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Synthesis, Structure, and Reactivity of *N*-Benzoyl Iminophosphoranes *Ortho* Lithiated at the Benzoyl Group

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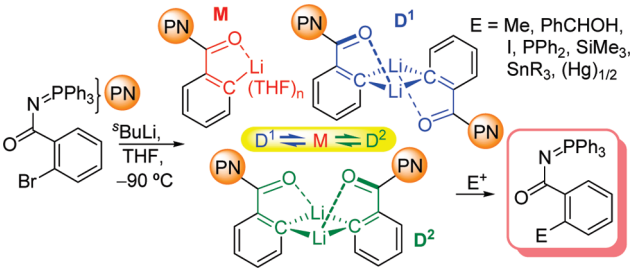

Ortho lithiation of *N*-benzamido-*P*,*P*,*P*-triaryliminophosphoranes through deprotonation with alkyllithium bases was achieved with *ortho*-C=O and *ortho*-P=N chemoselectivity. However, the synthetic scope of these processes was rather limited. *Ortho*-lithiated *N*-benzamido-*P*,*P*,*P*-triphenyliminophosphorane **8** was efficiently prepared via lithium/halogen exchange of the corresponding *ortho*-brominated precursor with *s*-BuLi in THF at −90 °C. The reaction of **8** with a variety of electrophiles provides an easy and mild method for the regioselective synthesis of *ortho*-modified iminophosphoranes via C−C (alkylation and hydroxyalkylation) and C−X (X = I, Si, P, Sn, and Hg) bond-forming reactions. NMR characterization of **8** in THF solution showed that **8** exists as an equilibrium mixture of one monomer and two dimers. The Li atoms of these species become members of five-membered rings through chelation by the *ortho*-metalated carbon and the carbonyl oxygen. The dimers differ in the relative orientation of the two chelates with respect to the plane defined by the C_2Li_2 core. The equilibrium between all species is established by splitting the dimers into monomers and subsequent recombination with formation of a different dimer.

Introduction

Selective *ortho* lithiation of aryl rings bearing heteroatom-containing functional groups is a powerful synthetic strategy in organic and organometallic synthesis.[1] From the organic chemistry point of view, the method gives access to *ortho* derivatives with excellent regiocontrol through reactions of the carbanions with a great variety of electrophiles (Scheme 1, compounds **4**).[2] On the other hand, the lithiated species may act as bidentate ligands that can be used in the preparation of

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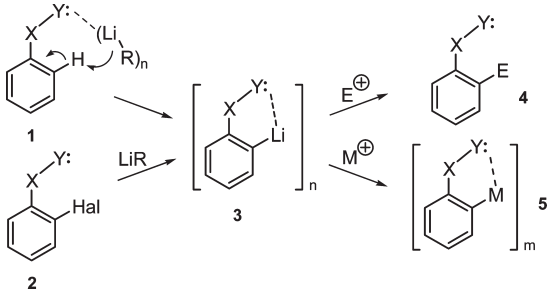
SCHEME 1. General Procedures of *Ortho*-Lithiation and Trapping Reactions



a number of metal complexes via transmetalation reactions (Scheme 1, complexes **5**).[3] *Ortho* lithiation is most commonly achieved through deprotonation reactions with organolithium bases. According to the CIPE (complex induced proximity effect) model, the polar group linked to the aromatic ring directs the approach of the base to the deprotonation site by coordination to the lithium atom (Scheme 1, complex **1**) and contributes to the stabilization of the *ortho*-lithiated species through intramolecular coordination (Scheme 1, complex **3**).[4] When the deprotonation method is not applicable due to the lack of reactivity or the required selectivity, among other factors, halogen−lithium exchange becomes a valuable alternative provided that the *ortho*-halogenated substrate **2** is readily available.[5]

