine, and $N(n\text{-}C_8H_{17})_3$



DOI: 10.1021/acs.inorgchem.8b02174
Inorg. Chem. XXXX, XXX, XXX−XXX

Table 1. $^{31}P\{^1H\}$ and ^1H NMR Chemical Shifts of $[N_{base}H]$-*rac-mer*-[**1**]

	$[N_{base}H]^+$-*mer*-$[\mathbf{1}]^-$	
compound	δ ^{31}P	δ $^1H_{acidic}$
$[PhNMe_2H]$-*rac-mer*-[**1**]	−107.7[a]	9.31[a]
$[PhNH_3]$-*rac-mer*-[**1**]	−133.6[b]	6.56[b]
[pyH]-*rac-mer*-[**1**]	−126.8[a]	16.37[c]
[isoquinolineH]-*rac-mer*-[**1**]	−104.7[a]	16.34[c]
[(−)-brucineH]-*rac-mer*-[**1**]	−135.2[b]	10.60[b]
[(−)-brucineH]-*mer*-[**1**]	−114.3, −114.6[c]	12.63[c]
$[(n\text{-}C_8H_{17})_3NH]$-*rac-mer*-[**1**]	−128.9[a]	10.40[c]
$[NEt_2H_2][P(C_6H_4CO_2)_3]$	−135.5[d]	NA
$[NEt_3H][P(C_6H_4CO_2)_3]$	−135.7[d]	NA

[a]In acetone-d_6. [b]In DMSO-d_6. [c]In dichloromethane-d_2. [d]In DMF-d_7.[8]

NMR spectrum of [(−)-brucineH]-*mer*-[**1**] recorded in DMSO-d_6 showed only a singlet resonance (δ = −135.2), that recorded in CD_2Cl_2 displays two resonances (δ = −114.3 and −114.6), see Figure 3. Importantly, these signals cannot be

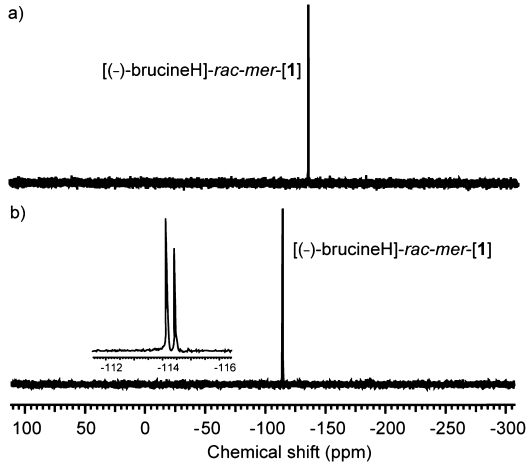


Figure 3. $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C) spectra of (a) [(−)-brucineH]-*rac-mer*-[**1**] recorded in $(CD_3)_2SO$ and (b) [(−)-brucineH]-*rac-mer*-[**1**] recorded in CD_2Cl_2 solvent.

assigned to the protonated form of *mer*-$[\mathbf{1}]^-$ (i.e., **2**). Therefore, we speculate that these observations indicate ion-pairing in the solvent of lower polarity (i.e., CD_2Cl_2) to afford the distinct diastereomers [(−)-brucineH]-Δ-*mer*-[**1**] and [(−)-brucineH]-Λ-*mer*-[**1**], which have slightly different chemical shifts than that of free *mer*-$[\mathbf{1}]^-$ ion. Although we cannot rule out the possibility of isomerization to *fac*-$[\mathbf{1}]^-$ form, it is highly unlikely given that the two signals are in a 1:1 ratio immediately upon dissolution. Such a rapid isomerization would be inconsistent with the slow rate we have previously observed for *mer*- to *fac*-isomerization of the related anion, $[P(OC_6H_4NMe)_3]^-$.[9]

The new ammonium salts were also characterized by ^1H NMR spectroscopy and the spectra were consistent with the assigned formulation $[N_{base}H]$-*rac-mer*-[**1**]. In each case, signals assigned to the acidic protons of $[N_{base}H]$-*rac-mer*-[**1**] were detected. Their chemical shifts will be discussed below and compared to those of related salts. It must be noted that in addition to anion−cation interactions, the ^1H chemical shifts of the $[N_{base}H]^+$ depend on the amount of base present, the solvent, the concentration, and the temperature. These signals displayed a wide range of chemical shifts. For instance, the signal assigned to the $[N_{base}H]^+$ proton of CD_2Cl_2 solutions of the isoquinolinium and pyridinium salts was 16.34 and 16.37 ppm, respectively. For comparison, the same proton of the pyridinium salt, $[pyH][As(N_3)_6]$, resonates slightly upfield [δ = 13.6 (in CD_2Cl_2)].[10] The chemical shifts of the acidic protons in the tertiary ammonium salts were similar to each other and at higher field to those described for the more acidic isoquinolinium and pyridinium salts {$[PhNMe_2H]$-*rac-mer*-[**1**]: δ = 9.31 in acetone-d_6; $[(n\text{-}C_8H_{17})_3NH]$-*rac-mer*-[**1**]: δ = 9.76 in acetone-d_6, 10.40 in CD_2Cl_2; [(−)-brucineH]-*rac-mer*-[**1**]: δ = 10.60 in DMSO-d_6; [(−)-brucineH]-Λ-*mer*-[**1**]: δ = 12.63 in CD_2Cl_2}. For comparison, the dimethylanilinium salt featuring a weakly coordinating fluoroarylborate anion, $[PhNMe_2H][HB(C_6F_5)_3]$, resonates at 8.88 ppm in CD_2Cl_2.[11] In contrast, the signal for the anilinium salt, $[PhNH_3]$-*rac-mer*-[**1**], appears at a much higher field [δ = 6.56 in DMSO-d_6] than the aforementioned salts and $[PhNH_3][BF_4]$ [δ = 8.20 in CD_3CN].[12]

Additional insight into the solution behavior of the new salts was gained from their $^{13}C\{^1H\}$ NMR spectra. Although the spectra displayed signals consistent with the assigned formulations, the signals assigned to the carboxylate ligands within *mer*-$[\mathbf{1}]^-$ for all salts were inequivalent and suggests a lowering of the predicted C_2 symmetry, perhaps due to weak ion pairing. Specifically, three distinct signals were observed that were assigned to the C=O moieties (range: δ = 163.9−170.7) and 18 resolved signals were observed that were assigned to the aromatic carbons. In the case of [(−)-brucineH]-*rac-mer*-[**1**], the $^{13}C\{^1H\}$ NMR spectrum revealed that most signals assigned to the anion were broadened or split when compared to those of enantiomerically pure [(−)-brucineH]-Λ-*mer*-[**1**]. This is most likely attributable to diastereotopism resulting from weak cation−anion interactions that differentiates [(−)-brucineH]-Δ-*mer*-[**1**] and [(−)-brucineH]-Λ-*mer*-[**1**]. A similar phenomenon was postulated above to account for the observed ^{31}P NMR spectrum of this compound. In conclusion, the $^{13}C\{^1H\}$ NMR spectroscopic data suggest a lowering of the expected symmetry of anion *mer*-$[\mathbf{1}]^-$ in solution that has not previously been observed with salts featuring the TRISPHAT anion, $[P(O_2C_6Cl_4)_3]^-$.[13,14] This asymmetry of *mer*-$[\mathbf{1}]^-$ will be discussed further in the next section, which describes the solid-state structures.

X-ray Crystallographic Characterization. Several of the new salts featuring $[\mathbf{1}]^-$ afforded single-crystals suitable for X-ray crystallographic analysis. Interestingly, each complex crystallizes as the *mer*-$[\mathbf{1}]^-$ isomer, and each has solvent molecules of crystallization. The molecular structures of $[PhNMe_2H]$-*rac-mer*-[**1**]·Me_2C=O, [pyH]-*rac-mer*-[**1**]·0.5 Me_2C=O, [isoquinolineH]-*rac-mer*-[**1**]·isoquinoline, and enantiomerically pure [(−)-brucineH]-Λ-*mer*-[**1**]·2 CH_2Cl_2 are displayed in Figure 4. The assignment of the Λ-configuration of *mer*-$[\mathbf{1}]^-$ in the latter structure is supported by the Flack parameter of 0.05(8).

