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$HL_2[P(1,2\text{-}O_2C_6H_4)_3]$ (L = DMSO or DMF): A Convenient Proton Source with a Weakly Basic Phosphorus(V) Anion

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Treating phosphorus pentachloride with catechol (3 equiv) followed by the addition of dimethylsulfoxide (DMSO) or dimethylformamide (DMF) affords isolable Brønsted acids of the tris(*o*-phenylenedioxy)phosphate anion, $[P(1,2\text{-}O_2C_6H_4)_3]^-$. Specifically, $H(DMSO)_2[P(1,2\text{-}O_2C_6H_4)_3]$ and $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)_3]$ have been isolated as crystalline solids. The downfield shifts of the acidic proton in their ^1H NMR spectra are consistent with its expected high acidity. The molecular structures of $H(DMSO)_2[P(1,2\text{-}O_2C_6H_4)_3]$ and $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)_3]$ reveal that the protons in each are O-bound by either DMSO (×2) or DMF (×2). The N−H stretching frequency for the $Oct_3NH[P(1,2\text{-}O_2C_6H_4)_3]$ ($\bar{\nu}_{N-H} = 3129$ cm^{-1}) is identical to that observed for trioctylammonium tetrafluoroborate ($\bar{\nu}_{N-H} = 3129$ cm^{-1}), suggesting that the basicity of these two weakly coordinating anions is similar. A preliminary investigation of the effectiveness of $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)_3]$ in the protonolysis of metal−alkyl bonds was undertaken. Treating $(dppe)PdMe_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] with $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)_3]$ affords either $[(dppe)Pd(NCMe)Me][P(1,2\text{-}O_2C_6H_4)_3]$ (1:1 ratio) or $[(dppe)Pd(NCMe)_2][P(1,2\text{-}O_2C_6H_4)_3]_2$ (1:2 ratio), both of which are structurally characterized.

Introduction

The stabilization of coordinatively unsaturated cations, which are often found as reactive intermediates or active catalysts, necessitates the presence of charge-balancing anions with minimal nucleophilicity, the so-called weakly coordinating anions (WCAs).[1] A number of sophisticated approaches have been designed to prepare large, charge-delocalized WCAs such as fluoroarylborates, carboranes, fluoroalkoxyaluminates, and teflates, among others.[2−5] Classical WCAs have often served as inspiration for the design of improved WCAs. For example, the classical anion $[BF_4]^-$ may be envisaged, at least formally, as the predecessor to the larger and more charge delocalized $[BPh_4]^-$. The formal evolution of $[BF_4]^-$ ultimately led to the popular fluoroarylborate anions $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ and $[B(C_6F_5)_4]^-$.[6,7] Although fluoroarylborates have permitted important advancements in both fundamental and

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applied chemistry,[8,9] their often difficult preparation leaves open the possibility to develop alternative WCAs with simple and convenient preparative routes.

We have been inspired by the aforementioned evolution of $[BF_4]^-$ to explore the possible analogous evolution of classical WCA $[PF_6]^-$, which has thus far received very little attention for improvement. Investigation of $[PF_6]^-$ derivatives could potentially pave the way to new classes of weakly nucleophilic anions with poor coordinating ability. A logical first step in the evolution of $[PF_6]^-$ is the preparation of $[PPh_6]^-$; however, this unknown species would likely suffer from undesirable redox chemistry. Therefore, we have chosen the relatively large tris(*o*-phenylenedioxy)phosphate anion $[\mathbf{1}]^-$ [10-12] as a candidate for our preliminary studies of the WCA properties of hexacoordinated phosphorus. Despite the fact that anion $[\mathbf{1}]^-$ has been studied extensively,[13-17] it has not yet been explored for WCA applications. We are particularly interested in preparing Brønsted acids containing $[\mathbf{1}]^-$ due to their potential to serve as catalyst activators through the protonolysis of metal−alkyl bonds, particularly when more sophisticated WCAs are not necessarily essential.

Herein, we describe the preparation and characterization of two solid Brønsted acids containing the tris(*o*-phenylenedioxy)phosphate anion $[\mathbf{1}]^-$. Specifically, $H(DMF)_2[\mathbf{1}]$ and $H(DMSO)_2[\mathbf{1}]$ have been prepared and structurally characterized. In contrast to the preparation of other protic salts of WCAs, the route to these new Brønsted acids is simple and straightforward, beginning with conveniently available inexpensive precursors: phosphorus(V) chloride, catechol, and DMF or DMSO. It will be shown that $H(DMF)_2[\mathbf{1}]$ is effective in the stoichiometric activation of the metal−alkyl bonds of $(dppe)PdMe_2$ and that the coordinating nature of the anion $[\mathbf{1}]^-$ is comparable to the classical WCA $[BF_4]^-$.

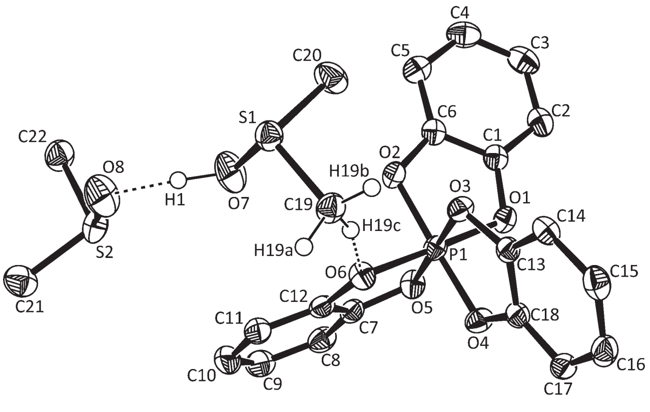
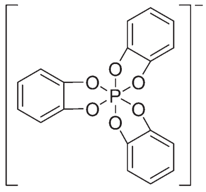


Figure 1. Molecular structure of $H(DMSO)_2[\mathbf{1}]$. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity, except for H(1), H(19a), H(19b), and H(19c). Selected bond lengths (Å) and angles (deg): O(1)−P(1) = 1.726(1); O(2)−P(1) = 1.716(1); O(3)−P(1) = 1.725(1); O(4)−P(1) = 1.709(1); O(5)−P(1) = 1.705(1); O(6)−P(1) = 1.713(1); O(7)−H(1) = 1.00(3); O(8)−H(1) = 1.45(3); O(7)−O(8) = 2.445(6); O(6)-H(19c) = 2.421 (1); O(2)−P(1)−O(1) = 90.85(5); O(2)−P(1)−O(3) = 87.11(5); O (3)−P(1)−O(1) = 92.00(5); O(4)−P(1)−O(3) = 90.60(5); O(4)−P (1)−O(6) = 92.85(5); O(4)−P(1)−O(1) = 88.62(5); O(5)−P(1)−O(2) = 93.42(5); O(5)−P(1)−O(4) = 88.86(5); O(5)−P(1)−O(6) = 91.27(5); O(5)−P(1)−O(1) = 87.89(5); O(6)−P(1)−O(3) = 88.86(5); O(6)−P(1)−O(2) = 87.71(5); O(7)−H(1)−O(8) = 171(3).



