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Chelating Assistance of P–C and P–H Bond Activation at Palladium and Nickel: Straightforward Access to Diverse Pincer Complexes from a Diphosphine–Phosphine Oxide

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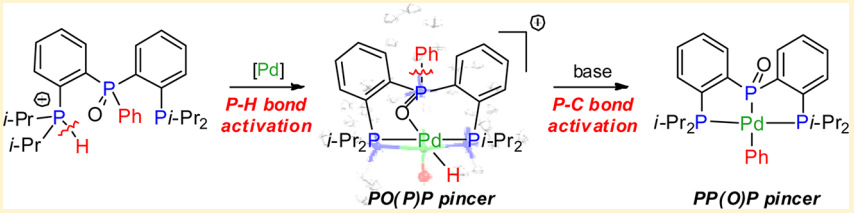
Supporting Information



ABSTRACT: The diphosphine–phosphine oxide (DPPO) {[*o*-*i*-Pr$_2$P-(C$_6$H$_4$)]$_2$P(O)Ph} (**1**) reacts with [Ni(cod)$_2$] (cod = 1,4-cyclooctadiene) to give the diphosphine–phosphide oxide $\kappa^{P,P(O),P}$ pincer complex **3**. According to DFT calculations, the Ph–P(O) bond activation involves a three-center P,C$_{ipso}$,Ni transition state. Reaction of the DPPO ligand **1** with [(nbd)Pd(ma)] (nbd = 2,5-norbornadiene and ma = maleic anhydride) affords the [(DPPO)Pd(ma)] complex **4**. Upon heating, the ma coligand is displaced and the $\kappa^{P,P(O),P}$ palladium pincer complex **2** is obtained. The dinuclear complex {(DPPO)[Pd(ma)]$_2$} (**6**) has also been authenticated. X-ray diffraction analysis showed an original situation in which the oxygen atom of the central phosphine oxide moiety bridges the two palladium centers. Addition of trifluoromethanesulfonic acid to DPPO **1** affords the trifunctional phosphine–phosphine oxide–phosphonium derivative **7**. Upon reaction with [Pd$_2$(dba)$_3$], the palladium hydride $\kappa^{P,O(P),P}$ pincer complex **8** is cleanly formed as the result of P$^+$–H bond activation. Complex **8** is readily deprotonated by DBU (DBU = 1,8-diazabicycloundec-7-ene), and spontaneous oxidative addition of the Ph–P(O) bond gives the diphosphine–phosphide oxide $\kappa^{P,P(O),P}$ pincer complex **2**. Conversely, addition of trifluoromethanesulfonic acid on **2** does not give back the palladium hydride **8** but leads to the diphosphine–hydroxy phosphine $\kappa^{P,P(OH),P}$ pincer complex **9**.

INTRODUCTION

Over the past few years, our group has been investigating the formation, electronic structure, and reactivity of transition-metal complexes deriving from polyfunctional ligands. We are particularly interested in ligands combining a central group 13, 14, or 15 element with phosphine buttresses.[1−7] Such chelate systems have proven extremely useful for the coordination of Lewis acids as σ-acceptor ligands,[1−4] and using the same strategy, interesting results have been obtained recently on the coordination and activation of σ bonds (Figure 1).[5−7] In this context, we have shown that the Ph–P(O) bond of the diphosphine–phosphine oxide (DPPO) **1** readily undergoes oxidative addition at palladium to give the diphosphine–phosphide oxide complex **2** (Scheme 1).[7]

Thanks to their chelating rigid structure, pincer complexes display unique properties, and over the last two decades, they have attracted enormous interest.[8] In this area, pincer complexes derived from PEP ligands occupy a forefront position, and the nature of the central moiety has been extensively varied (E = C,[9] N,[10] Si,[11] B,[12] ...). Notably, however, PPP frameworks have been comparatively poorly explored,[13,14] and complex **2** represents a rare example of a PP(O)P pincer complex.[15] This prompted us to explore further the coordination of diphosphine–phosphine oxide ligands. DPPO **1** was found to remain intact and behave as a mono-, bi-, or tridentate ligand upon coordination to gold, silver, and rhodium.[16] In this work, the coordination of **1** to Pd and Ni has been comprehensively studied, with special interest paid to the oxidative addition of the Ph–P(O) bond. The formation of a palladium hydride complex by P$^+$–H oxidative addition of a phosphine–phosphine oxide–phosphonium derivative is also described. Upon deprotonation of the palladium hydride

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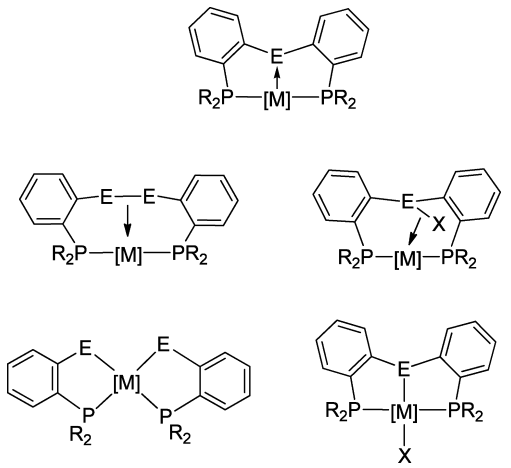
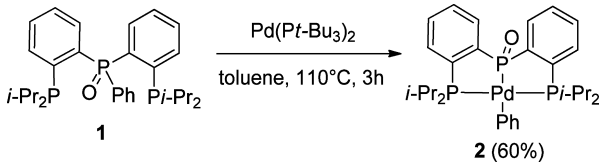


Figure 1. Schematic representations of the different types of complexes obtained upon coordination of PEP, PEEP, and PE(X)P ligands (E = group 13−15 elements).

Scheme 1. Formation of the Diphosphine−Phosphide Oxide Pd Pincer Complex 2 upon P(O)−Ph Bond Activation of 1

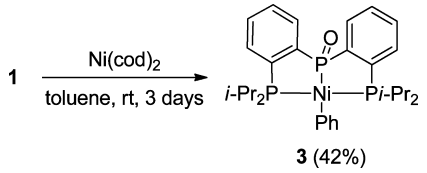


complex, spontaneous Ph−P(O) bond activation occurs to give the diphosphine−phosphide oxide complex **2**.