In each salt, the closest cation−anion contact was a hydrogen-bonding interaction between the acidic N−H proton and the oxygen of a C=O moiety in $[\mathbf{1}]^-$. Specifically, these O···H distances were much shorter for $[PhNMe_2H]$-*rac-mer*-[**1**] [O(2)···H(1) = 1.67(3) Å] than [pyH]-*rac-mer*-[**1**] [O(2)···H(1) = 1.92(4) Å] and [(−)-brucineH]-Λ-*mer*-[**1**] [O(2)···H(1) = 1.88(1) Å]. In each case, these contacts are well within the sum of the van der Waals radii for oxygen and

DOI: 10.1021/acs.inorgchem.8b02174
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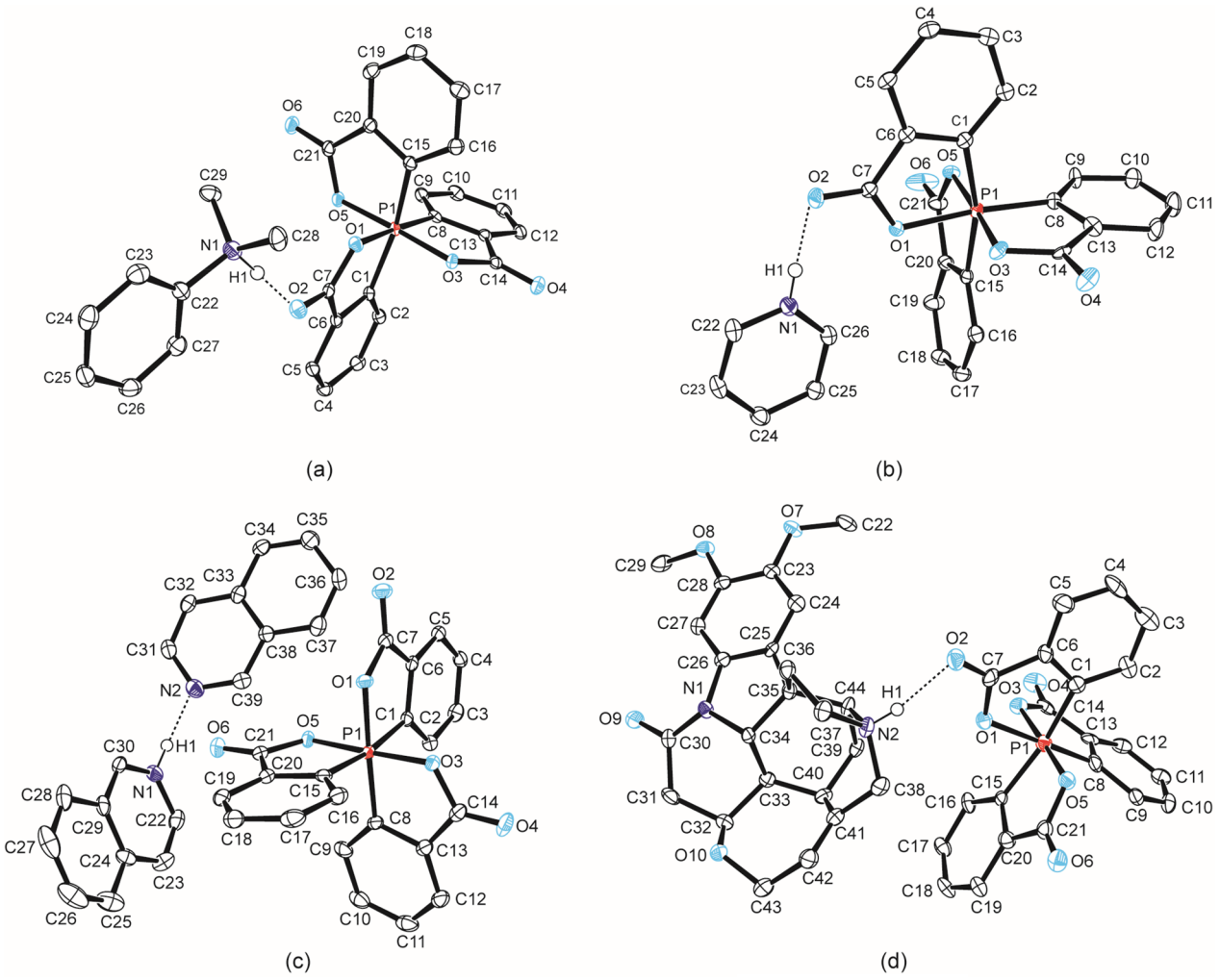


Figure 4. Molecular structures of: (a) [PhNMe$_2$H]-*rac-mer*-[**1**]·Me$_2$C═O (Λ isomer is shown); (b) [pyH]-*rac-mer*-[**1**]·0.5 Me$_2$C═O (Δ isomer is shown); (c) [isoquinolineH]-*rac-mer*-[**1**]·(C$_9$H$_7$N) (Δ isomer is shown); (d) [(−)-brucineH]-Λ-*mer*-[**1**]·2.02 CH$_2$Cl$_2$. Ellipsoids are drawn at the 50% probability level. Solvents of crystallization and hydrogen atoms are omitted for clarity, except for H(1). Only one enantiomer is shown in (a−c), whereas (d) is enantiomerically pure.

hydrogen [r_{vdw} = 2.72 Å] and suggest significant ion-pairing.[15] In contrast, the analogous O···H distance in [isoquinolineH]-*rac-mer*-[**1**] is 3.13(9) Å [O(6)···H(1)] suggesting little to no significant cation−anion interaction. This may be a consequence of the presence of a second hydrogen bonding interaction involving the isoquinoline solvent molecule [N(2)···H(1) = 1.76(8) Å, cf. r_{vdw} = 2.75 Å].[15] Similar H-bonding interactions have been reported for [isoquinoline-H]$_4$[isoquinoline]$_2$[Mo$_8$O$_{26}$] [N(3)···H(1A) = 1.84(1) Å].[16] No such interactions between the acidic N−H proton and solvent are present in the other salts.

Furthermore, there is a short cation−anion interaction in each salt involving the acidic nitrogen and the oxygen of a C═O moiety of [**1**]$^-$. These O···N distances were within the sum of the van der Waals radii for oxygen and nitrogen [r_{vdw} = 3.07 Å][16] and suggest some degree of ion-pairing {O(2)···N(1) = 2.713(3) Å, [PhNMe$_2$H]-*rac-mer*-[**1**]; O(2)···N(1) = 2.771(2) Å, [pyH]-*rac-mer*-[**1**]; O(2)···N(1) = 2.741(10) Å, [(−)-brucineH]-Λ-*mer*-[**1**]; and O(6)···N(1) = 2.936(6) Å, [isoquinolineH]-*rac-mer*-[**1**]}.