$[\mathbf{1}]^-$

Results and Discussion

The tris(*o*-phenylenedioxy)phosphate anion $[\mathbf{1}]^-$ was first isolated as its triethylammonium salt,[10] and the presence of hexacoordinate phosphorus in its structure was confirmed by X-ray diffraction.[11,12] Recently, the salt $Li[\mathbf{1}]$ has attracted attention as an electrolyte for use in lithium batteries and was reported to have good thermal stability (up to 150 °C).[13] We postulated that its large size combined with high thermal stability should make $[\mathbf{1}]^-$ a promising candidate for WCA applications. Particularly attractive, from the standpoint of the activation of metal−carbon bonds, would be the preparation of Brønsted acids containing the tris(*o*-phenylenedioxy)phosphate anion $[\mathbf{1}]^-$. Consequently, we set out to prepare $H[\mathbf{1}]$ in the presence of weakly basic solvents in an effort to prepare isolable compounds that would serve as solid, weighable, proton sources.

Brønsted Acids of Tris(*o*-phenylenedioxy)phosphate. 1. Synthesis and Spectroscopic Characterization. It has been reported that the treatment of PCl_5 with catechol (3 equiv) affords an equilibrium mixture of monomer **2** and catechol-bridged **3**.[14] Interestingly, previous studies of catechol-containing phosphorus(V) compounds in DMF or DMSO provided evidence for the formation of protic acids of $[\mathbf{1}]^-$,

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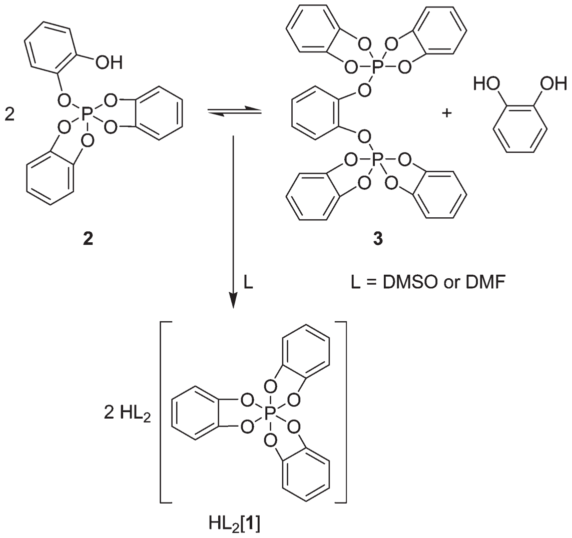
however no compounds were isolated nor were structural data obtained. The presence of HL[**1**] was inferred on the basis of ^{31}P NMR spectroscopic data, which suggested the presence of [**1**]$^-$ ($\delta = -83.5$).[15,16]

Inspired by this previous work, a solid mixture of **2** and **3** was prepared from PCl_5 and catechol (3 equiv), and subsequently, the mixture was dissolved in DMSO. Following an identical procedure, the mixture of **2** and **3** was dissolved in DMF. Analysis of each reaction mixture using ^{31}P NMR spectroscopy revealed that the resonances at −28.8 and −29.4 ppm, attributed to **2** and **3**, respectively, had been consumed and were replaced by a signal at ca. −80 ppm (DMSO: $\delta = -80.5$; DMF: $\delta = -80.0$), which is similar to those reported previously.[15,16]



In contrast to previous studies, we have successfully isolated and crystallographically characterized protic salts of [**1**]$^-$ with $[H(DMSO)_2]^+$ and $[H(DMF)_2]^+$ as counterion. The molecular structures are presented in Figures 1 and 2, and the metrical parameters will be discussed later. In addition to ^{31}P NMR spectroscopy, each compound was characterized using ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of CD_3CN solutions of the crystalline solids are shown in Figures 3 and 4. Of particular importance is the broad downfield signal that is assigned to the acidic proton of $H(DMSO)_2$[**1**] (δ = 13.3) and $H(DMF)_2$[**1**] (δ = 15.3). Importantly, the integrated ratio of the signal assigned to acidic proton and the DMSO protons (δ = 2.83) or the DMF signals (δ = 8.06, 3.07, and 2.95) are consistent with the molecular structure determined by X-ray crystallography (vide infra). The slight downfield shift observed for the complex in comparison to free DMSO (δ = 2.50) or free DMF (δ = 7.92, 2.89, and 2.77) provides evidence that the $[HL_2]^+$ moiety is retained in solution (L = DMSO or DMF).

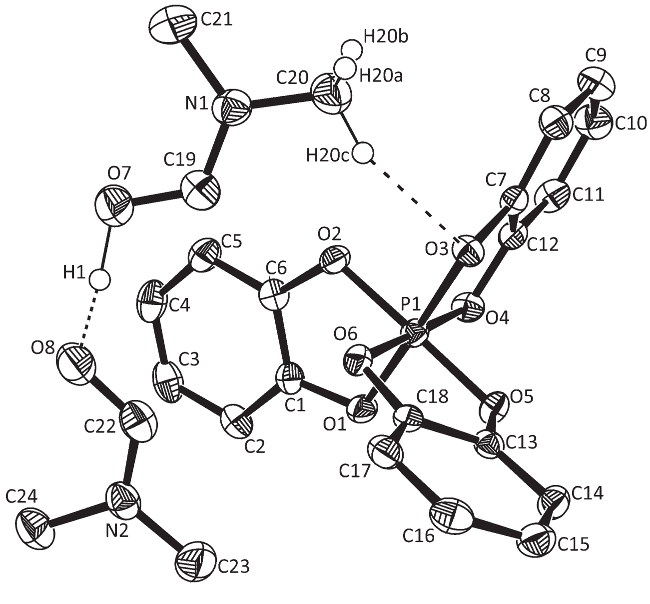


Figure 2. Molecular structure of $H(DMF)_2$[**1**]. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity, except for H(1), H(20a), H(20b), and H(20c). Selected bond lengths (Å) and angles (deg): O(1)−P(1) = 1.706(1); O(2)−P(1) = 1.715(1); O(3)−P(1) = 1.708(1); O(4)−P(1) = 1.708(1); O(5)−P(1) = 1.700(1); O(6)−P(1) = 1.730(1); O(7)−H(1) = 1.13(4); O(8)−H(1) = 1.31(4); O(7)−O(8) = 2.438(2); O(3)−H(20c) = 2.375(1); O(1)−P(1)−O(2) = 90.96(6); O(1)−P(1)−O(4) = 88.78(7); O(1)−P(1)−O(6) = 92.32(7); O(2)−P(1)−O(6) = 87.79(6); O(3)−P(1)−O(2) = 87.54(6); O(3)−P(1)−O(6) = 87.86(6); O(4)−P(1)−O(2) = 92.66(7); O(4)−P(1)−O(3) = 91.05(6); O(5)−P(1)−O(1) = 89.23(6); O(5)−P(1)−O(3) = 92.27(7); O(5)−P(1)−O(4) = 89.08(7); O(5)−P(1)−O(6) = 90.46(6); O(7)−H(1)−O(8) = 176(4).