RESULTS AND DISCUSSION

First, the DPPO ligand **1** was reacted with the nickel(0) precursor $Ni(cod)_2$ (cod = 1,4-cyclooctadiene) to substantiate the generality of the P(O)−Ph bond activation process. After 3 days at room temperature in toluene, the pincer complex **3** was obtained as the sole product (Scheme 2). After workup, it was

Scheme 2. P(O)−Ph Bond Activation of the Diphosphine−Phosphine Oxide 1 at Nickel, Leading to the Pincer Complex 3



isolated as a yellow powder (42% isolated yield) and fully characterized. The spectroscopic data for **3** are very close to those of the palladium complex **2**, indicating that P(O)−Ph bond activation had occurred similarly at Ni(0). In particular, the ^{31}P NMR spectrum displays a triplet at δ 134.6 ppm (P(O)) and a doublet at δ 61.8 ppm ($P(i\text{-}Pr)_2$) with a J_{PP} coupling constant of 43 Hz. Also diagnostic is the ^{13}C NMR signal observed at 158.2 ppm (doublet of triplets, J_{CP} = 75 and 24 Hz) for the C_{ipso} atom of the Ph group at Ni. C−X (X = I, Br), C−O, and C−S bond activations at Ni are common,[17] but phosphines have only been occasionally reported to undergo C−P bond cleavage at Ni,[18] and to the best of our knowledge, C−P(O) bond activation had not been observed so far with this metal.[19]

To shed light on the C−P(O) bond activation leading to complex **3**, DFT calculations were performed on the actual system.[20] The energy profile computed for the Ni species (Figure 2) very much resembles that found previously for Pd.[7] The oxidative addition product **3*** is favored thermodynamically by 26 kcal/mol over the corresponding DPPO·Ni^0 complex **4*** (in which the low-valent Ni center is stabilized by π coordination of the phenyl ring at the phosphine oxide). The C−P(O) bond activation proceeds via a three-center P,C_{ipso},Ni transition state, and the activation barrier from **4*** to **3*** is relatively low (9 kcal/mol).

Complexes **2** and **3** are obtained directly upon reaction of the DPPO ligand **1** with $[Pd(Pt\text{-}Bu_3)_2]$ and $[Ni(cod)_2]$. No intermediate was detected spectroscopically before oxidative addition of the Ph−P(O) bond occurred. To gain more insight into the formation of the pincer complexes, we became interested in the reaction of the DPPO **1** with other Pd(0) precursors and turned our attention to [Pd(nbd)(ma)][21] (nbd = 2,5-norbornadiene, ma = maleic anhydride). This choice was stimulated by the labile character of the nbd coligand (in comparison with $Pt\text{-}Bu_3$) and the ability of ma to stabilize low-valent Pd centers.[22] The DPPO **1** was first treated with 1 equiv of [Pd(nbd)(ma)] in dichloromethane at room temperature. After 30 min, the new complex **5** was obtained predominantly (~90%, according to NMR) along with a small amount of the side product **6** (~10%) (Scheme 3). Complex **5** could be obtained in pure form using a slight excess of DPPO (1.2 equiv with respect to Pd). Its NMR data are consistent with the general formula (DPPO)Pd(ma). According to ^1H NMR, the nbd coligand has been displaced but ma is retained. In addition, the ^{31}P NMR data indicate symmetric coordination of the two phosphine moieties of DPPO to Pd: two singlets of relative integrations 1:2 are observed at δ 39.1 and 34.8 ppm for the P(O)Ph and $Pi\text{-}Pr_2$ moieties, respectively. The molecular structure of **5** was unambiguously assessed by X-ray diffraction (Figure 3a). In agreement with the spectroscopic data, the DPPO ligand **1** is intact and coordinates symmetrically to Pd (P2−Pd = 2.388(1) and P3−Pd = 2.326(1) Å). The oxygen atom of the central phosphine oxide moiety points toward the metal but remains too far to interact significantly with it (O−Pd

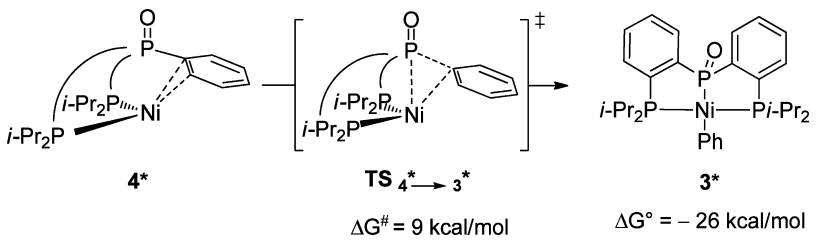


Figure 2. P(O)−Ph bond activation at Ni, as calculated at the B3PW91/SDD+f (Ni) and 6-31G** (other atoms) level of theory.

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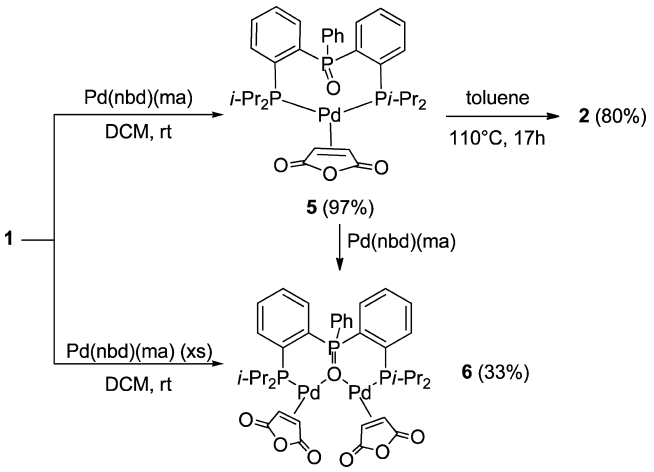
Scheme 3. Synthesis of the Mono- and Dinuclear Palladium Complexes 5 and 6 and Thermal Activation of 5 Leading to the Pincer Complex 2



distance 2.870(2) Å). η^2 Coordination of ma completes the coordination sphere of Pd (Pd−C8 = 2.096(2) and Pd−C5 = 2.125(3) Å).

Complex **5** simply results from the displacement of the nbd coligand at Pd by the two phosphine moieties of DPPO. As the result of this chelating coordination, the central phosphine oxide fragment is positioned close to the metal, but ma stabilizes the Pd(0) center and prevents oxidative addition of the P(O)−Ph bond. In fact, ma dissociation and activation of the DPPO ligand can be achieved upon heating, and **5** was converted into the pincer complex **2** after 17 h of reflux in toluene (spectroscopic yield of 80%).