The ammonium salts show N−H distances within the cation that are typical of those found in related salts. For instance, the dimethylanilinium salt has an N−H distance of 1.04(3) Å [N(1)−H(1)], which is at the long end of the typical range [range: 0.84(5)−1.083(2) Å].[17] The pyridinium salt features a slightly shorter N−H distance of 0.85(4) Å [N(1)−H(1)] that is within the range found in related salts featuring [pyH]$^+$ [range: 0.77(6)−0.88(2) Å].[18] The analogous distance within [isoquinolineH]-*rac-mer*-[**1**] is 0.94(7) Å [N(1)−H(1)], which fits in the middle of the normal range [range: 0.848(8)−1.13(3) Å].[16,19] Likewise, the N−H distance in [(−)-brucineH]-Λ-*mer*-[**1**] [N(2)−H(1) = 0.88(9) Å] is also in the typical range [range: 0.80(3)−0.96(5) Å].[20]

As mentioned earlier, the solution NMR spectroscopic studies suggested that there was asymmetry within the phosphorus(V) anion [**1**]$^-$. In the solid state, this is immediately apparent on examination of the P−O bond lengths. In each case, the P−O bond to the carboxylate moiety that is H-bonded to the ammonium cation is significantly longer than the uncoordinated P−O bonds. For instance, the H-bonded P(1)−O(1) bond length in [PhNMe$_2$H]-*rac-mer*-[**1**] [1.92(1) Å] is significantly elongated relative to non-H-bonded P(1)−O(3) and P(1)−O(5) [1.778(1) and 1.774(1) Å], respectively. For comparison, these P(V)−O bond lengths are longer than those found in related hexacoordinate P(V) anions {e.g., 1.72 Å in [P(1,2-O$_2$C$_6$H$_4$)$_3$]$^-$, 1.71 Å in [P(1,2-

DOI: 10.1021/acs.inorgchem.8b02174
Inorg. Chem. XXXX, XXX, XXX−XXX

$O_2C_6Cl_4)_3]^-$, 1.69 Å in $[P(C_2O_4)_3]^-$}.[3,13,21,22] Virtually identical metrical parameters to those described above are observed in the molecular structures of [pyH]-*rac*-*mer*-[**1**] and [(−)-brucineH]-Λ-*mer*-[**1**]. Likewise, analogous observations were made with the previously characterized $[NEt_2H_2]$[**1**] and $[Et_3NH]$[**1**] $avg_{P(V)-O}$: 1.853(3) and 1.856(8) Å, respectively, which displays considerable asymmetry within *mer*-[**1**]$^-$ [$range_{P(V)-O}$: 1.746(1)−1.91(1) Å].[8]

Placement of [1]$^-$ on IR Scale for WCAs. On the basis of the above results which suggest significant coordinating properties for *mer*-[**1**]$^-$, we analyzed *mer*-[**1**]$^-$ in the context of the simple infrared scale proposed by Reed and co-workers to assess WCA properties.[23] Since there is no absolute scale to compare the WCA properties of specific anions,[24] this analysis provides a rough idea of the donor properties of *mer*-[**1**]$^-$. Specifically, we compared the N−H stretching frequencies of tri(*n*-octyl)ammonium salts of various anions, including *mer*-[**1**]$^-$, in the solid state and in solution. Solution spectra were recorded in carbon tetrachloride, where $(n\text{-}C_8H_{17})_3N^+$−H···A$^-$ contact ion pairs are typically formed to varying extents dependent upon the anion. The results for *mer*-[**1**]$^-$ and for common anions are presented in Table 2. The stretching

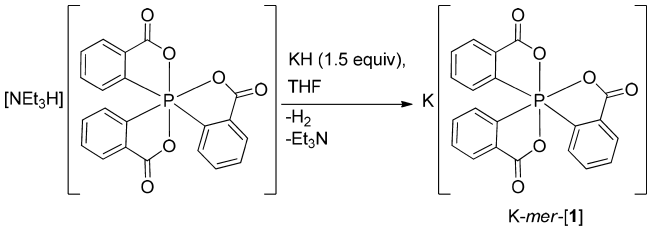
Table 2. ν_{N-H} Frequencies for $[(n\text{-}C_8H_{17})_3NH]^+$[anion]$^-$ Salts in CCl_4 and Solid State

[anion]$^-$	ν_{N-H} [cm^{-1}] in CCl_4 solution	ν_{N-H} [cm^{-1}] solid or wax	ref
$[B(C_6F_5)_4]^-$	3233	3241	23
$[PF_6]^-$	3191	3219	23
$[BF_4]^-$	3133	3156	23
$[P(1,2\text{-}O_2C_6H_4)_3]^-$	3129		25
$[N(SO_2CF_3)_2]^-$	3086		23
[**1**]$^-$	3069	3064	this work
$[ClO_4]^-$	3050	3098	23
$[CF_3SO_3]^-$	3031, 2801	3056, 2815	23
$[NO_3]^-$	2451	2571	23
$[Cl]^-$	2330	2452	23

frequency for $[(n\text{-}C_8H_{17})_3$ NH]-*rac*-*mer*-[**1**] in CCl_4 (ν_{N-H} = 3069 cm^{-1}, 0.01 M) was close to those of classical WCAs such as $[ClO_4]^-$ (ν_{N-H} = 3050, 2801 cm^{-1}) and $[N(SO_2CF_3)_2]^-$ (ν_{N-H} = 3086 cm^{-1}). For comparison, very weakly donating $[B(C_6F_5)_4]^-$ and $[CMeB_{11}F_{11}]^-$ rank much higher (ν_{N-H} = 3233 and 3219 cm^{-1}, respectively), whereas the strongly donating Cl$^-$ ranks much lower (ν_{N-H} = 2330 cm^{-1}). The results in the solid state also suggest that the WCA properties of *mer*-[**1**]$^-$ are comparable to perchlorate and triflamide according to this simple scale and are entirely consistent with the moderate cation−anion interactions described for *mer*-[**1**]$^-$ in solution and in the solid-state.

K$^+$ and H$^+$ Salts of [1]$^-$. With several ammonium salts in hand and a preliminary ranking of *mer*-[**1**]$^-$ on the WCA scale, we explored the potential synthesis of alkali metal based salts and stronger Brønsted acids featuring *mer*-[**1**]$^-$. Treating a THF solution of $[NEt_3H]$[**1**] with KH (1.5 equiv) resulted in the immediate evolution of a gaseous species (presumably H_2) (Scheme 2). Over 2 h, a colorless precipitate was observed that was separated and dried. The solid was dissolved in methanol-d_4, and the solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. A singlet resonance was observed at −127.6 ppm, consistent with the preservation of the anion *mer*-[**1**]$^-$. K-*mer*-[**1**] dissolves in H_2O. Analysis by ^{31}P NMR spectroscopy reveals one signal at −94.0 ppm, tentatively assigned to [**1**]$^-$. No change in the spectrum was observed after a few hours. Additional characterization by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as well as mass spectrometry {ESI (negative mode): *m*/*z* = 391.0, *mer*-[**1**]$^-$} supported the formulation of the product as K-*rac*-*mer*-[**1**].

Scheme 2. Synthetic Route to K-*mer*-[1]



Confirmation of this tentative assignment was obtained by X-ray crystallographic analysis of crystals obtained from the methanol-d_4 solution. The molecular structure is shown in Figure 5 and reveals that K-*rac*-*mer*-[**1**] is a coordination polymer with K$^+$ ions bridging the anion centers. There are two crystallographically unique *mer*-[**1**]$^-$ anions and three unique K$^+$ cations. Interestingly, K(2) is bound by two short and two long contacts to four different *mer*-[**1**]$^-$ anions [K(2)···O(6) = 2.660(2) Å, K(2)···O(8) = 2.668(2) Å, K(2)···O(12) = 2.926(2) Å, K(2)···O(2) = 3.019(2) Å] and by three methanol molecules [K···O_{avg} = 2.762(5) Å]. In contrast, K(1) and K(3) both sit on special positions and are bound by eight oxygen atoms. In each case, there are two short and two long K···O = C contacts [avg. = 2.727(3) and 3.038(3) Å], two K···O−P contacts [avg. 3.028(3) Å] and two K···OMe contacts [avg. = 2.787(5) Å]. The longer contacts involve binding of K$^+$ by two chelating CO_2 moieties of anion *mer*-[**1**]$^-$ (i.e., four K···O interactions), which are related by inversion symmetry around K$^+$. For comparison, a survey of the Cambridge Crystallographic Database revealed K···O = C contacts [between 2.678(2) and 3.135(3) Å][26] and K···O−Me contacts of methanol [2.750(2)−3.369(3) Å][27] Thus, the two short K···O=C contacts to anion *mer*-[**1**]$^-$ and the K···O−Me contacts are at the short end of this range. The two long K···O=C contacts are at the long end of this range. The K···O−P cation−anion contacts in K-*rac*-*mer*-[**1**] [avg. 3.028(3) Å] are slightly shorter than those found in related compounds {e.g., Δ,Δ-$K_2(DMSO)_6[P(1,2\text{-}O_2C_6H_4)_3]\cdot C_7H_8$ [avg. 2.855(3) Å],[28] $\{K(CH_3CN)_2[P(1,2\text{-}O_2C_6H_4)_3]\}_6$ [avg. 2.883(2) Å],[28] $K[P(C_{14}H_{20}O_2)_3]\cdot 1.5\ C_6H_6\cdot 2.5\ CH_3CN$ [avg. 2.783(5) Å],[29] and $K[P(H_2O_4)C_6H_4NO_2]\cdot CH_3OH$ [avg. 2.798(3) Å]}.[30]