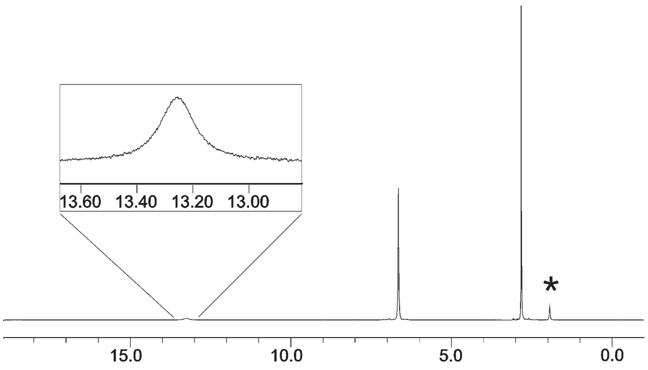


Figure 3. ^{1}H NMR (300 MHz) spectrum of $H(DMSO)_2$[**1**] in CD_3CN at room temperature (* = residual protonated solvent).

A rough indication of the acidity of the *H* in the $[H(DMSO)_2]^+$ and $[H(DMF)_2]^+$ cations and the innocence of the [**1**]$^-$ anion may be obtained from the ^{1}H NMR chemical shift for the acidic proton. At room temperature the chemical shift for $[H(DMSO)_2]^+$ is 13.3 ppm, whereas for $[H(DMF)_2]^+$ it is observed further downfield at 15.3 ppm, suggesting a higher acidity for the latter, which is inconsistent with the relative pK_a's for $[HDMSO]^+$ (pK_a = −2.01[18]) and $[HDMF]^+$ (pK_a = −1.2 ± 0.5[19]). A plausible rationale for this inconsistency has been proposed previously by considering that the positive charge is better delocalized through resonance stabilization in monosolvated protons when compared to disolvated protons.[20] The significant deshielding of the acidic proton is consistent with that observed for acids of other weakly coordinating anions. For comparison, chemical shifts of the acidic proton in related compounds such as

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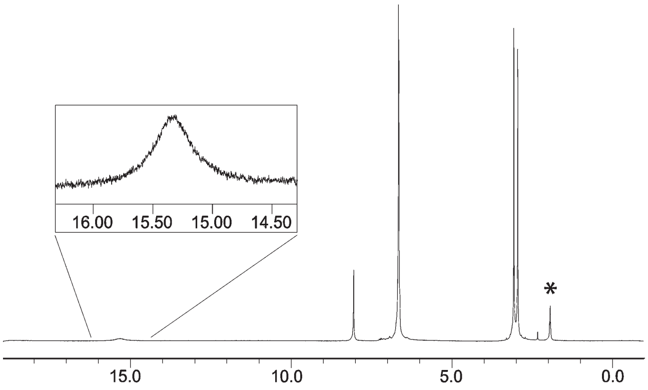

Figure 4. ^1H NMR (300 MHz) spectrum of $H(DMF)_2$[**1**] in CD_3CN at room temperature (* = residual protonated solvent).

$H_2(DMF)_4[TeBr_6]$ and $H(DMF)_2[OTf]$ are 16.8 and 16.9, respectively,[21] whereas those of the widely used $[H(OEt)_2][B(3,5-(CF_3)_2C_6H_3)_4]$ and $[H(OEt)_2][B(C_6F_5)_4]$ are 11.1 and 15.5, respectively.[7a,7b]

The Brønsted acid $H(DMF)_2$[**1**] exhibits excellent stability. For example, a solid sample of $H(DMF)_2$[**1**] that was stored at room temperature in a glovebox showed no change in its ^1H or ^{31}P NMR spectrum when monitored for over one month. Remarkably, neither the ^1H nor the ^{31}P NMR spectra of a solution of $H(DMF)_2$[**1**] in CD_3CN show any change when monitored for one month. In contrast, the ^{31}P NMR spectrum of a solution of $H(DMSO)_2$[**1**] in CD_3CN shows evidence of decomposition after several hours.

2. X-ray Crystallography. Details of the solution and refinement for $H(DMSO)_2$[**1**] and $H(DMF)_2$[**1**] are given in Table 1 and in the Experimental Section. The phosphorus atom of anion [**1**]$^-$ in each compound shows very minor deviation from perfect octahedral geometry. The P−O bond lengths in HL_2[**1**] [av: 1.711(3) Å, L = DMF; 1.716(3) Å, L = DMSO] are longer than those typically observed for P−O single bonds in triarylphosphates [1.59(1) Å][22] and are similar to those found in the ammonium salt Et_3NH[**1**] [av: 1.715(6)].[12]

Consistent with the ^1H NMR spectroscopic data, the molecular structures of the Brønsted acids of [**1**]$^-$ revealed that their cationic components consist of a single proton coordinated through the oxygen atom of two ligand molecules. In each case the acidic hydrogen atom, H(1), was located in the difference map and was refined isotropically. The H−O bond lengths in the $[H(DMSO)_2]^+$ cation differ considerably [O−H = 1.00(3) and 1.45(3) Å], which is consistent with that observed in related compounds: $[H(DMSO)_2]_2[TeCl_6]$, $H(DMSO)_2[7,8\text{-}C_2B_9H_{12}]$, and $H(DMSO)_2$[*trans*-$RuCl_4(DMSO)_2$] [O−H = 0.9(1), and 1.5(1) Å;[23] 0.95(4) and 1.45(4) Å;[24] 1.12(6) and 1.30(6) Å,[25] respectively]. Similarly, the $[H(DMF)_2]^+$ cation is also bound asymmetrically [O−H = 1.13(4) and 1.31(4) Å]. Asymmetric hydrogen bonding is quite common for protons bound by oxygen donors such as DMF and DMSO.[23,24] The O···O distance in the O−H−O moiety of the $[HL_2]^+$ ion is generally accepted as being more indicative of the strength of hydrogen bonding than the H−O distance, which is difficult to determine accurately.[23,25−29] The O···O distance for the O−H−O moiety in $H(DMSO)_2$[**1**] is 2.445(6) Å and in $H(DMF)_2$[**1**] is 2.438(2) Å, which are comparable to those observed in related compounds {$H(DMSO)_2$[*trans*-$RuCl_4(DMSO)_2$] (2.423(5) Å[25]), $[H(DMSO)_2]_2[TeBr_6]$ (2.448(4) Å[29]), and $[H(DMF)_2]_2[TeBr_6]$ (2.44(2) Å)[21]}. Noteworthy, is the fact that the distance between the oxygen atoms of the two DMF molecules in $H(DMF)_2$[**1**] [O(7)···O(8) = 2.438(2) Å] is longer than partially chlorinated tris(*o*-phenylenedioxy) phosphate, $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)(1,2\text{-}O_2C_6Cl_4)_2]$ (2.413 Å).[30] The above data suggest that there is strong hydrogen bonding present in the Brønsted acids of [**1**]$^-$.