We were intrigued by the aforementioned minor product **6** and also carried out an X-ray diffraction study to reveal its structure (Figure 3b). Quite surprisingly, it is a dinuclear complex in which a single DPPO ligand coordinates two Pd atoms. Each metal center is surrounded by one *i*-Pr_2P fragment and a ma coligand. In addition, the oxygen atom of the central phosphine oxide moiety bridges symmetrically the two Pd centers. The corresponding OPd distances (O−Pd1 = 2.219(2) and O−Pd2 = 2.214(2) Å) fall in the higher range of those observed in terminal phosphine oxide Pd complexes (1.968−2.276 Å according to a Cambridge database search). Despite the bridging coordination of DPPO, the two Pd centers are too far away from each other to interact (Pd1−Pd2 distance 3.448(1) Å). The ability to bridge metal centers is well-established for P═S moieties[23] but comparatively rare for P═O groups. Only a few examples of P═O bridging coordination have been reported to date with group 10 metals (all involving Ni).[24] Note that complex **6** can be obtained preparatively (33% isolated yield) by reacting the free ligand DPPO **1** or the mononuclear complex **5** with an excess of [Pd(nbd)(ma)].

As briefly discussed in the Introduction, chelating assistance is a very useful method to support unusual metal−ligand interactions and original bond activation processes. Also, pincer complexes are now commonly prepared by E−H bond activation (E = C,[9] N,[10] Si,[11] B,[12] P,[13,14] ...) of polyfunctional ligands. It is also well-known that oxidative addition of C−E bonds (E = Si, O, S, N, ...)[25] and E−E bonds (E = C, Si, ...)[26] can be efficiently promoted by appending donor groups.

At this point, we became interested in taking advantage of the chelating approach to promote P^+−H bond activation and thereby prepare hydride complexes, using DPPO as a precursor. Tertiary phosphonium salts R_3PH^+,X^- are stable and easy-to-handle precursors for phosphines. Upon reaction with transition metals in the presence of a base, they readily form phosphine complexes, a route that is frequently used to generate electron-rich Pd complexes.[27] However, oxidative addition of R_3P^+−H bonds at transition metals has only rarely been observed. As far as Pd is concerned, Stephan recently described the formation of a zwitterionic Pd hydride complex upon oxidative addition of the phosphonium−borate $Cy_2P^+H-C_6F_4-B^-F(C_6F_5)_2$ to $[Pd(PPh_3)_4]$,[28a] while Caporaso and Mecking reported a somewhat similar process starting from the phosphonium−sulfonate $(o\text{-An})_2P^+H-C_6H_4-SO_3^-$ and $[Pd(Pt\text{-}Bu_3)_2]$.[28b] In order to study further such P^+−H bond activation processes, we envisioned converting our DPPO ligand **1** into a trifunctional derivative combining phosphine,

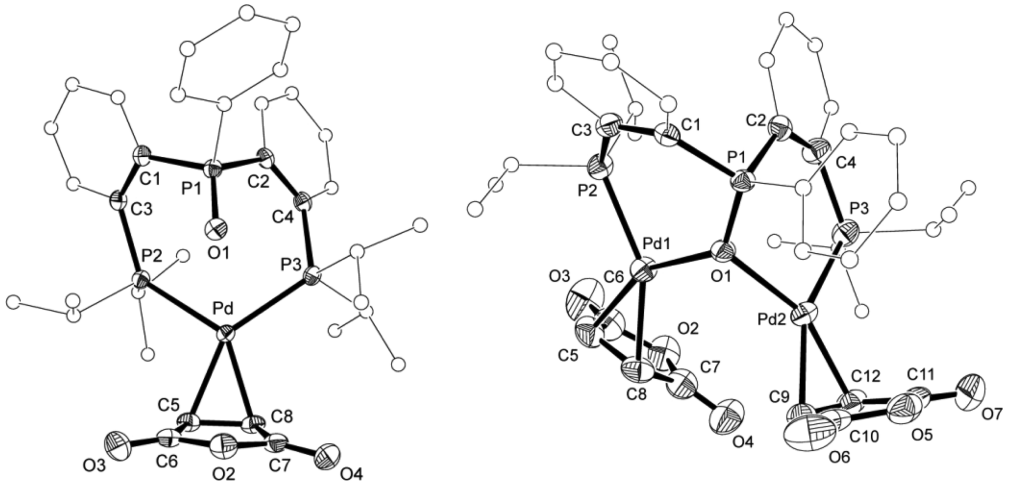


Figure 3. Molecular view of complexes **5** (a, left) and **6** (b, right). For clarity, hydrogen atoms are omitted and isopropyl/phenyl groups at phosphorus are simplified. Selected bond lengths (Å) and bond angles (deg) are as follows. **5**: P2−Pd, 2.388(1); P3−Pd, 2.326(1); P1−O, 1.480(2); Pd−C5, 2.125(3); Pd−C8, 2.096(2); C5−C8, 1.424(4); P2−Pd−P3, 111.48(2); C5−Pd−C8, 39.4(1). **6**: P2−Pd1, 2.308(1); P3−Pd2, 2.283(1); P1−O, 1.520(2); Pd1−C5, 2.062(4); Pd1−C8, 2.146(2); Pd2−C12, 2.065(4); Pd2−C9, 2.132(4); C5−C8, 1.425(6); C9−C12, 1.408(6); P2−Pd1−O1, 95.21(6); P3−Pd2−O1, 94.01(6); C5−Pd1−C8, 39.5(2); C9−Pd2−C12, 39.2(2).

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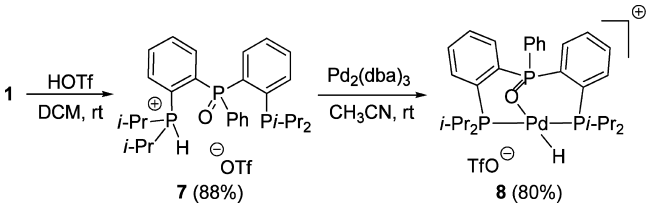
phosphine oxide, and phosphonium fragments. Reaction of **1** with trifluoromethanesulfonic acid (1.1 equiv) in dichloromethane readily afforded the desired compound **7** (Scheme 4).