Analogous to the aforementioned ammonium salts, the phosphorus(V) anion, *mer*-[**1**]$^-$, displays significant asymmetry. For instance, the P(1)−O(1) bond length [1.906(2) Å] is significantly longer than the P(1)−O(3) and P(1)−O(5) bonds [1.765(2) and 1.786(2) Å]. The situation is identical for P(2) with one long bond [P(2)−O(11) = 1.902(3) Å] and two short bonds [P(2)−O(7) = 1.785(2) Å, P(2)−O(9) = 1.767(2) Å]. It is peculiar that the elongated P−O bond in *mer*-[**1**]$^-$ is not involved in binding to K$^+$ in K-*rac*-*mer*-[**1**]. In contrast, the elongated P−O moiety within the anions of [PhNMe$_2$H]-*rac*-*mer*-[**1**], [pyH]-*rac*-*mer*-[**1**] and [(−)-brucineH]-Λ-*mer*-[**1**] is the atom involved in hydrogen bonding to the cation. In all salts we have crystallographically characterized, the P−C bond lengths in *mer*-[**1**]$^-$ do not show significant differences.

DOI: 10.1021/acs.inorgchem.8b02174
Inorg. Chem. XXXX, XXX, XXX−XXX

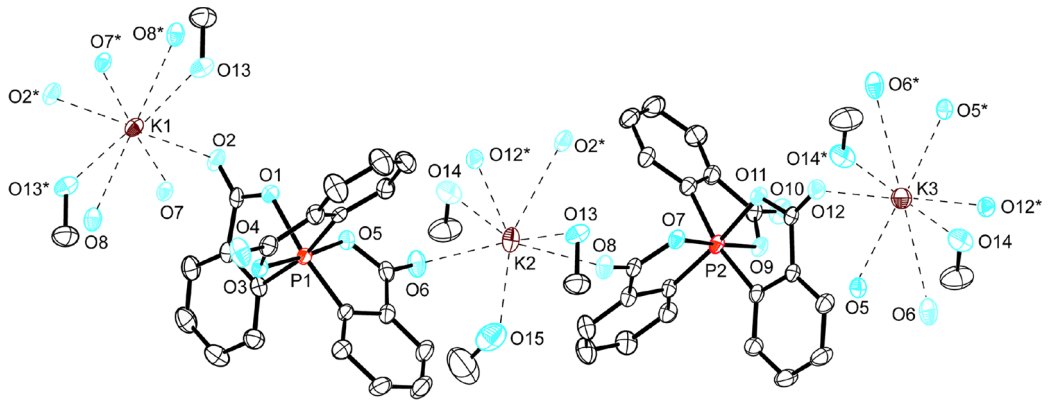


Figure 5. Extended structure showing the coordination polymer formed by K-*rac*-*mer*-[**1**]·3 CH_3OH (K-Δ,Δ-*mer*-[**1**] is shown). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. O(13), O(14), and O(15) are methanol solvate oxygen atoms. Oxygen atoms O(2), O(5), O(6), O(7), O(8), and O(12) are associated with anion *mer*-[**1**]$^-$ related by inversion symmetry and translation around K^+ with O(13)*, O(13), O(7)*, O(8)*, O(2)*, O(5)*, O(6)*, O(14)*, O(12)*, O(14), O(6), O(5), O(12)*, and O(2)*.

Finally, the potential synthesis of strong Brønsted acids of *mer*-[**1**]$^-$ was explored by dissolving phosphorane **2** in weakly basic solvents such as DMF. Heating the reaction mixture to 120 °C and monitoring the reaction progress by $^{31}P\{^1H\}$ NMR spectroscopy suggested the quantitative formation of *mer*-[**1**]$^-$ after 1 month. Namely, the signal assigned to phosphorane **2** (δ = −55.9) was replaced by two sharp singlet resonances at −134.6 and −138.9 ppm (ca. 9:1 ratio) (see Figure 6). The

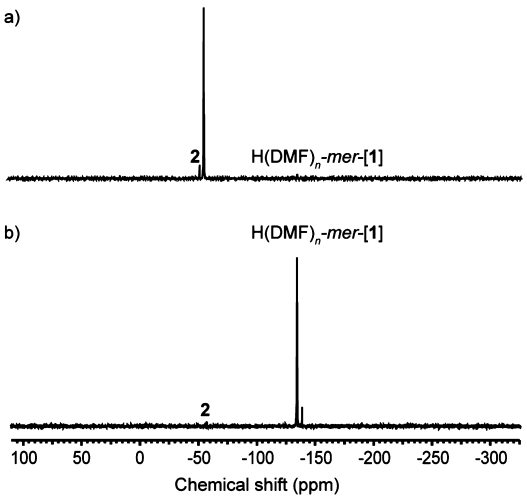
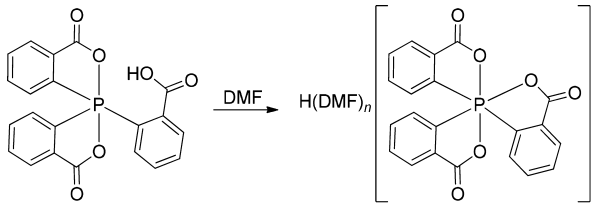


Figure 6. $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C) spectra of (a) reaction mixture of H(DMF)$_n$-*mer*-[**1**] recorded after 2 days and (b) reaction mixture of H(DMF)$_n$-*mer*-[**1**] recorded after ca. 4 weeks. **2** is phosphorane $P(C_6H_4CO_2)_2(C_6H_4COOH)$.

chemical shift of the signals assigned to these anions is consistent with that previously observed for anion *mer*-[**1**]$^-$ (Table 1). The presence of two signals may suggest that both *mer*-and *fac*-isomers are present or, similar to that postulated for [(−)-brucineH]-*mer*-[**1**], strong ion-pairing is observed. Although attempts to isolate or crystallize this product were not successful, the major signal in the electrospray mass spectrum (ESI−MS, negative mode) was consistent with the formulation of [**1**]$^-$ (m/z = 390.9; calcd mass of *mer*-[**1**]$^-$ = 391.0). Moreover, the positive mode ESI-MS showed a signal that may be consistent with the cation [H(DMF)]$^+$ (m/z = 74.4; calcd for $C_3H_8N_1O_1$: m/z = 74.1). On the basis of these preliminary data, efforts are underway to isolate this postulated Brønsted acid of *mer*-[**1**]$^-$ (Scheme 3).

Scheme 3. Proposed Route to H(DMF)$_n$-*mer*-[1] ($n \geq 1$)



SUMMARY

The synthesis, isolation, and characterization of a series of salts incorporating the hexacoordinate phosphorus(V) anion *mer*-[**1**]$^-$ has been reported. These compounds were conveniently obtained by treating phosphorane $P(C_6H_4CO_2)_2(C_6H_4COOH)$ with an N-containing base or KH. Significantly, the crystal structures of [pyH]-*rac*-*mer*-[**1**], [isoquinolineH]-*rac*-*mer*-[**1**], [(−)-brucineH]−Λ-*mer*-[**1**], [PhNMe$_2$H]-*rac*-*mer*-[**1**], and K-*rac*-*mer*-[**1**] were obtained. In the case of enantiomerically pure (−)-brucine, the solution data suggests two diastereomers in solution whereas the solid state structure determined was for enantiomerically pure [(−)-brucineH]-Λ-*mer*-[**1**]. The solid-state structure of K-*rac*-*mer*-[**1**] reveals a coordination polymer with K^+ ions bridging the anion centers. A preliminary assessment of the basicity of the *mer*-[**1**]$^-$ was conducted and revealed that the tri(*n*-octylammonium) salt has a ν_{N-H} frequency similar to those of the salts of $[ClO_4]^-$ and $[CF_3SO_3]^-$. Finally, preliminary evidence for the potential synthesis of the Brønsted acid, H(DMF)$_n$-*mer*-[**1**], has been obtained. Future work will explore the potential isolation of these novel protic species and the possible applications of the *mer*-[**1**]$^-$ ion as a novel WCA for application in catalysis and polymerization.