Importantly, the metrical parameters for $H(DMSO)_2$[**1**] and $H(DMF)_2$[**1**] reveal that there are weak interactions between the cation and anion [**1**]$^-$. Specifically, the closest contact between $[H(DMSO)_2]^+$ and [**1**]$^-$ involves an oxygen atom in the catecholate anion and an H atom of the methyl group of DMSO [O(6)···H(19c) = 2.421(1) Å]. Likewise, the closest contact between $[H(DMF)_2]^+$ and [**1**]$^-$ involves a methyl group of DMF and an oxygen atom of [**1**]$^-$ [O(3)···H(20c) = 2.375(1) Å]. In both cases, the closest ion-pair distances are within the sum of van der Waals radii for oxygen and hydrogen [r_{vdw} = 2.72 Å], consistent with weak cation−anion interactions.[31]

3. Placement of [1]$^-$ on an Infrared Scale for Weakly Basic Anions. Given our interest in the potential use of [**1**]$^-$ as a weakly coordinating anion, we are interested in comparing the coordinating ability [**1**]$^-$ with other anions. A convenient scale of coordinating ability in solution has been proposed that involves measuring the N−H stretching frequency for ammonium salts of different anions.[32] In an effort to place [**1**]$^-$ on this scale, we synthesized and characterized the trioctylammonium salt of [**1**]$^-$. Analysis of a CCl_4 solution of Oct_3NH[**1**] by infrared spectroscopy following the literature protocol revealed a N−H stretching frequency of 3129 cm^{-1}. Interestingly, this value is comparable to $Oct_3NH[BF_4]$ [$\bar{\nu}_{N-H}$ = 3133 cm^{-1},[32] 3129 cm^{-1} (our data)], suggesting that [**1**]$^-$ has a similar basicity to $[BF_4]^-$. For comparison, the most likely candidates for the title of “weakest coordinating anion”, $[B(C_6F_5)_4]^-$ and $[CMeB_{11}F_{11}]^-$, have N−H stretching frequencies of 3233 and 3219 cm^{-1}, respectively.[32] In contrast, the chloride anion is the most basic of those previously measured, and Oct_3NHCl possesses an N−H stretching frequency of 2330 cm^{-1}.[32]

Application of HL_2[1] in Metal−Carbon Bond Protonolysis. The results from the previous section suggest that the coordinating ability of tris(*o*-phenylenedioxy)phosphate anion [**1**]$^-$ should be comparable to tetrafluoroborate. Although more coordinating than perfluoroarylborate and carborane anions, the relative ease of synthesis of

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Table 1. X-ray Crystallographic Data of $H(DMSO)_2$[1], $H(DMF)_2$[1], [(dppe)Pd(NCMe)Me][Λ-1], [(dppe)Pd(NCMe)Me][Δ-1], and $[(dppe)Pd(NCMe)_2][1]_2$

	$H(DMSO)_2$[1]	$H(DMF)_2$[1]	[(dppe)Pd(NCMe)Me]-[Λ-1]·CH_3CN	[(dppe)Pd(NCMe)Me]-[Δ-1]·CH_3CN	$[(dppe)Pd(NCMe)_2]$ $[1]_2$·$2CH_3CN$
formula	$C_{22}H_{25}O_8PS_2$	$C_{24}H_{27}N_2O_8P$	$C_{49}H_{45}N_2O_6P_3Pd$	$C_{49}H_{45}N_2O_6P_3Pd$	$C_{70}H_{60}N_4O_{12}P_4Pd$
fw	512.51	502.45	957.18	957.18	1379.50
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1$	$P\bar{1}$
color	colorless	colorless	colorless	colorless	yellow
a (Å)	12.767(3)	11.5961(9)	10.036(1)	10.030(2)	12.173(1)
b (Å)	13.932(3)	14.877(1)	17.318(2)	17.331(3)	15.673(2)
c (Å)	13.625(3)	13.831(1)	13.035(2)	13.073(3)	18.048(2)
α (deg)	90	90	90	90	81.711(5)
β (deg)	108.507(7)	97.807(4)	95.200(5)	95.079(7)	83.998(5)
γ (deg)	90	90	90	90	68.021(5)
V (Å^3)	2298.2(9)	2364.0(3)	2256.2(5)	2263.6(8)	3154.8(6)
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Z	4	4	2	2	2
μ(Mo Kα) (mm^{-1})	0.349	0.169	0.569	0.567	0.463
cryst size (mm^3)	1.1 × 0.7 × 0.5	0.5 × 0.3 × 0.2	0.9 × 0.8 × 0.3	0.8 × 0.6 × 0.5	0.40 × 0.35 × 0.15
D_{calcd} (Mg m^{-3})	1.481	1.406	1.409	1.404	1.452
2θ(max) (deg)	55.8	55.88	56.0	55.82	56.7
no. of reflns	39 445	38 168	19 836	37 561	67 930
no. of unique data	5373	5664	9813	10 816	15 158
R(int)	0.0319	0.0493	0.0205	0.0216	0.0476
refln/param ratio	14.37	17.48	17.75	19.56	18.40
R_1 $[I > 2\sigma(I)]^a$	0.0324	0.0423	0.0245	0.0216	0.0375
wR_2 [all data]^b	0.0836	0.1131	0.0621	0.0518	0.0816
GOF	1.019	1.020	1.042	1.032	1.004

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2[\text{all data}]) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

$H(DMSO)_2$[1] and $H(DMF)_2$[1] compared to protic salts of fluoroarylborate or carboranes makes them attractive as catalyst activators where a moderately coordinating anion can be tolerated. Moreover, they represent convenient protonating agents because they are isolable in solid form and may be readily weighed.[33] Protic acids of weakly coordinating anions are of importance for the protonolysis of metal−alkyls to generate active catalysts. Readily available anhydrous Brønsted acids, such as $HOSO_2CF_3$, $HOSO_2F$, HBF_4/Et_2O, and $HF·SbF_5$, can be effective in metal−alkyl bond activation; however, they are available only in solution or in liquid form. Weighable solid Brønsted acids of moderate molecular weight, such as $H(DMSO)_2$[1] and $H(DMF)_2$[1], are less common; however, they are attractive for catalytic applications since, due the small amount of catalyst typically used, they enable more precise control of stoichiometry. In this section, the activation of palladium(II)−methyl bonds using $H(DMF)_2$[1] will be explored.

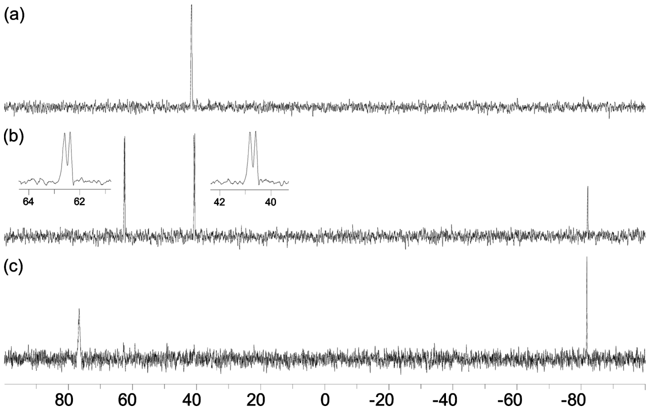

Figure 5. (a) ^{31}P NMR (162 MHz) spectrum of $(dppe)PdMe_2$ in CD_3CN at room temperature. (b) $^{31}P\{^1H\}$ NMR (121 MHz) spectrum of [(dppe)Pd(NCMe)Me][1] in CD_3CN at room temperature. (c) ^{31}P NMR (162 MHz) spectrum of $[(dppe)Pd(NCMe)_2][1]_2$ in CH_3CN at room temperature.