Scheme 4. Synthesis of the Phosphine−Phosphine Oxide−Phosphonium Derivative 7 and Its Reaction with $[Pd_2(dba)_3]$



The protonation takes place at one of the $P(i\text{-}Pr)_2$ moieties, and three distinct signals are observed in the ^{31}P NMR spectrum. The signals are broad at room temperature but sharpen at low temperature (− 40 °C), indicating that some exchange occurs slowly on the NMR time scale. Compound **7** was then reacted with different Pd(0) precursors. Complex mixtures of unidentified products were obtained with $Pd[P(t\text{-}Bu)_3]_2$ and [Pd(nbd)(ma)], but **7** reacted cleanly with $[Pd_2(dba)_3]$ in acetonitrile at room temperature to give the new complex **8**. The $^{31}P\{^1H\}$ NMR spectrum of **8** displays a doublet at δ 50.3 ppm for the two $P(i\text{-}Pr)_2$ groups and a triplet at δ 48.9 ppm for the central P(O)Ph moiety, with a J_{PP} coupling constant of 8 Hz. The presence of a hydride at Pd is clearly apparent from the multiplet observed at δ −16.5 ppm in the ^1H NMR spectrum (the J_{PH} coupling constants are too small to be resolved). This chemical shift falls in the lower limit of those reported for Pd hydrides ($\delta(^1H)$ from −3 to −12 ppm).[29]

Crystals were obtained by diffusion of diethyl ether into an acetonitrile solution of **8**, and an X-ray diffraction study was carried out (Figure 4a). Complex **8** adopts an ion pair structure, and the Pd center is tetracoordinated. The two phosphine fragments $i\text{-}Pr_2P$ coordinate symmetrically (P2−Pd = 2.299(1) and P3−Pd = 2.279(1) Å). The hydrogen at Pd was unambiguously located in the difference Fourier map, and the Pd−H distance was refined at 1.50(2) Å. The coordination sphere is completed by the oxygen atom of the central phosphine oxide moiety. The P═O bond of **8** (1.512(2) Å) is noticeably elongated in comparison to that of **5** (1.480(2) Å), in which the phosphine oxide remains pendant. Also, despite the strong trans influence of the hydride (O−Pd−H bond angle 179°), the O−Pd distance (2.116(2) Å) exceeds the sum of covalent radii by only 5%.[30]

The reaction of **7** with $[Pd_2(dba)_3]$ thus proceeds via oxidative addition of the P^+−H bond at Pd, and the in situ reconstituted DPPO ligand coordinates to Pd via the two lateral phosphine groups as well as the central phosphine oxide fragment. Such tridentate coordination is reminiscent of that observed upon coordination of DPPO to $[Rh(CO)]^+$,[16] and the Pd hydride complex **8** provides the second example of such a PO(P)P pincer complex.

Formally, the cationic Pd hydride complex **8** differs from **2** only by a proton, raising the question of the possible interconversion of these two species. It is known that strong bases are able to depronotate palladium hydrides,[31] and accordingly, deprotonation of **8** was envisioned to generate transiently a low-valent Pd(0) complex. At this stage, oxidative addition of the P(O)−Ph bond should proceed spontaneously, leading to the neutral Pd(II) complex **2**. This hypothesis was verified experimentally. Upon addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane at room temperature, complex **8** was converted quantitatively and quasi-instantaneously into **2** (Scheme 5).

The reversibility of this transformation, that is reductive elimination of P(O)−Ph at Pd upon protonation, was then explored. To this end, complex **2** was treated with trifluoromethanesulfonic acid in dichloromethane. A clean reaction occurred immediately. According to NMR data, it did not give back the Pd hydride **8** but led to the new complex **9**, whose structure was determined by X-ray crystallography (Figure 4b). The overall structure of the precursor **2** is retained in **9** (the Pd center is surrounded by the three phosphorus atoms and the phenyl group, organized in a square-planar arrangement), but the oxygen atom has been protonated so that the central phosphide oxide of **2** has been converted into a hydroxyphosphine moiety in **9**. Such transformation of an X-type into a L-type ligand upon protonation is rather common,

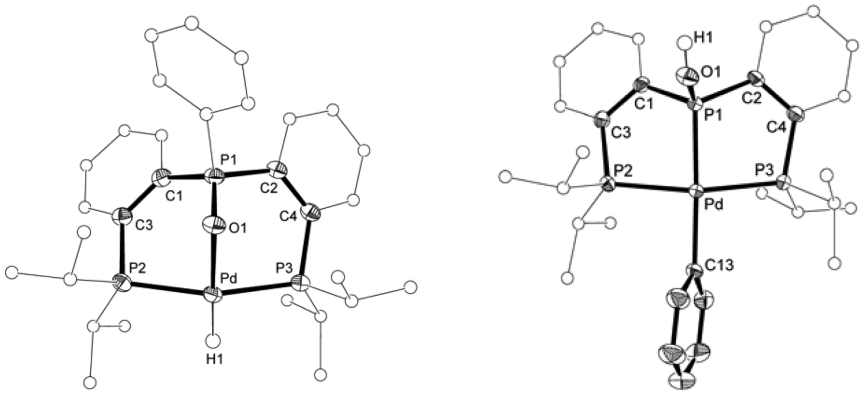


Figure 4. Molecular view of complex **8** (a, left) and **9** (b, right). For clarity, the triflate counteranion and hydrogen atoms (except that at Pd for **8** and that at O for **9**) are omitted and isopropyl/phenyl groups at phosphorus are simplified. Selected bond lengths (Å) and bond angles (deg) are as follows. **8**: P3−Pd, 2.279(2); P2−Pd, 2.299(2); P1−Pd, 2.934(2); O−Pd, 2.116(2); P1−O, 1.512(2); Pd−H, 1.50(2); P2−Pd−P3, 157.17(2); P3−Pd−H, 88(1); P2−Pd−H, 93(1); P3−Pd−O1, 90.92(4); P2−Pd−O1, 88.52(4). **9**: P2−Pd, 2.317(21); P3−Pd, 2.302(1); P1−Pd, 2.251(1); C13−Pd, 2.079(2); P1−O1, 1.588(2); O1−H, 0.840(2); P2−Pd−P3, 160.88(2); P2−Pd−P1, 84.91(2); P3−Pd−P1, 85.72(2); P1−Pd−C13, 176.99(7); P2−Pd−C13, 93.28(7); P3−Pd−C13, 96.69(7).