EXPERIMENTAL SECTION

All experiments were performed using standard Schlenk or glovebox techniques under nitrogen atmosphere. CH_2Cl_2 (Sigma-Aldrich) was deoxygenated with nitrogen and dried by passing through a column containing activated, basic alumina. Subsequently, the CH_2Cl_2 was

DOI: 10.1021/acs.inorgchem.8b02174
Inorg. Chem. XXXX, XXX, XXX−XXX

dried over CaH_2, freshly distilled, and freeze−pump−thaw (×3) degassed. Acetonitrile (Sigma-Aldrich) and DMF (Fisher Scientific) were dried over calcium hydride, freshly distilled, and freeze−pump−thaw (×3) degassed. Acetone (Fisher Scientific) was dried over calcium sulfate and freshly distilled. For extended periods of storage (1 day to 2 weeks), anhydrous solvents were stored over 3 Å molecular sieves. THF (Fisher Scientific) was freshly distilled from sodium/benzophenone ketyl immediately prior to use. Potassium hydride (30 wt % dispersion in mineral oil) was purchased from Sigma-Aldrich, washed with hexanes, and dried *in vacuo* prior to use. (−)-Brucine (Sigma-Aldrich) was dried under vacuum at 40 °C prior to use. Aniline (Sigma-Aldrich) and *N*,*N*′-dimethylaniline (Sigma-Aldrich) were dried over CaH_2 and freshly distilled under partial vacuum at 40 °C. Pyridine (Fisher Scientific), trimethylamine (Fisher Scientific), isoquinoline (Sigma-Aldrich), and *N*,*N*′-dimethylaniline (Acros Organics) were distilled under partial vacuum at 30−50 °C. Tri(*n*-octyl)amine, $[N(n\text{-}C_8H_{17})_3]$ (Sigma-Aldrich), was degassed with N_2 gas prior to use. $(C_6H_4CO_2)_2P(C_6H_4CO_2H)$, **2**,[31] and $[HNEt_3][P(C_6H_4CO_2)_3]$[8] were prepared following literature procedure. Elemental analyses, mass spectrometry, and NMR spectra were performed in the University of British Columbia Facilities. Low resolution electrospray ionization mass spectra, ESI-LRMS, were recorded on Bruker Esquire LC mass spectrometer. High-resolution electrospray ionization mass spectra, ESI-HRMS, were recorded on Micromass LCT time-of-flight (TOF) mass spectrometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 400 MHz spectrometers at ambient temperature unless noted. H_3PO_4 (85%) was used as external standard for ^{31}P NMR spectra with δ = 0.0. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were referenced to deuterated solvents. Infrared spectra were recorded either in powder form or in CCl_4 solution {0.01 M for $[(n\text{-}C_8H_{17})_3NH][$**1**$]$} on a PerkinElmer FT-IR Frontier spectrometer.

Synthesis of [PhNMe$_2$H]-*mer*-[1]. $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.11 g, 0.28 mmol) was dissolved in anhydrous acetone (3 mL). To the colorless solution was added anhydrous *N*,*N*′-dimethylaniline (0.16 mL, 0.15 g, 1.23 mmol). The solution was stirred overnight and concentrated *in vacuo* to afford a colorless precipitate. The crude product was washed with a minimal amount of acetone and dried *in vacuo*. Single crystals suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of the crude product in anhydrous acetone (−30 °C, ca. 2 weeks). Yield = 0.23 g (includes acetone of crystallization).

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$, 25 °C): δ −107.7. ^1H NMR (400 MHz, $(CD_3)_2CO$, 25 °C): δ 9.31 (br s, 1H, $N(CH_3)_2C_6H_5H$), 8.14−8.04 (m, 5H, Ar−*H*), 7.89−7.81 (m, 4H, Ar−*H*), 7.63−7.55 (m, 2H, Ar−*H*), 7.34−7.29 (m, 1H, Ar−*H*), 7.28−7.24 (m, 2H, $N(CH_3)_2C_6H_5H$), 6.95−6.91 (m, 2H, $N(CH_3)_2C_6H_5H$), 6.84−6.80 (tt, J_{HH} = 7.3 Hz, 1H, $N(CH_3)_2C_6H_5H$), 2.97(s, 6H, $N(CH_3)_2C_6H_5H$). $^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2CO$, 25 °C): δ 168.2 (s, *C*═O), 168.1 (s, *C*═O), 165.2 (s, *C*═O), 149.4 (s, $N(CH_3)_2C_6H_5H$), 141.2 (s, Ar−*C*), 140.8 (s, Ar−*C*), 139.7 (s, Ar−*C*), 138.8 (s, Ar−*C*), 135.1 (s, Ar−*C*), 134.9 (s, Ar−*C*), 134.3 (s, Ar−*C*), 134.1 (s, Ar−*C*), 133.6 (d, J_{CP} = 3.7 Hz, Ar−*C*), 132.5 (s, Ar−*C*), 132.3 (d, J_{CP} = 5.1 Hz, Ar−*C*), 132.2 (s, Ar−*C*), 130.4 (s, Ar−*C*), 130.3 (s, Ar−*C*), 130.1 (d, J_{CP} = 5.1 Hz, Ar−*C*), 129.3 (s, Ar−*C*), 129.1 (s, $N(CH_3)_2C_6H_5H$), 129.0 (s, Ar−*C*), 128.9 (s, Ar−*C*), 126.7 (s, $N(CH_3)_2C_6H_5H$), 126.5 (s, $N(CH_3)_2C_6H_5H$), 118.1 (s, $N(CH_3)_2C_6H_5H$), 114.0 (s, $N(CH_3)_2C_6H_5H$), 40.9 (s, $N(CH_3)_2C_6H_5H$). IR (neat) ν: 3405 (vw), 3055 (vw), 3035 (vw), 2966 (vw), 2670 (vw), 1700 (s), 1644 (m), 1633 (sh, m), 1592 (m), 1574 (m), 1511 (m), 1495 (m), 1452 (m), 1353 (m), 1299 (vw), 1277 (s), 1241 (s), 1195 (w), 1159 (w), 1125 (s), 1110 (s), 1061(s), 1024 (w), 994 (w), 904 (m), 852 (s), 769 (m), 748 (s), 728 (sm), 700 (s), 684 (s) cm^{-1}. LRMS (ESI, positive mode) m/z = 122.3 $[M]^+$. HRMS (ESI/TOF, negative mode) m/z = $[M]^-$ calcd for $C_{21}H_{12}O_6P_1$ 391.0372, found 391.0373.

Synthesis of [PhNH$_3$]-*mer*-[1]. $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.15 g, 0.38 mmol) was dissolved in anhydrous *N*,*N*-dimethylformamide (4 mL). The white suspension was stirred at ambient temperature for 40 min until fully dissolved. Upon addition of anhydrous aniline (2.00 mL, 2.05 g, 22.0 mmol), a colorless solution was obtained, which was concentrated *in vacuo* to give a colorless oil. The oily residue was washed with anhydrous dimethylformamide. Yield = 0.28 g (includes *N*,*N*-dimethylformamide). A ∼5 mg sample was prepared for elemental analysis by drying *in vacuo* for ca. 1 day at 40 °C.