It is known that the reaction of $(P^\wedge P)PdMe_2$ (where $P^\wedge P$ is a bidentate ligand) with $H(OEt_2)_2[B(3,5-(CF_3)_2C_6H_3)_4]$ affords $[(P^\wedge P)Pd(solvent)Me][B(3,5-(CF_3)_2C_6H_3)_4]$,[34,35] an active catalyst for alternating polymerization of carbon monoxide and ethylene.[36−38] Consequently, we investigated the reaction of $(dppe)PdMe_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) with $H(DMF)_2$[1] in Et_2O/CH_3CN solution as a starting point to test the effectiveness of acids of $[1]^-$ to protonate metal−alkyl moieties. We chose to study the use of $H(DMF)_2$[1] rather than $H(DMSO)_2$[1] due to the greater stability of the former at room temperature. Cooling the reaction mixture to −30 °C resulted in the precipitation of a colorless solid. The ^{31}P NMR spectrum of a CD_3CN solution of the powder is shown in Figure 5 and is consistent with the successful formation of [(dppe)Pd(NCMe)Me][1]. Importantly, the spectrum reveals two inequivalent coupled phosphine moieties [δ = 62.5, 40.7; $^2J_{PP}$ = 28 Hz] and a singlet resonance assigned to the anion $[1]^-$ [δ = −82.0]. For comparison, similar resonances are observed for the phosphine moieties in [(dppe)Pd(NCMe)Me][OTf] [δ = 60.4, 35.2; $^2J_{PP}$ = 27 Hz][39] and $[(dppe)Pd(NCMe)Me][PF_6]$

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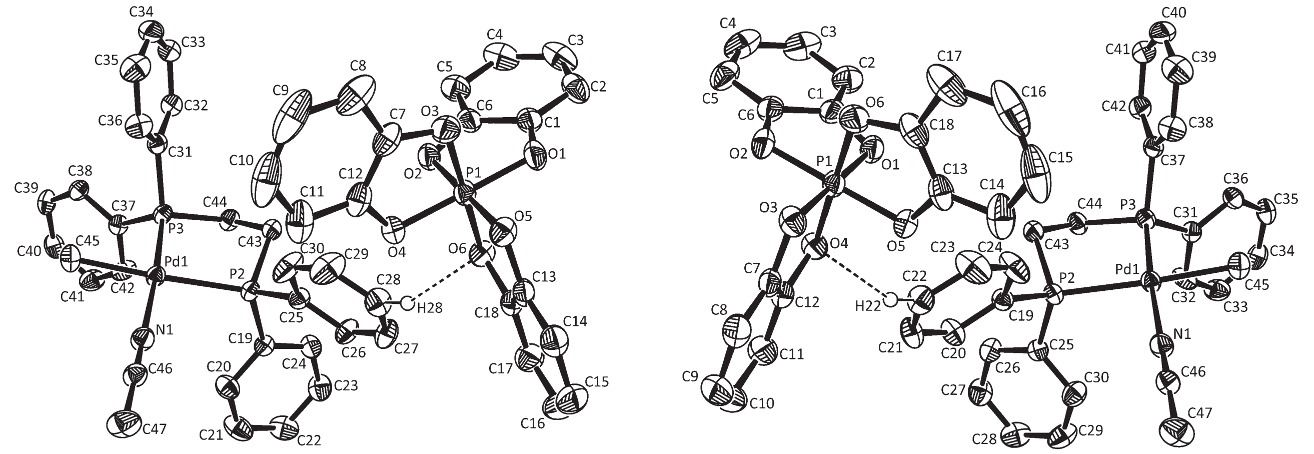
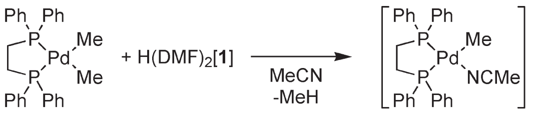


[(dppe)Pd(NCMe)Me][Λ-**1**] [(dppe)Pd(NCMe)Me][Δ-**1**]

Figure 6. Molecular structures of [(dppe)Pd(NCMe)Me][Λ-**1**] and [(dppe)Pd(NCMe)Me][Δ-**1**]. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity, except for H(28) for [(dppe)Pd(NCMe)Me][Λ-**1**] and H(22) for [(dppe)Pd(NCMe)Me][Δ-**1**]. In both cases, solvents of crystallization (CH_3CN) are also omitted for clarity. Selected bond lengths (Å) and angles (deg): [(dppe)Pd(NCMe)Me][Λ-**1**]: O(1)−P(1) = 1.705(2); O(2)−P(1) = 1.703(2); O(3)−P(1) = 1.712(2); O(4)−P(1) = 1.708(2); O(5)−P(1) = 1.712(2); O(6)−P(1) = 1.707(2); P(2)−Pd(1) = 2.3368(6); P(3)−Pd(1) = 2.2022(6); N(1)−Pd(1) = 2.063(2); C(45)−Pd(1) = 2.084(2); O(6)−H(28) = 2.551(2); O(1)−P(1)−O(3) = 88.60(9); O(1)−P(1)−O(5) = 88.68(8); O(1)−P(1)−O(6) = 92.10(8); O(2)−P(1)−O(1) = 91.28(8); O(2)−P(1)−O(3) = 92.01(9); O(2)−P(1)−O(4) = 88.54(8); O(2)−P(1)−O(6) = 88.23(8); O(4)−P(1)−O(3) = 90.74(8); O(4)−P(1)−O(5) = 91.51(8); O(5)−P(1)−O(3) = 88.59(9); O(6)−P(1)−O(4) = 88.56(8); O(6)−P(1)−O(5) = 91.17(8); N(1)−Pd(1)−C(45) = 89.17(9); C(45)−Pd(1)−P(3) = 87.26(7); N(1)−Pd(1)−P(2) = 96.76(6); P(3)−Pd(1)−P(2) = 86.73(2); [(dppe)Pd(NCMe)Me][Δ-**1**]: O(1)−P(1) = 1.706(1); O(2)−P(1) = 1.708(1); O(3)−P(1) = 1.716(1); O(4)−P(1) = 1.711(1); O(5)−P(1) = 1.710(1); O(6)−P(1) = 1.714(2); P(2)−Pd(1) = 2.3381(6); P(3)−Pd(1) = 2.2076(6); N(1)−Pd(1) = 2.069(2); C(45)−Pd(1) = 2.087(2); O(4)−H(22) = 2.550(1); O(1)−P(1)−O(2) = 91.06(7); O(1)−P(1)−O(4) = 88.38(7); O(1)−P(1)−O(5) = 88.80(6); O(1)−P(1)−O(6) = 92.08(7); O(2)−P(1)−O(3) = 88.92(7); O(2)−P(1)−O(4) = 92.25(7); O(2)−P(1)−O(6) = 88.38(7); O(4)−P(1)−O(3) = 90.99(7); O(5)−P(1)−O(3) = 91.23(7); O(5)−P(1)−O(4) = 88.50(7); O(5)−P(1)−O(6) = 90.87(7); O(6)−P(1)−O(3) = 88.56(7); N(1)−Pd(1)−C(45) = 89.36(7); C(45)−Pd(1)−P(3) = 87.31(6); N(1)−Pd(1)−P(2) = 96.52(5); P(3)−Pd(1)−P(2) = 86.75(2).