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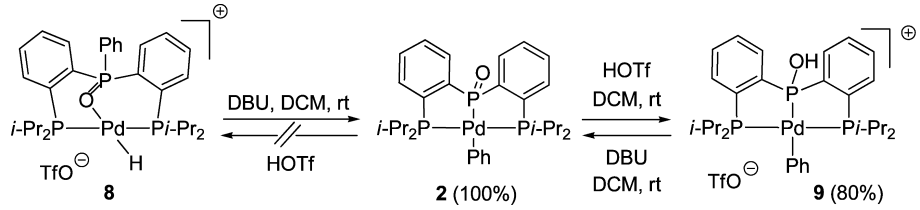
Scheme 5. Synthesis of 2 by Deprotonation of the Palladium Hydride Complex 8 and Addition of Trifluoromethanesulfonic Acid to 2 Giving the Diphosphine−Hydroxyphosphine Complex 9



including in pincer complexes.[32] The conversion of **2** into **9** provides the first example of this transformation happening via phosphide oxide protonation. The reverse transformation, namely deprotonation of hydroxyphosphine complexes, is comparatively well-known.[33] And actually, complex **8** gives back **2** upon treatment with DBU.

CONCLUSION

Coordination of the diphosphine−phosphine oxide DPPO to various Pd and Ni precursors has provided further insight into the Ph−P(O) bond activation process. The reaction proceeds similarly at Pd and Ni, involving a P,C_{ipso},M transition state. The presence of a maleic anhydride coligand at Pd disfavors the oxidative addition process, and complex **5**, in which the two phosphines are symmetrically coordinated but the P(O)Ph moiety remains pendant, has been isolated. Complete characterization of the dinuclear complex **6**, obtained as a byproduct of **5**, revealed an original coordination mode for a phosphine oxide moiety: namely, symmetric bridging of two palladium centers.

The chelating approach was then extended to P^+−H bond activation. The original derivative **7** combining three different phosphorus moieties (phosphine, phosphine oxide, and phosphonium) was readily prepared by chemoselective protonation of DPPO. Its coordination to Pd proceeds with oxidative addition of the P^+−H bond, and the ensuing hydride complex **8** adopts a rare PO(P)P pincer structure. Upon deprotonation, the palladium hydride complex **8** undergoes spontaneous Ph−P(O) bond activation to afford the diphosphine−phosphine oxide pincer complex **2**, while protonation of **2** selectively occurs at the oxygen atom to give the diphosphine−hydroxyphosphine pincer complex **9**.

This work substantiates the versatility of diphosphine−phosphine oxide ligands such as **1**. Indeed, a variety of coordination modes, including $\kappa^{PO(P)P}$, $\kappa^{PP(O)P}$, and $\kappa^{PP(OH)P}$, have been authenticated in the ensuing pincer complexes. Future work in our laboratory will seek to develop further the chelating approach of bond activation, and the reactivity of the ensuing complexes will be explored.

EXPERIMENTAL SECTION

General Comments. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker Avance 500 or 300 spectrometer. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ^{1}H (7.24 ppm) and ^{13}C (77.16 ppm) solvent signals, $CFCl_3$ (0.00 ppm), and 85% H_3PO_4 (0 ppm), respectively. Unless otherwise stated, NMR was recorded at 298 K. The *N* values corresponding to $^1/_2[J(AX) - J(A'X)]$ are provided when second-order AA′X or AA′MX systems were observed in ^{1}H or ^{13}C NMR spectra.[34] Mass spectra were recorded on a Waters LCT mass spectrometer. The DDPO ligand **1** was prepared as previously described.[7]

Ni Complex 3. In a Schlenk flask containing Ni(cod)$_2$ (55 mg, 0.20 mmol) was added a solution of diphosphine−phosphine oxide **1** (102 mg, 0.20 mmol, 1 equiv) in toluene (2 mL). The progress of the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, and after ∼3 days, most of the DPPO had been consumed. The solvent was removed under vacuum, and trituration with pentane (2 × 5 mL) followed by a pentane wash (3 × 5 mL) gave complex **3** (48 mg, 0.084 mmol, 42% yield) in ∼99% purity, as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR (500.33 MHz, $CDCl_3$): δ 8.27 (m, 2H, H_3), 7.98−7.82 (br, $\omega_{1/2}$ = 23 Hz, 1H, H_o), 7.72−7.62 (m, 2H, H_6), 7.62−7.56 (m, 2H, H_4), 7.55−7.47 (m, 2H, H_5), 7.42−7.30 (br, 1H, H_o), 7.07 (m, 2H, H_m), 6.89 (m, 1H, H_p). 2.85 (br, $\omega_{1/2}$ = 30 Hz, 2H, H_7), 2.66 (br, $\omega_{1/2}$ = 30 Hz, 2H, H_7), 1.26 (m, 12H, H_8), 0.95 (m, 6H, H_8), 0.79 (m, 6H, H_8). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$): δ 158.2 (dt, $^2J_{CP}$ = 75 Hz, $^2J_{CP}$ = 24 Hz, C_i), 154.2 (AA′MX, *N* = 20 Hz, $^2J_{PC}$ = 42 Hz, C_2), 140.9 (br, $\omega_{1/2}$ = 15 Hz, C_o), 137.6 (AA′MX, *N* = 19 Hz, $^2J_{PC}$ = 46 Hz, C_1), 136.9 (br, $\omega_{1/2}$ = 12 Hz, C_o), 130.9 (m, C_4), 130.6 (d, $^2J_{CP}$ = 17.3 Hz, C_6), 130.2 (s, C_5), 129.7 (AA′X, *N* = 7 Hz, C_3), 126.8 (br, $\omega_{1/2}$ = 16 Hz, C_m), 125.3 (br, $\omega_{1/2}$ = 16 Hz, C_m), 121.8 (s, C_p), 27.3 (AA′X, *N* = 12 Hz, C_7), 22.7 (AA′X, *N* = 12 Hz, C_7), 19.2 (s, C_8), 18.1 (s, C_8), 17.9 (s, C_8), 17.6 (s, C_8). ^{31}P NMR (202.54 MHz, $CDCl_3$): δ 134.6 (t, J_{PP} = 43 Hz, 1P, P(O)Ph), 61.8 (d, J_{PP} = 43 Hz, 2P, P(*i*-Pr)$_2$).