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2SO$, 25 °C): δ −133.6. ^1H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ 7.84−7.22 (m, 11H, Ar−*H*), 7.17−6.78 (m, 5H, $PhNH_3$−Ar−*H*), 6.56 (br s, 3H, $PhNH_3$), 6.10 (dd, J_{HH} = 7.4 Hz, 1H, Ar−*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2SO$, 25 °C): δ 168.6 (s, *C*═O), 167.2 (s, *C*═O), 167.1 (s, *C*═O), 156.9 (s, Ar−*C*), 154.0 (s, Ar−*C*), 145.0 (s, $PhNH_3$, Ar−*C*), 142.3 (s, Ar−*C*), 133.6 (s, Ar−*C*), 133.4 (s, Ar−*C*), 132.7 (s, Ar−*C*), 132.4 (s, Ar−*C*), 131.6 (s, Ar−*C*), 131.4 (s, Ar−*C*), 129.9 (s, Ar−*C*), 129.5 (s, $PhNH_3$, Ar−*C*), 129.4 (d, J_{CP} = 6.1 Hz, Ar−*C*), 129.1 (d, J_{CP} = 3.3 Hz, Ar−*C*), 126.7 (s, Ar−*C*), 126.3 (d, J_{CP} = 14.4 Hz, Ar−*C*), 125.0 (s, Ar−*C*), 124.8 (s, Ar−*C*), 121.2 (s, Ar−*C*), 119.7 (s, Ar−*C*), 119.2 (s, $PhNH_3$, Ar−*C*), 116.6 (s, $PhNH_3$, Ar−*C*). IR (neat) ν: 3354 (vw), 3081 (vw), 3021 (vw), 2935 (vw), 2864 (vw), 1721 (m), 1754 (s), 1653 (s), 1594 (m), 1498 (w), 1483 (w), 1458 (s), 1397 (w), 1338 (m), 1292, (s), 1276 (s), 1253 (m), 1242 (s), 1123 (s), 1108 (s), 1063 (s), 1023 (w), 967 (w), 855 (s), 816 (m), 745 (s), 729 (m), 698 (s), 687 (s) cm^{-1}. Elem. anal. calcd for $C_{27}H_{20}N_1O_6P_1{\cdot}0.15\ C_3H_7N_1O_1$: C, 66.42; H, 4.27; N, 3.27. Found: C, 66.57; H, 4.07; N, 3.51.

Synthesis of [pyH]-*mer*-[1]. To a solution of $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.36 g, 0.92 mmol) in anhydrous acetone (7 mL) was added pyridine (0.10 mL, 0.10 g, 1.26 mmol), and the colorless reaction mixture was stirred for 2 h at ambient temperature to afford a colorless precipitate. The precipitate was filtered, washed with cold acetone (1.2 mL), and dried *in vacuo*. Yield = 0.26 g, 60%. Single crystals suitable for X-ray crystallography were isolated by cooling a saturated solution of the crude product in CH_2Cl_2/hexane (1:1) to −30 °C.

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$, 25 °C): δ −126.8. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ −118.1. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 16.37 (s, 1H, C_5H_5NH), 8.45 (d, J_{HH} = 7.3 Hz, 2H, Ar−*H*), 8.11−8.02 (m, 5H, Ar−*H*), 7.73−7.69 (m, 4H, Ar−*H*), 7.54−7.48 (m, 3H, C_5H_5NH), 7.46−7.41(m, 1H, C_5H_5NH), 7.11 (d, J_{HH} = 6.4 Hz, 1H, C_5H_5NH), 7.06 (d, J_{HH} = 7.3 Hz, 1H, Ar−*H*). ^1H NMR (400 MHz, $(CD_3)_2CO$, 25 °C): δ 15.18 (br s, 1H, N−*H*). $^{13}C\{^1H\}$ NMR (101 MHz CD_2Cl_2, 25 °C): δ 170.2 (s, *C*═O), 170.1 (s, *C*═O), 166.0 (s, *C*═O), 146.2 (s, C_5H_5NH), 141.2 (s, Ar−*C*), 140.1 (s, Ar−*C*), 139.8 (s, C_5H_5NH), 138.1 (s, Ar−*C*), 134.9 (s, Ar−*C*), 134.7 (s, Ar−*C*), 134.1 (s, Ar−*C*), 133.9 (s, Ar−*C*), 133.2 (d, J_{CP} = 2.9 Hz, Ar−*C*), 132.4 (d, J_{CP} = 2.9 Hz, Ar−*C*), 132.1 (s, Ar−*C*), 131.9 (s, Ar−*C*), 131.2 (s, Ar−*C*), 131.1 (s, Ar−*C*), 130.1 (d, J_{CP} = 3.7 Hz, Ar−*C*), 129.3 (s, Ar−*C*), 129.2 (s, Ar−*C*), 129.0 (s, Ar−*C*), 128.9 (s, Ar−*C*), 126.8 (s, C_5H_5NH), 126.7 (s, C_5H_5NH), 125.0 (s, C_5H_5NH). IR (neat) ν: 3187 (vw), 3132 (vw), 3101 (w), 3068 (vw), 2141 (vw), 1721 (m), 1699 (s), 1638 (m), 1613 (sh, m), 1593 (sh, m), 1574 (w), 1548 (m), 1482 (m), 1455 (m), 1399 (vw), 1352 (m), 1309 (w), 1274 (s), 1239 (s), 1159 (m), 1127 (m), 1112 (s), 1065 (m), 1059 (m), 1025 (w), 1001 (w), 881 (vw), 854 (s), 819 (w), 759 (s), 730 (m), 669 (s), 661 (s) cm^{-1}. Elem. anal. calcd for $C_{26}H_{18}NO_6P_1{\cdot}0.2\ CH_2Cl_2$: C, 64.87; H, 3.81; N, 2.89. Found: C, 64.96; H, 4.06; N, 2.80.

Synthesis of [IsoquinolineH]-*mer*-[1]. To a stirred solution of $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.21 g, 0.54 mmol) in anhydrous acetone (9 mL) was added isoquinoline (0.11 mL, 0.12 g, 0.93 mmol) via syringe. The reaction mixture was stirred for 2 days at ambient temperature and the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2/hexane (4 mL, 3 mL) and stored at −30 °C to afford a colorless precipitate. The precipitate was filtered, washed with CH_2Cl_2 (ca. 1 mL), and dried *in vacuo*. Yield = 0.19 g, 68%. The aforementioned filtrate was cooled (−30 °C) to afford single crystals suitable for X-ray crystallography.

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$, 25 °C): δ −104.7. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 16.34 (s, 1H, N*H*), 9.19 (s, 1H, isoquinoline−Ar−*H*), 8.29 (d, 1H, isoquinoline−Ar−*H*), 8.09−8.04 (m, 5H, isoquinoline−Ar−*H*), 8.02−7.41 (m, 11H, Ar−*H*), 6.99 (dd,

DOI: 10.1021/acs.inorgchem.8b02174
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J_{HH} = 7.8 Hz, 1H, Ar−*H*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 170.7 (s, *C*═O), 170.6 (s, *C*═O), 166.8 (s, *C*═O), 148.9 (s, isoquinolineH, Ar−*C*), 145.0 (s, Ar−*C*), 144.12 (s, Ar−*C*), 143.44 (s, Ar−*C*), 142.1 (s, Ar−*C*), 137.4 (s, isoquinolineH, Ar−*C*), 136.1 (s, isoquinolineH, Ar−*C*), 134.0 (s, Ar−*C*), 133.9 (d, J_{CP} = 2.2 Hz, Ar−*C*), 133.7 (s, Ar−*C*), 132.2 (d, J_{CP} = 2.9 Hz, Ar−*C*), 132.0 (s, Ar−*C*), 131.0 (s, Ar−*C*), 130.9 (s, Ar−*C*), 130.8 (s, Ar−*C*), 129.7 (d, J_{CP} = 3.7 Hz, Ar−*C*), 129.3 (s, isoquinolineH, Ar−*C*), 129.1 (s, isoquinolineH, Ar−*C*), 128.3 (s, Ar−*C*), 128.1 (s, Ar−*C*), 127.9 (s, Ar−*C*), 127.8 (s, Ar−*C*), 127.6 (s, Ar−*C*), 126.9 (s, isoquinolineH, Ar−*C*), 126.8 (s, isoquinolineH, Ar−*C*), 126.6 (s, isoquinolineH, Ar−*C*), 123.1 (s, isoquinolineH, Ar−*C*). IR (neat) ν: 3417 (vw), 3132 (vw), 3067 (w), 3009 (vw), 2998 (vw), 2930 (vw), 2764, 2112 (vw), 1975 (vw), 1709 (s), 1651 (s), 1616 (m), 1593 (w), 1575 (w), 1494 (w), 1452 (m), 1397 (w), 1341 (m), 1278 (s), 1242 (s), 1154 (m), 1128 (s), 1114 (s), 1065 (s), 1029 (vw), 976 (w), 951 (w), 853 (s), 824 (m), 802 (m), 746 (s), 731 (s), 717 (m), 700 (s), 696 (s), 685 (s) cm^{-1}. HRMS (ESI/TOF, positive mode) m/z = $[M]^+$ calcd for $C_9H_8N_1$ 130.0657, found 130.0658. HRMS (ESI/TOF, negative mode) m/z = $[M]^-$ calcd for $C_{21}H_{12}O_6P_1$ 391.0372; found 391.0376.