[$\delta = 61.2, 39.5$; $^2J_{PP} = 27$ Hz].[40] Further analysis of the product by ^1H and ^{13}C NMR spectroscopy provided further evidence for the formulation of the product as [(dppe)Pd(NCMe)Me][**1**].



(1)

We were also interested in whether or not H(DMF)$_2$[**1**] could doubly activate (dppe)PdMe$_2$ and whether or not the dication [(dppe)Pd(NCMe)$_2$]$^{2+}$ would be stable in the presence of [**1**]$^-$. Complexes containing the [(dppe)Pd(solvent)$_2$]$^{2+}$ are effective for numerous catalytic transformations.[41] A solid mixture of (dppe)PdMe$_2$ and H(DMF)$_2$[**1**] (2 equiv) was dissolved in acetonitrile, and an immediate color change to yellow was observed. After the reaction mixture was stirred for a total of 3 h, the ^{31}P NMR spectrum was consistent with the quantitative formation of [(dppe)Pd(NCMe)$_2$][**1**]$_2$ [δ = 76.5 (s), −82.1 (s), respectively] (see Figure 5). Upon standing, a pale yellow solid precipitated from the reaction solution, and this solid was separated, washed, and dried. Analyses of a DMSO-d_6 solution of the solid product by ^{31}P, ^1H, and ^{13}C NMR spectroscopy were consistent with the dication salt [(dppe)Pd(NCMe)$_2$][**1**]$_2$. For comparison, we treated (dppe)PdMe$_2$ with hydrogen chloride in acetonitrile solution, which afforded (dppe)PdCl$_2$ rather than [(dppe)Pd(NCMe)$_2$]Cl$_2$

The molecular structures of [(dppe)Pd(NCMe)Me][**1**] and [(dppe)Pd(NCMe)$_2$][**1**]$_2$ determined using X-ray crystallography (Figures 6 and 7, respectively) confirmed the formulations proposed from NMR spectroscopy. Details of the solution and refinement are provided in Table 1 and in the Experimental Section. The metrical parameters within the anion [**1**]$^-$ in each molecular structure are similar to those found in the HL_2^+ salts discussed above and will not be discussed further. Noteworthy is the fact that [(dppe)Pd(NCMe)Me][**1**] crystallizes in a chiral space group, $P2_1$. Remarkably, the analysis of two different crystals revealed that the Λ- and Δ-isomers of [**1**]$^-$ are resolved in the presence of [(dppe)Pd(NCMe)Me]$^+$. Careful comparison of the molecular structures of [(dppe)Pd(NCMe)Me][Λ-**1**] with [(dppe)Pd(NCMe)Me][Δ-**1**] reveals an asymmetrical twist

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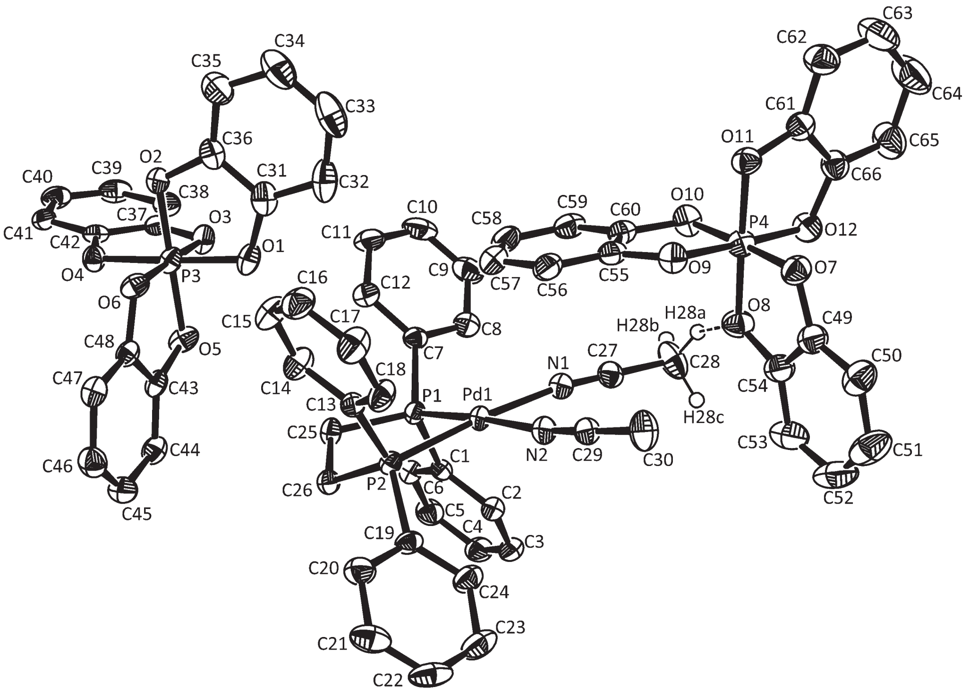

Figure 7. Molecular structure of [(dppe)Pd(NCMe)$_2$][**1**]$_2$. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity, except for H(28a), H(28b), and H(28c). Solvents of crystallization (2 × CH_3CN) are also omitted for clarity. Selected bond lengths (Å) and angles (deg): O(1)−P(3) = 1.708(2); O(2)−P(3) = 1.709(2); O(3)−P(3) = 1.715(2); O(4)−P(3) = 1.708(2); O(5)−P(3) = 1.720(2); O(6)−P(3) = 1.723(2); O(7)−P(4) = 1.711(2); O(8)−P(4) = 1.713(2); O(9)−P(4) = 1.703(2); O(10)−P(4) = 1.717(2); O(11)−P(4) = 1.717(2); O(12)−P(4) = 1.711(2); P(1)−Pd(1) = 2.2492(6); P(2)−Pd(1) = 2.2370(7); N(1)−Pd(1) = 2.080(2); N(2)−Pd(1) = 2.093(2); O(8)-H(28a) = 2.318(2); O(1)−P(3)−O(2) = 90.84(8); O(1)−P(3)−O(3) = 88.38(8); O(1)−P(3)−O(5) = 88.59(8); O(1)−P(3)−O(6) = 92.96(8); O(2)−P(3)−O(3) = 93.60(8); O(2)−P(3)−O(6) = 88.72(8); O(3)−P(3)−O(5) = 87.46(8); O(4)−P(3)−O(2) = 87.11(8); O(4)−P(3)−O(3) = 91.17(8); O(4)−P(3)−O(5) = 93.46(8); O(4)−P(3)−O(6) = 87.57(8); O(5)−P(3)−O(6) = 90.24(7); O(7)−P(4)−O(11) = 88.65(8); O(7)−P(4)−O(8) = 90.85(8); O(8)−P(4)−O(10) = 87.43(8); O(9)−P(4)−O(10) = 91.02(8); O(9)−P(4)−O(11) = 88.16(8); O(9)−P(4)−O(7) = 88.04(8); O(9)−P(4)−O(8) = 93.11(9); O(11)−P(4)−O(10) = 93.09(8); O(12)−P(4)−O(10) = 88.46(8); O(12)−P(4)−O(11) = 90.47(8); O(12)−P(4)−O(7) = 92.53(9); O(12)−P(4)−O(8) = 88.26(8); N(1)−Pd(1)−N(2) = 87.38(8); N(2)−Pd(1)−P(2) = 93.50(6); N(1)−Pd(1)−P(1) = 93.74(6); P(2)−Pd(1)−P(1) = 85.09(2).