Pd Complex 5. In a Schlenk flask containing a light yellow suspension of Pd(nbd)(ma) (102 mg, 0.34 mmol) in dichloromethane (2 mL) was added diphosphine-phosphine oxide **1** (211 mg, 0.41 mmol, 1.2 equiv) in dichloromethane (2 mL). The resulting mixture was stirred for 30 min to give an orange solution with a black precipitate. The suspension was filtered, and the solvent was evaporated from the supernatant under vacuum. Trituration with pentane (3 × 5 mL), followed by pentane wash (3 × 5 mL), gave Pd(DPPO)(ma) (**5**; 235 mg, 0.33 mmol, 97% yield) as an orange powder. ^{1}H NMR (500.33 MHz, 253 K, $CDCl_3$): δ 7.66−7.65 (m, 2H, H_6), 7.60 − 7.48 (m, 9H, H_3, H_5, H_o, H_m, H_p), 7.36 (AA′X, *N* = 7.3 Hz, 2H, H_4), 4.22 (d, J_{HP} = 5.0 Hz, 2H, =C−H ma), 2.86−2.81 (sept br, $^3J_{HH}$ = 5.0 Hz, 2H, H_7), 2.68−2.60 (sept br, $^3J_{HH}$ = 5.0 Hz, 2H, H_7), 1.29−1.24 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 5.0 Hz, 6H, H_8), 1.16−1.10 (m, 12H, H_8), 0.91−0.87 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 5.0 Hz, 6H, H_8). ^{13}C{^{1}H} NMR (125.81 MHz, 253 K, $CDCl_3$): δ 172.9 (s, C=O), 138.6−138.5 (m, C_2), 138.4 (AA′MX, *N* = 8 Hz, $^2J_{PC}$ = 99 Hz, C_1), 135.5 (d, $^1J_{CP}$ = 107 Hz, C_i), 134.8 (AA′MX, *N* = 4 Hz, $^2J_{PC}$ = 13 Hz, C_3), 134.1 (d, J_{CP} = 12 Hz, C_6), 131.7 (s, C_p), 131.6 (d, $^2J_{CP}$ = 10 Hz, C_o), 130.1 (s, C_m), 129.1 (d, $^3J_{CP}$ = 12 Hz, C_5), 128.7 (d, $^4J_{CP}$ = 12 Hz, C_4), 51.4 (dt, J_{CP} = 24 Hz, J_{CP} = 12 Hz, =C−H ma), 30.0 (t, $^1J_{CP}$ = 10 Hz, C_7), 23.8 (m, C_7), 20.6 (t, $^2J_{CP}$ = 4 Hz, C_8), 19.7 (s br, C_8), 19.0 (m, C_8), 17.4 (s br, C_8). ^{31}P{^{1}H} NMR (202.54 MHz, 253 K, $CDCl_3$): δ 39.1 (s, 1P, P(O)Ph), 34.8 (s, 2P, P(*i*-Pr)$_2$). HRMS (CI, CH_4): exact mass (monoisotopic) calcd for [M − ma]H$^+$, 617.1483; found, 617.1514. Mp: 184−186 °C.

Preparation of Complex 2 from 5. An orange solution of Pd(DPPO)(ma) (**5**; 15 mg, 0.02 mmol) in toluene was heated at reflux in a Schlenk flask. The progress of the reaction was monitored over time by ^{31}P{^{1}H} NMR spectroscopy. After 17 h, all of the Pd(DPPO)(ma) had been consumed to give complex **2** in 80% yield, as determined by ^{31}P{^{1}H} NMR spectroscopy.

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Preparation of Complex 6 from 5. In a Schlenk flask containing a light yellow suspension of Pd(nbd)(ma) (**5**; 60 mg, 0.20 mmol, 3 equiv) in dichloromethane (1 mL) was slowly added a solution of diphosphine−phosphine oxide **1** (34 mg, 0.067 mmol, 1 equiv) in dichloromethane (3 mL). The resulting mixture was stirred for 1 h to give an orange solution with a black precipitate. The reaction mixture was filtered, the solvent was evaporated from the supernatant under vacuum, and a pale yellow solid was obtained after trituration with pentane (3 × 5 mL). The sample was recrystallized by slow diffusion of diethyl ether (5 mL) into a concentrated solution of **6** in dichloromethane (1 mL) to give yellow crystals with a small amount of elemental palladium. The crystalline sample was redissolved in dichloromethane and filtered to remove the remaining elemental palladium. The solvent was removed under vacuum, and trituration with pentane (3 × 5 mL) gave $[(DPPO)(Pd(ma))_2]$ (**6**; 20 mg, 0.022 mmol, 33% yield). ^{1}H NMR (300.13 MHz, 295 K, CD_2Cl_2): δ 7.85−7.75 (m, 2H, H_{spacer}), 7.73−7.60 (m, 4H, $3H_{spacer}$ and H_{Ph}), 7.51 (br, $\omega_{1/2} \approx 62$ Hz, 2H, H_{Ph}), 7.36 (m, 3H, H_{spacer}), 6.86 (br, $\omega_{1/2} = 51$ Hz, 2H, H_{Ph}), 3.80−4.40 (br, 4H, =C−H ma), 2.38 (br, $\omega_{1/2} = 56$ Hz, 4H, H_7), 1.30−0.78 (m, 24H, H_8). ^{31}P{^{1}H} NMR (121.44 MHz, 295 K, CD_2Cl_2): δ 50.8 (br, $\omega_{1/2} = 45$ Hz, 1P, P(O)Ph), 38.8 (br, $\omega_{1/2} = 115$ Hz, 2P, P(*i*-Pr)$_2$).