Synthesis of [(−)-BrucineH]-*mer*-[1]. To a solution of P-$(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.19 g, 0.48 mmol) in anhydrous acetone (6.5 mL) was slowly added a solution of (−)-brucine (0.22 g, 0.56 mmol) in anhydrous acetone (4 mL). The reaction mixture was stirred for 1 h to afford a colorless precipitate. The precipitate was filtered, washed with anhydrous acetone, and dried *in vacuo*. Yield = 0.30 g, 79%. Cooling a concentrated solution of the crude product (80 mg) in CH_2Cl_2 (5 mL) afforded colorless crystals (−30 °C, ca. 5 days). Yield = 38 mg, 48%. A crystal was selected for X-ray crystallographic analysis without drying. In addition, a concentrated solution of the crude product was dissolved in DMSO-d_6 solvent. Single crystals suitable for X-ray diffraction analysis were obtained upon standing for 20 min at ambient temperature.

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2SO$, 25 °C): δ −135.2; δ (CD_2Cl_2) −114.3, −114.6. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 12.63 (s, 1H, N*H*), 8.01−7.94 (m, 3H, Ar−*H*), 7.79 (s, 1H, (−)-brucinium, Ar−*H*), 7.75−7.35 (m, 8H, Ar−*H*), 6.77 (s, 1H, (−)-brucinium, Ar−*H*), 6.45 (dd, J_{HH} = 7.4 Hz, 1H, Ar−*H*), 6.18 (t, J_{HH} = 6.2 Hz, 1H, (−)-brucinium, C*H*), 4.35−4.32 (m, 1H, (−)-brucinium, O−C*H*), 4.27−4.21 (m, 2H, (−)-brucinium, OCH_2), 4.10 (dd, J_{HH} = 8.8 Hz, 1H, (−)-brucinium, C*H*), 3.93 (s, 1H, (−)-brucinium, −N−C*H*−C−), 3.91 (s, 3H, (−)-brucinium, OCH_3), 3.88 (s, 3H, (−)-brucinium, OCH_3), 3.82 (d, J_{HH} = 13.7 Hz, 1H, (−)-brucinium, −N−CH_2−), 3.63−3.59 (m, 1H, brucinium, CH_2), 3.14 (s, 1H, (−)-brucinium, C*H*), 3.09 (t, J_{HH} = 8.8 Hz, 1H, (−)-brucinium, CH_2), 3.02−2.94 (m, 1H, (−)-brucinium, C*H*), 2.87 (d, J_{HH} = 14.7 Hz, 1H, (−)-brucinium, C*H*), 2.67 (dd, J_{HH} = 3.9 Hz, 1H, (−)-brucinium, C*H*), 2.00−1.86 (m, 3H, (−)-brucinium, 3 × C*H*), 1.47 (d, J_{HH} = 14.7 Hz, 1H, (−)-brucinium, C*H*), 1.33 (dt, J_{HH} = 10.8 Hz, 1H, (−)-brucinium, C*H*). ^1H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ 10.60 (br s, 1H, N−*H*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 172.5 (s, (−)-brucinium, *C*═O), 172.2 (s, *C*═O), 168.3 (s, C═O), 168.1 (s, C═O), 150.5 (s, Ar−*C*), 148.9 (s, Ar−*C*), 146.9 (s, Ar−*C*), 136.0 (s, Ar−*C*), 135.5 (s, Ar−*C*), 133.4 (s, Ar−*C*), 133.2 (s, Ar−*C*), 133.0 (s, (−)-brucinium, Ar−*C*), 132.8 (s, (−)-brucinium, Ar−*C*), 132.5 (s, Ar−*C*), 132.3 (s, Ar−*C*), 131.7 (s, Ar−*C*), 131.5 (s, Ar−*C*), 129.9 (s, (−)-brucinium), 129.1 (s, (−)-brucinium), 127.2 (s, (−)-brucinium), 127.0 (s, Ar−*C*), 126.5 (s, Ar−*C*), 126.3 (s, Ar−*C*), 125.9 (s, Ar−*C*), 125.7 (s, Ar−*C*), 125.1 (s, Ar−*C*), 124.9 (s, Ar−*C*), 118.8 (s, (−)-brucinium), 105.6 (s, (−)-brucinium), 101.0 (s, (−)-brucinium), 77.3 (s, (−)-brucinium), 64.0 (s, (−)-brucinium), 61.2 (s, (−)-brucinium), 59.2 (s, (−)-brucinium), 56.6 (s, (−)-brucinium), 56.1 (s, (−)-brucinium), 52.1 (s, (−)-brucinium), 52.0 (s, (−)-brucinium), 50.2 (s, (−)-brucinium), 46.9 (s, (−)-brucinium), 42.0 (s, (−)-brucinium), 40.5 (s, (−)-brucinium), 30.4 (s, (−)-brucinium), 24.7(s, (−)-brucinium). IR (neat) ν: 3494 (vw), 3061 (vw), 3056 (vw), 2997 (vw), 2959 (vw), 2872 (vw), 2829 (vw), 1708 (sh, m), 1668 (s), 1648 (sh, s), 1594 (m), 1577 (w), 1502 (m), 1451 (m), 1414 (m), 1362 (w), 1331 (w), 1283 (s), 1245 (m), 1220 (m), 1198 (m), 1176 (w), 1111 (s), 1088 (w),1071 (m), 1065 (w), 1027 (m), 1012 (w), 986 (m), 964 (w), 938 (vw), 885 (vw), 849 (s), 817 (sh, w), 790 (w), 762 (sh, w), 728 (s), 719 (m), 701 (s), 684 (m) cm^{-1}. Elem. anal. calcd for $C_{45}H_{41}N_2O_{10}P{\cdot}0.7\ CH_2Cl_2{\cdot}0.9\ C_3H_6O$: C, 63.71; H, 5.30; N, 3.06. Found: C, 63.81;H, 5.40; N, 3.10.

Synthesis of [(*n*-$C_8H_{17})_3NH$]-*mer*-[1]. To a suspension of $P(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.23 g, 0.58 mmol) in anhydrous acetone (6 mL) was added degassed tri(*n*-octyl)amine, N(*n*-$C_8H_{17})_3$, (0.50 mL, 0.40 g, 1.13 mmol). Within seconds, the reaction mixture dissolved and was stirred overnight. Subsequently, the solvent was removed *in vacuo* to afford pale yellow oil. The oily residue was washed with *n*-hexane, filtered, and heated *in vacuo* at 140 °C for 4 h to remove residual solvent. Yield = 0.31 g, 73%.