conformation of the palladacycle, which results in the opposite enantiomer for the cation in each structure. Such twisting is commonly observed for square-planar palladium(II) compounds containing the dppe ligand.[42] The molecular structure of [(dppe)Pd(NCMe)$_2$][**1**]$_2$ shows similar behavior; however, both enantiomers of the cation and anion are present and are related by symmetry in the $P\bar{1}$ space group.[43]

The metrical parameters within the [(dppe)Pd(NCMe)Me]$^+$ and [(dppe)Pd(NCMe)$_2$]$^{2+}$ cations are comparable to those observed in analogous species. As represented by a dashed line in Figure 6, the closest ion contact in [(dppe)Pd(NCMe)Me][Λ-**1**] and [(dppe)Pd(NCMe)Me][Δ-**1**] is between a phenyl-H of the dppe ligand and an oxygen atom from the catecholate anion [ca. 2.55 Å]. In contrast, Figure 7 shows that the closest contact in [(dppe)Pd(NCMe)$_2$][**1**]$_2$ is between an acetonitrile hydrogen and an oxygen atom of the [**1**]$^-$ [2.318(2) Å]. In both compounds, these approaches are slightly less than the sum of the van der Waals radii for oxygen and hydrogen [r_{vdw} = 2.72 Å][31] and suggest weak interactions between the cation and anion.

Summary

The preparation of two novel Brønsted acids containing the tris(*o*-phenylenedioxy)phosphate anion [**1**]$^-$, H(DMF)$_2$[**1**] and H(DMSO)$_2$[**1**], was accomplished following a straightforward procedure from PCl_5, catechol, and the appropriate solvent (DMF or DMSO). Both compounds were characterized spectroscopically and through X-ray crystallographic analysis. Their high acidities were suggested by the downfield shifts of the acidic proton in their ^1H NMR spectra. The basicity of anion [**1**]$^-$ was determined to be similar to the classical weakly coordinating anion [BF_4]$^-$, based on identical N−H stretching frequency for the Oct$_3$NH[**1**], and to that observed for Oct$_3$NH[BF_4]. H(DMF)$_2$[**1**] was shown to be effective in the stoichiometric activation of the metal−alkyl bonds of (dppe)PdMe$_2$ to afford either [(dppe)Pd(NCMe)Me][**1**] (1:1 ratio) or [(dppe)Pd(NCMe)$_2$][**1**] (1:2 ratio), both of which were structurally characterized. Future work is underway to determine the effectiveness of H(DMF)$_2$[**1**] in the protonolysis of other metal−alkyls to generate catalytically active species. The potential resolution of [**1**]$^-$, or its derivatives, to afford compounds containing enantiomerically pure anions may lead to exciting possibilities in enantioselective synthesis.

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[43] The absolute configuration of anion [**1**]$^-$ components of **5(Λ)** and **5 (Δ)** were determined on the basis of their Flack values. Their final Flack values were refined to be 0.006(12) for **5(Λ)** and −0.012(10) for **5(Δ)**. Flack, H. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 876.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk or glovebox techniques under nitrogen atmosphere. Toluene and Et_2O were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. CD_3CN, CD_2Cl_2, and DMSO-d_6 were purchased from Cambridge Isotope Laboratories Inc. in 1 g sealed ampules and dried over 3 Å molecular sieves before use. Trioctylamine and HPLC grade carbon tetrachloride were purchased from Aldrich and dried over 3 Å molecular sieves before use. DMSO and DMF were dried over 3 Å molecular sieves and distilled before use. Acetonitrile was distilled from CaH_2 before use. PCl_5 (Aldrich) was sublimed prior to use. Anhydrous HCl (BOC Gases) and catechol (Aldrich) were used as received. Mixture **2**/**3**[14] and $[(dppe)Pd(CH_3)_2]$[44] were prepared following literature procedures. ^1H, $^{13}C\{^1H\}$, ^{31}P, and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. 85% H_3PO_4 was used as an external standard (δ 0.0) for ^{31}P and $^{31}P\{^1H\}$ NMR spectra. ^1H NMR spectra were referenced to residual protonated solvent, and $^{13}C\{^1H\}$ NMR spectra were referenced to the deuterated solvent. Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer equipped with an inlet attached to a nitrogen supply. The sample chamber was purged with nitrogen until a constant concentration level of moisture, and carbon dioxide was obtained for the background. IR spectra of 0.005−0.01 M solutions of trioctylammonium salts in carbon tetrachloride were obtained using a cell with KBr windows and recorded in the 4000−500 cm^{-1} range under a flow of nitrogen.

$H(DMSO)_2$[1]. To a solid mixture of **2** and **3** (1.0 g, 2.8 mmol) was added DMSO (5.0 g, 64 mmol), and the resultant pale purple solution was stirred for 20 min. Subsequently, toluene (90 mL) was added to afford a colorless precipitate, which was collected by filtration. The solid was redissolved in CH_3CN (10 mL), reprecipitated with toluene (90 mL), and collected by filtration. The crude product was dried in vacuo. Yield = 1.4 g (98%). Crystals suitable for X-ray crystallography were obtained from slow diffusion of toluene into a DMSO solution of $H(DMSO)_2$[**1**] (ca. 5 days).

^{31}P NMR (162 MHz, CH_3CN): δ −80.5. ^1H NMR (300 MHz, CD_3CN): δ 13.3 (s, 1H, *H*-$DMSO_2$), 6.65 (s, 12H, Ar-*H*), 2.83 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): 145.4 (d, J_{CP} = 4 Hz), 118.6 (s), 108.9 (d, J_{CP} = 17 Hz), 40.4 (s). Anal. Calcd for $C_{22}H_{25}O_8PS_2$: C, 51.55; H, 4.92. Found: C, 51.68; H, 4.93.

$H(DMF)_2$[1]. To a solid mixture of **2** and **3** (1.0 g, 2.8 mmol) was added DMF (5.0 g, 68 mmol), and the resultant white suspension was stirred for 60 min. Subsequently, toluene (40 mL) was added and the colorless precipitate was collected by filtration. The solid was redissolved in CH_3CN (10 mL), reprecipitated with toluene (90 mL), and collected by filtration. The crude product was dried in vacuo. Yield = 1.1 g (78%). Crystals suitable for X-ray diffraction were obtained from slow diffusion of toluene into a solution of $H(DMF)_2$[**1**] in DMF.

^{31}P NMR (162 MHz, CH_3CN): δ −80.0. ^1H NMR (300 MHz, CD_3CN): δ 15.3 (br s, 1H, *H*-DMF_2), 8.06 (s, 2H, *H*C=O), 6.69−6.65 (m, 12H, Ar-*H*), 3.07 (s, 6H, CH_3), 2.95 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): 165.5 (s), 146.6 (d, J_{CP} = 4 Hz), 120.3 (s), 110.4 (d, J_{CP} = 16 Hz), 39.3 (s), 33.8 (s). Anal. Calcd for $C_{24}H_{27}N_2O_8P$: C, 57.37; H, 5.42; N, 5.58. Found: C, 57.52; H, 5.45; N, 5.64.