Phosphine−Phosphonium−Phosphine Oxide Derivative 7. Neat trifluoromethanesulfonic acid (63 μL, 0.71 mmol, 1.1 equiv) was added to a Schlenk flask containing a solution of diphosphine−phosphine oxide **1** (330 mg, 0.64 mmol) in dichloromethane (2 mL). The solution was stirred for 20 min, and the solvent was removed under vacuum. Trituration with pentane (3 × 5 mL), followed by pentane wash (3 × 5 mL), gave compound **7** (370 mg, 0.56 mmol, 88% yield) as a white powder in >99% purity. ^{1}H NMR (500.33 MHz, 293 K, CD_2Cl_2): δ 8.40−7.90 (br, 1H, H_{11}), 7.81 (br, $\omega_{1/2} = 23$ Hz, 3H, H_3, H_{12} and H_{14}), 7.67 (m, 4H, H_4, H_o and H_p), 7.58 (m, 2H, H_m), 7.46−7.10 (br, 3H, H_5, H_6 and H_{13}), 6.10 (d br, $^1J_{PH} = 408$ Hz, 1H, (*i*-Pr$_2$)P*H*$^+$), 4.02 (br in baseline, 1H, H_{15}), 3.46 (br in baseline, 1H, H_{15}), 2.25 (br in baseline, 2H, H_7), 1.75−0.60 (br, 24H, H_8 and H_{16}). ^{1}H NMR (500.33 MHz, 233 K, CD_2Cl_2): δ 8.20 (dd, $^3J_{PH} = 16$ Hz, $^4J_{PH} = 7$ Hz, 1H, H_{11}), 7.85−7.77 (m, 3H, H_3, H_{12}, and H_{14}), 7.69 (t, $^3J_{HH} = 7$ Hz, 1H, H_4), 7.67−7.58 (m, 3H, H_o and H_p), 7.57−7.50 (m, 2H, H_m), 7.47−7.39 (m, 2H, H_5 and H_{13}), 7.15 (dd, $^3J_{PH} = 13$ Hz, $^4J_{PH} = 7$ Hz, 1H, H_6), 6.04 (dt, $^1J_{PH} = 414$ Hz, $^3J_{HH} = 9$ Hz, 1H, (*i*-Pr$_2$)P*H*$^+$), 4.04 (br, 1H, H_{15}), 3.52 (m, 1H, H_{15}), 2.10 (m, 1H, H_7), 2.04 (m, 1H, H_7), 1.55 (dd, $^3J_{PH} = 22$ Hz, $^3J_{HH} = 6$ Hz, 3H, H_{16}), 1.53 (dd, $^3J_{PH} = 22$ Hz, $^3J_{HH} = 6$ Hz, 3H, H_{16}), 1.20 (dd, $^3J_{PH} = 22$ Hz, $^3J_{HH} = 7$ Hz, 3H, H_{16}), 1.00 (dd, $^3J_{PH} = 15$ Hz, $^3J_{HH} = 7$ Hz, 3H, H_8), 0.95 (dd, $^3J_{PH} = 15$ Hz, $^3J_{HH} = 6$ Hz, 3H, H_8), 0.76−0.65 (m, 6H, H_{16}), 0.59 (dd, $^3J_{PH} = 12$ Hz, $^3J_{HH} = 6$ Hz, 3H, H_{16}). ^{13}C{^{1}H} NMR (75.47 MHz, 233 K, CD_2Cl_2): δ 142.8 (dd, $^1J_{CP} = 26$ Hz, $^2J_{CP} = 12$ Hz, C_2), 140.7 (AA′X, $N = 10$ Hz, C_{11}), 137.7 (dd, $^1J_{CP} = 108$ Hz, $^2J_{CP} = 31$ Hz, C_1), 137.6 (dd, $^1J_{CP} = 99$ Hz, $^2J_{CP} = 9$ Hz, C_9), 135.1 (dd, $^2J_{CP} = 11$ Hz, $^3J_{CP} = 2$ Hz, C_3), 134.5 (m, C_6), 134.4 (m, C_{13}), 134.3 (m, C_{14}), 132.9 (m, C_{12}), 132.8 (m, C_4), 132.7 (d, $^4J_{CP} = 3$ Hz, C_p), 131.6 (d, $^2J_{CP} = 12$ Hz, C_o), 131.3 (d, $^1J_{CP} = 107$ Hz, C_{ipso}), 129.2 (d, $^3J_{CP} = 9$ Hz, C_m), 129.0 (d, $^3J_{CP} = 12$ Hz, C_5), 120.8 (dd, $^1J_{CP} = 80$ Hz, $^2J_{CP} = 6$ Hz, C_{10}), 26.8 (d, $^1J_{CP} = 44$ Hz, C_{15}), 26.7 (dd, $^1J_{CP} = 44$ Hz, $^4J_{CP} = 8$ Hz, C_{15}), 25.6 (d, $^1J_{CP} = 13$ Hz, C_7), 24.9 (d, $^1J_{CP} = 13$ Hz, C_7), 20.0 (d, $^2J_{CP} = 19$ Hz, C_8), 19.9 (d, $^2J_{CP} = 17$ Hz, C_8), 19.9 (br, C_{16}), 19.8 (d, $^2J_{CP} = 9$ Hz, C_{16}), 19.7 (br, C_{16}), 19.6 (d, $^2J_{CP} = 14$ Hz, C_8), 19.1 (br, C_8), 18.2 (br, C_{16}). ^{31}P{^{1}H} NMR (121.44 MHz, 293 K, CD_2Cl_2): δ 57.6 (br, $\omega_{1/2} = 120$ Hz, $^1J_{PH} = 440$ Hz, 1P, (*i*-Pr$_2$)P*H*$^+$), 33.9 (br, $\omega_{1/2} = 83$ Hz, 1P, P(O)Ph), −2.5 (br, $\omega_{1/2} = 220$ Hz, 1P, P(*i*-Pr$_2$)$_2$). ^{31}P{^{1}H} NMR (121.44 MHz, 233 K, CD_2Cl_2): δ 60.6 (d, $^3J_{PP} = 3$ Hz, $^1J_{PH} = 440$ Hz, 1P, PH(*i*-Pr)$_2$), 33.2 (dd, $^3J_{PP} = 19$ Hz, $^3J_{PP} = 5$ Hz, 1P, P(O)Ph), −4.7 (d, $^3J_{PP} = 18$ Hz, 1P, P(*i*-Pr)$_2$). ^{19}F{^{1}H} NMR (282.23 MHz, 298 K, $CDCl_3$): δ −78.2 (s, OTf).