$^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$, 25 °C): δ −128.9; δ (CD_2Cl_2) − 125.6; ^1H NMR (400 MHz, $(CD_3)_2CO$, 25 °C): δ 9.76 (br s, 1H, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 8.50−7.20 (m, 11H, Ar−*H*), 6.29 (dd, J_{HH} = 7.3 Hz, 1H, Ar−*H*), 3.04 (t, $^3J_{HH}$ = 8.3 Hz, 6H, ($CH_3(CH_2)_5CH_2CH_2)_3NH$), 1.69 (m, 6H, ($CH_3(CH_2)_5CH_2CH_2)_3NH$), 1.31 (br s, 30H, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 0.89 (t, $^1J_{HH}$ = 6.9 Hz, 9H, $(CH_3(CH_2)_5CH_2CH_2)_3NH$). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 10.40 (s, 1H, $(CH_3(CH_2)_5CH_2CH_2)_3NH$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, 25 °C): δ 169.4 (s, *C*═O), 169.3 (s, *C*═O), 163.9 (s, C═O), 156.5 (s, Ar−*C*), 154.3 (s, Ar−*C*), 135.8 (s, Ar−*C*), 135.7 (s, Ar−*C*), 134.9 (s, Ar−*C*), 134.8 (s, Ar−*C*), 132.3 (s, Ar−*C*), 132.1 (s, Ar−*C*), 131.7 (s, Ar−*C*), 131.5 (s, Ar−*C*), 130.7 (d, J_{CP} = 3.7 Hz, Ar−*C*), 130.6 (s, Ar−*C*), 130.4 (s, Ar−*C*), 128.5 (d, J_{CP} = 4.4 Hz, Ar−*C*), 127.2 (s, Ar−*C*), 127.0 (s, Ar−*C*), 124.8 (d, J_{CP} = 2.2 Hz, Ar−*C*), 124.7 (s, Ar−*C*), 52.5 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 31.6 (s, ($CH_3(CH_2)_5CH_2CH_2)_3NH$), 29.0 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 28.9 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 26.4 (s, ($CH_3(CH_2)_5CH_2CH_2)_3NH$), 23.3 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 22.4 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$), 13.5 (s, $(CH_3(CH_2)_5CH_2CH_2)_3NH$). IR ($CCl_4$) ν: 3069 (vw), 2955 (m), 2927 (m), 2879 (w), 2857 (m), 1709 (s), 1653 (m), 1596 (m), 1579 (w), 1454 (m), 1378 (vw), 1280 (s), 1242 (s), 1127 (s), 1112(m), 1071 (m), 1061(s), 1023 (w), 984 (m), 856 (s), 809 (w), 784 (s), 757 (s), 731 (sh, m), 700(m), 686 (w). IR (neat) ν: 3064 (vw), 3021 (vw), 2954 (m), 2925 (m), 2870 (w), 2856 (m), 1707 (s), 1653 (m), 1595 (m), 1579 (w), 1453 (m), 1378 (vw), 1277 (s), 1240 (s), 1125 (s), 1113 (s), 1071 (m), 1061(s), 1022 (w), 984 (m), 855 (s), 809 (w), 784 (s), 757 (s), 731 (sh, m), 699 (s), 686 (m) cm^{-1}.

Synthesis of K-*mer*-[1]. To a colorless solution of $[NEt_3H][P(C_6H_4CO_2)_3]$ (0.17 g, 0.34 mmol) in anhydrous THF (12 mL) was slowly added a suspension of potassium hydride (0.02g, 0.52 mmol) in anhydrous THF (6 mL) at ambient temperature. The immediate evolution of gas (i.e., H_2) was observed and the reaction mixture was stirred for 2 h at ambient temperature to afford a colorless precipitate. The precipitate was filtered and washed with minimal amount of anhydrous THF and dried *in vacuo*. Yield = 0.12 g, 82%. Single crystals suitable for X-ray diffraction were obtained by cooling a concentrated solution of the crude product (44 mg) in MeOH-d_4 (1.5 mL) (−30 °C, ca. 9 days).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD, 25 °C): δ −127.6, δ ($(CD_3)_2CO$) −136.4. ^1H NMR (400 MHz, CD_3OD, 25 °C): δ 7.94−7.28 (m, 11H, Ar−*H*), 6.26 (dd, J_{HH} = 7.6 Hz, 1H, Ar−*H*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, 25 °C): δ 170.7 (s, *C*═O), 169.9 (s, C═O), 169.8 (s, C═O), 155.4 (s, Ar−C), 154.3 (s, Ar−C), 153.2 (s, Ar−C), 133.3 (s, Ar−C), 133.1 (s, Ar−C), 132.3 (s, Ar−C), 132.1 (d, J_{CP} = 2.9 Hz, Ar−C), 130.2 (s, Ar−C), 130.1 (s, Ar−C), 129.0 (d, J_{CP} = 2.9 Hz, Ar−*C*), 128.9 (s, Ar−C), 128.7 (d, J_{CP} = 3.7 Hz, Ar−*C*), 128.6 (s, Ar−C), 126.0 (s, Ar−C), 125.9 (s, Ar−C), 125.8 (s, Ar−C), 124.7 (s, Ar−C), 124.5 (s, Ar−C). IR (neat) ν: 2962 (vw), 1689 (s), 1632 (sh, w), 1595 (m), 1580 (w), 1453 (m), 1391 (w), 1332 (w), 1282 (s), 1244 (s), 1120 (s), 1071 (m), 1062 (m), 1025 (w), 855 (s), 813 (w), 745 (s), 729 (s), 718 (w), 697 (s), 684 (m) cm^{-1}; LRMS (ESI, negative mode) m/z = 391.0 $[M]^-$.

Attempted Synthesis of H(DMF)$_n$-*mer*-[1]. To P-$(C_6H_4CO_2)_2(C_6H_4COOH)$ (0.20 g, 0.57 mmol) was added

DOI: 10.1021/acs.inorgchem.8b02174
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anhydrous *N*,*N*-dimethylformamide (5 mL). The initially cloudy solution cleared within a few seconds and was subsequently stirred for ca. 16 h. Despite heating to 120 °C over ca. 4 weeks, no additional changes were observed in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture. An aliquot was removed from the reaction mixture for mass spectrometric analysis.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $N(CH_3)_2COH$, 25 °C): δ −55.9, −34.6, −138.9. LRMS (ESI, negative mode) m/z = 391.0 $[M]^-$.

X-ray Crystallography. All single crystals were immersed in oil and mounted on a glass fiber. Data were collected on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo Kα radiation, integrated using the Bruker SAINT software package,[32] and corrected for absorption effect using SADABS.[33] All structures were solved by direct methods and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were not refined with the exception of N−H hydrogens, which were located in a difference map and refined isotropically. All data sets were corrected for Lorentz and polarization effects. All refinements were performed using the SHELXT-2015[34] via the Olex2 interface.[35]

[$PhNMe_2H$]-*rac*-*mer*-[**1**] crystallizes with one molecule of solvent acetone in the asymmetric unit. [pyH]-*rac*-*mer*-[**1**] was solved using nonoverlapped data from a major twin component. Subsequent refinements were carried out using a data set containing complete data from component one and any overlaps from component two. The material crystallizes with one-half-molecule of acetone in the asymmetric unit. Additionally, one coordinated benzoic acid ligand is disordered and is modeled in two orientations. The compound [isoquinolineH]-*rac*-*mer*-[**1**] crystallizes as a twin, with a ∼9:1 ratio between the major and minor twin components. [(−)-BrucineH]-Λ-*mer*-[**1**] crystallizes with two molecules of solvent methylene chloride in the asymmetric unit. One of these solvent molecules is disordered and was modeled in three orientations, such that their combined site occupancies summed to one. K-*rac*-*mer*-[**1**] crystallizes with three MeOH molecules coordinated to the potassium cation. Additionally, the material crystallizes with disordered free MeOH in the lattice. The disorder could not be reasonably modeled; therefore, the PLATON/SQUEEZE[36] program was used to generate a data set free of disordered solvent. O−H hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions. Additional crystal data and details of data collection are given in the Supporting Information. All crystallographic data has been deposited with the Cambridge Structural Database: CCDC−1857626 [isoquinolineH]-*rac*-*mer*-[**1**], CCDC−1857627 [$PhNMe_2H$]-*rac*-*mer*-[**1**], CCDC−1857628 [pyH]-*rac*-*mer*-[**1**], CCDC−1857629 K-*rac*-*mer*-[**1**], and CCDC−1857630 [(−)-brucineH]-*rac*-*mer*-[**1**].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02174.

NMR spectra, X-ray crystallographic data, tabulated metrical parameters (PDF)

Accession Codes

CCDC 1857626−1857630 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Counsel (NSERC) of Canada for financial support of this work in the form of Discovery, Collaborative Research & Development, and Research Tools grants to D.P.G.

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DOI: 10.1021/acs.inorgchem.8b02174
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