[(dppe)Pd(NCMe)Me][1]. To a solid mixture of [(dppe)$PdMe_2$] (50 mg, 0.093 mmol) and $H(DMF)_2[P(1,2\text{-}O_2C_6H_4)_3]$ (47 mg, 0.094 mmol) was added Et_2O (ca. 1 mL). Acetonitrile was added dropwise to the stirred suspension until all the solids dissolved (ca. 10 drops). The solution was stirred at room temperature for 15 min, after which it was cooled −30 °C to afford a colorless precipitate. The supernatant liquid was decanted from the precipitate and the solid was dried in vacuo. Yield = 72 mg (85%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of [(dppe)Pd(NCMe)Me][**1**] in Et_2O/CH_3CN.

$^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN): δ 62.5 (d, $^2J_{PP}$ = 28 Hz, dppe), 40.7 (d, $^2J_{PP}$ = 28 Hz, dppe), −82.0 (s, anion). ^1H NMR (300 MHz, CD_3CN): δ 7.69−7.52 (m, 20H, Ar-*H* of dppe), 6.65−6.58 (m, 12H, Ar-*H* of anion), 2.73−2.55, 2.41−2.24 (m, 4H, CH_2CH_2), 1.96 (s, 3H, Pd-NCCH_3), 0.52 (dd, $^3J_{HP}$ = 6 Hz, $^3J_{HP}$ = 3 Hz, 3H, Pd−CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 146.3 (d, J_{CP} = 5 Hz), 133.8 (d, J_{CP} = 12 Hz), 133.2 (d, J_{CP} = 14 Hz), 132.8 (d, J_{CP} = 3 Hz), 132.3 (s), 130.1 (d, J_{CP} = 9 Hz), 130.4 (d, J_{CP} = 34 Hz), 130.0 (d, J_{CP} = 12 Hz), 127.9 (d, J_{CP} = 57 Hz), 123.7 (s), 119.4 (s), 109.9 (d, J_{CP} = 18 Hz), 31.3 (dd, J_{CP} = 35 Hz, J_{CP} = 21 Hz), 24.2 (dd, J_{CP} = 28 Hz, J_{CP} = 8.1 Hz), 8.6 (d, J_{CP} = 88 Hz), 3.0 (s).

[(dppe)Pd(NCMe)$_2$][1]$_2$. To a solid mixture of (dppe)$PdMe_2$ (45 mg, 0.084 mmol) and $H(DMF)_2$[**1**] (85 mg, 0.17 mmol) was added CH_3CN (2 mL). The resulting cloudy yellow mixture was stirred for 3 h, and the supernatant was decanted to afford a yellow solid. The solid was washed with cold CH_3CN (3 × 2 mL) and was dried in vacuo. Yield = 66 mg (61%). Crystals, suitable for X-ray diffraction, were obtained after a concentrated solution of $[(dppe)Pd(NCCH_3)_2]$[**1**]$_2$ in CH_3CN was left in the glovebox overnight.

^{31}P NMR (162 MHz, CH_3CN): δ 76.5 (s, dppe), −82.1 (s, anion). ^1H NMR (400 MHz, CD_3CN): δ 7.79−7.61 (m, 20H, Ar-*H* on dppe), 6.64−6.58 (m, 24H, Ar-*H* on anion), 2.92−2.77 (m, 4H, CH_2CH_2 on dppe), 1.96 (s, 6H, PdNCCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): 145.5 (d, J_{CP} = 4 Hz), 133.5 (d, J_{CP} = 12 Hz), 129.7 (d, J_{CP} = 12 Hz), 125.3 (d, J_{CP} = 55 Hz), 118.6 (s), 118.0 (s), 108.9 (d, J_{CP} = 17 Hz), 26.9 (dd, J_{CP} = 39 Hz, J_{CP} = 8 Hz), 1.1 (s).

Reaction of (dppe)$PdMe_2$ with HCl. Anhydrous HCl was bubbled through a stirred solution of (dppe)$PdMe_2$ in CH_3CN (10 mL) at 0 °C for a few minutes. The solvent was removed in vacuo to afford a white solid. The ^{31}P NMR spectrum of the isolated solid was identical to that of an authentic sample of (dppe)$PdCl_2$ [δ = 68.1 in CH_3CN].[45]

[$(C_8H_{17})_3NH$][1]. Trioctylamine (1.7 g, 4.8 mmol) and a solid mixture of **2** and **3** (1.0 g, 2.8 mmol) were dissolved in CH_2Cl_2 (5 mL). After 3 h, the solvent was removed in vacuo and the resultant colorless oil was heated in vacuo at 140 °C. Subsequently, hexanes (15 mL) was added to the colorless oil, and this mixture was ultrasonicated for 15 min to afford a white solid. [$(C_8H_{17})_3NH$][**1**] was isolated by filtered, washed with hexanes (10 mL), and dried in vacuo. Yield = 1.3 g (63%).

^{31}P NMR (121 MHz, $CDCl_3$): δ −83.8. ^1H NMR (300 MHz, $CDCl_3$): δ 8.61 (br s, 1H, *H*-N), 6.70 (s, 12H, Ar-*H*), 3.20−3.12 (m, 6H, N-CH_2), 1.74−1.63 (m, 6H, NCH_2-CH_2), 1.26−1.17 (m, 30H, NC_2H_4-C_5H_{10}), 0.87 (t, $^3J_{HH}$ = 7 Hz, 9H, CH_3). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): 145.0 (d, J_{CP} = 4 Hz), 119.5 (s), 109.7 (d, J_{CP} = 19 Hz), 53.4 (s), 31.5 (s), 28.8 (s), 28.7 (s), 26.5 (s), 23.1 (s), 22.4 (s), 14.0 (s). Anal. Calcd for $C_{42}H_{64}NO_6P$: C, 71.06; H, 9.09; N, 1.97. Found: C, 71.12; H, 9.21; N, 2.12.

X-ray Crystallography. All single crystals were immersed in oil and were mounted on a glass fiber. Data were collected on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and subsequent Fourier difference techniques. Unless noted, all non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were included in calculated positions but not refined. All data sets were corrected for Lorentz

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and polarization effects. Calculations were performed using PARST[46,47] and SHELXL-97.[48,49] All refinements were performed using the SHELXTL[49,50] crystallographic software package from Bruker-AXS.

Compound H(DMSO)$_2$[**1**] has two disordered molecules of DMSO bound to H(1). H(1) was located using the difference map and refined isotropically. Each of the disordered DMSO molecules was modeled in two orientations. Their respective populations were refined to the final occupancy of 0.926(2), 0.074(2), 0.8570(16), and 0.1430(16). Due to the low occupancy values (0.074(2)) for C(19b) and C(20b), they were refined isotropically. Compound H(DMF)$_2$[**1**] has two molecules of DMF bound to H(1). H(1) was located using the difference map and refined isotropically. Crystal data and refinement paramenters are listed in Table 1. Additional data are available in the Supporting Information.

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Supporting Information Available: CIF files giving supplementary crystallographic data for the structures reported are available free of charge via the Internet at http://pubs.acs.org. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre as CCDC-727172 to CCDC-727176 via www.ccdc.cam.ac.uk/data_request/cif.

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