Palladium Hydride Complex 8. In a Schlenk flask containing a dark red solution of $Pd_2(dba)_3$ (69 mg, 0.079 mmol) in acetonitrile (2 mL) was slowly added a colorless solution of compound **7** (100 mg, 0.15 mmol, 2 equiv) in the same solvent (2 mL). The resulting mixture was stirred for 1 h and filtered via cannula to remove elemental Pd. The solvent was removed from the supernatant under vacuum, and the residue was washed with ether (4 × 5 mL) to give **8** (92 mg, 0.12 mmol, 80% yield) in ∼99% purity. A portion of the sample (70 mg, 0.088 mmol) was dissolved in a minimal amount of acetonitrile and recrystallized by solvent diffusion of diethyl ether (5 mL) to give yellow crystals (36 mg, 0.047 mmol, 53% yield) suitable for X-ray diffraction analysis. ^{1}H NMR (500.33 MHz, 298 K, CD_3CN): δ 8.03−7.92 (m, 4H, H_3 and H_6), 7.87−7.84 (m, 2H, H_4 or H_5), 7.75−7.72 (m, 1H, H_p), 7.72−7.68 (m, 2H, H_4 or H_5), 7.58−7.54 (m, 2H, H_m), 7.40−7.36 (m, 2H, H_o), 2.92−2.86 (m, 2H, H_7), 2.64−2.55 (m, 2H, H_7), 1.36−1.26 (m, 18H, H_8), 0.89−0.84 (m, 6H, H_8), −16.14 to −16.17 (m, 1H, PdH); ^{13}C{^{1}H} NMR (125.81 MHz, 298K, CD_3CN): δ 136.1 (AA′MX, $N = 4$ Hz, $^2J_{PC} = 14$ Hz, C_3 or C_6), 135.36 (AA′MX, $N = 6$ Hz, $^2J_{PC} = 100$ Hz, C_1 or C_{ipso}), 134.4 (d, $J_{CP} = 11$ Hz, C_3 or C_6), 133.8 (d, $^4J_{CP} = 3$ Hz, C_p), 133.4−133.3 (m, C_4 or C_5), 132.5 (d, $^2J_{CP} = 11$ Hz, C_o), 130.4 (d, $J_{CP} = 13$ Hz, C_4 or C_5), 129.99 (d, $^1J_{CP} = 13$ Hz, C_2), 129.3 (d, $^3J_{CP} = 13$ Hz, C_m), 114.5 (br, OTf), 27.5 (AA′X, $N = 11$ Hz, C_7), 21.2 (AA′X, $N = 11$ Hz, C_7), 19.0 (br, C_8), 18.7 (m, C_8), 18.4 (AA′X, $N = 6$ Hz, C_8), the peak due to C_1 or C_{ipso} is not observed. ^{31}P NMR (202.54 MHz, 298 K, CD_3CN): δ 50.3 (dd, $J_{PP} = 8$ Hz, $J_{PH} = 4$ Hz, 2P, P(*i*-Pr)$_2$), 48.9 (td, $J_{PP} = 8$ Hz, $J_{PH} = 2$ Hz, 1P, P(O)). ^{19}F{^{1}H} NMR (282.23 MHz, 298 K, CD_3CN): δ −79.3 (s, OTf).

Preparation of 2 from 8. In an NMR tube containing a colorless solution of **8** (8 mg, 0.01 mmol) in d_2-dichloromethane (0.5 mL) was slowly added at room temperature neat 1,8-diazabicyclo[5.4.0]undec-7-ene (1.6 μL, 0.01 mmol, 1 equiv). The ^{31}P{^{1}H} NMR spectrum recorded immediately afterward showed that there was 100% conversion of the starting material to the palladium complex **2**.

Cationic Palladium Complex 9. In a Schlenk flask containing a colorless solution of **2** (62 mg, 0.10 mmol) in dichloromethane (3 mL) was added at room temperature neat trifluoromethanesulfonic acid (8.9 μL, 0.10 mmol, 1 equiv). The resulting mixture was stirred for 15 min, the solution was condensed, and pentane (3−4 mL) was added to give **9** (63 mg, 0.08 mmol, 80% yield) as a white crystalline solid. **9** was crystallized in a 5/1 CH_2Cl_2/pentane mixture to give white crystals suitable for X-ray diffraction analysis. ^{1}H NMR (500.33 MHz, 295 K, $CDCl_3$): δ 9.5 (br, $\omega_{1/2} = 115$ Hz, 1H, OH), 8.76 (dd, $^3J_{HP} = 7$ Hz, $^3J_{HH} = 7$ Hz, 2H, H_6), 7.86 (t br, $^3J_{HH} = 7$ Hz, 2H, H_5), 7.85−7.73 (m, 6H, H_3, H_4 and H_o), 7.17 (m, 2H, H_m), 7.02 (t br, $^3J_{HH} = 7$ Hz, 1H, H_p), 2.88 (m, 2H, H_7), 2.59 (m, 2H, H_7), 1.22 (dd, $^3J_{HP} = 16$ Hz, $^3J_{HH} = 7$ Hz, 6H, H_8), 1.19 (dd, $^3J_{HP} = 16$ Hz, $^3J_{HH} = 7$ Hz, 6H, H_8), 1.09 (dd, $^3J_{HP} = 17$ Hz, $^3J_{HH} = 6$ Hz, 6H, H_8), 0.81 (dd, $^3J_{HP} = 17$ Hz, $^3J_{HH} = 6.0$ Hz, 6H, H_8). ^{13}C{^{1}H} NMR (125.81 MHz, 295 K, $CDCl_3$): δ 153.2 (dt, $^2J_{CP} = 134$ Hz, $^2J_{CP} = 7$ Hz, C_i), 144.9 (AA′MX, $N = 16$ Hz, $^2J_{PC} = 46$ Hz, C_2), 139.0 (AA′MX, $N = 18$ Hz, $^2J_{PC} = 70$ Hz, C_1), 133.0 (m, C_5), 132.9−132.7 (m, C_3, C_4 and C_6), 132.1 (d, $^3J_{CP} = 21$ Hz, C_o), 123.7 (s br, C_m and C_p), 115.5 (br, OTf), 27.4 (AA′X, $N = 11$ Hz, C_7), 23.7 (AA′X, $N = 11$ Hz, C_7), 18.9 (AA′X, $N = 2$ Hz, C_8), 18.6 (AA′X, $N = 2$ Hz, $CHCH_3$), 17.7 (s, C_8), 17.5 (AA′X, $N = 2$ Hz, C_8). ^{31}P{^{1}H} NMR (202.54 MHz, 295 K, $CDCl_3$, δ): 142.3 (t, $J_{PP} = 25$ Hz, 1P, P(OH)), 62.8 (d, $J_{PP} = 25$ Hz, 2P, P*Pr$^i_2$). ^{19}F{^{1}H} NMR (282.23 MHz, 298 K, $CDCl_3$): δ −78.4 (br, $\omega_{1/2} = 30$ Hz, OTf). Mp: 249−251 °C.

Crystallographic Analyses. Crystallographic data were collected at 193 K on a Bruker-AXS APEX-II QUAZAR diffractometer equipped with an air-cooled microfocus source (**5**, **6**, and **9**) or on Bruker-AXS SMART APEX-II (**8**), using Mo Kα radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were employed.[35] The structures were solved by direct methods (SHELXS-97),[36] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2. The molecular views were generated with ORTEP3.[37]

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, text, and CIF files giving multinuclear NMR spectra of **3**−**9**, computational details and Cartesian coordinates for the optimized structures, and X-ray crystallographic data for CCDC 919850 (**5**), 919851 (**6**), 919852 (**8**), and

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919853 (**9**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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