Some of us are interested in using iminophosphoranes as C,N-bidentate ligands for the synthesis of new transition metal complexes, due to their versatility, structural characteristics, and interesting applications.[3f,6] Among them, we have reported the use of Pd(II),[6a] Au(I), and Au(III)[3f,6i] complexes with *ortho*-metalated iminophosphoranes as catalysts, we have studied the orientation of the *ortho*-metalation on iminophosphoranes and phosphorus ylides,[6b,e] and we have prepared complexes with different nuclearities,[6f,g] or characterized unusual bonding modes.[6c] More

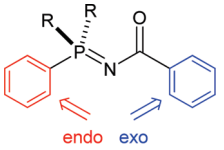
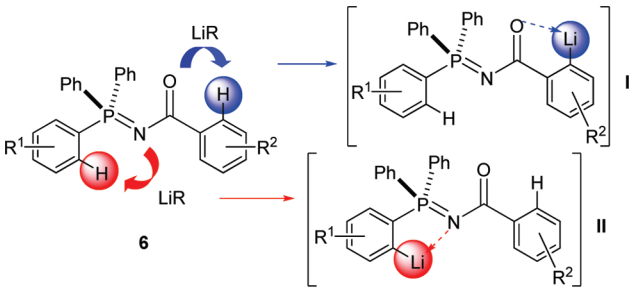


FIGURE 1. Different cyclometalation position on iminophosphoranes.

SCHEME 2. Possible Intermediates in the *Ortho*-Directed Lithiation of *N*-Benzoyliminophosphoranes 6



interestingly, we have determined that the *ortho*-palladation of imino-tri(aryl)phosphoranes contaning *N*-benzyl substituents can be oriented toward the benzyl ring (exo metalation) or toward the *P*-aryl rings (endo metalation) as a function of the reaction temperature,[6d] while palladation of *N*-benzoyl derivatives affords exclusively the exo derivatives.[6h] We have also studied the mechanism of the *ortho*-palladation by DFT methods, which showed that the exo metalation (Figure 1) is under kinetic control, while the product derived from endo metalation is thermodynamically more stable.[6d,h] Similar observations have been perfomed on *N*-naphthyliminophosphoranes.[6j] This control has deeper implications, and, for instance, it has allowed the selective functionalization of different substrates. In a recent example we have been able to functionalize regioselectively *N*-naphthyltri(aryl)phosphoranes, either at the *P*-aryl ring or at the *N*-naphthyl ring.[6k]

We are interested in the synthesis of new derivatives of transition metals containing *N*-benzoyliminophosphoranes **6** metalated at the benzoyl ring, that is, in exo position (Figure 1 and Scheme 2). While *ortho*-palladated complexes derived from this ligand can be easily obtained by C−H bond activation, this preparative strategy is not successful in other metals (for instance, in gold derivatives). Therefore, other synthetic procedures have to be considered. In order to expand the synthetic applications of iminophosphoranes, we thought that *ortho*-lithiated *N*-benzoyliminophosphoranes **6** would be valuable synthons for the preparation of new

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stable functionalized derivatives via carbon−carbon and carbon−heteroatom bond-forming reactions (Scheme 2).

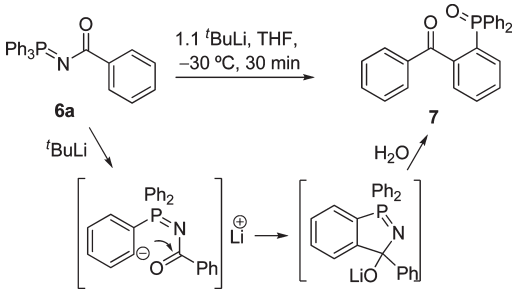
Iminophosphoranes **6** are bifunctional compounds containing a P=N linkage and a carboxamide moiety (CON) that might promote lithiation at their respective *ortho* positions. Examples of *ortho* lithiations directed by the CON[2a,7] and PN[8] groups are well known in the literature. *Ortho*-lithiated iminophosphoranes behave as bidentate ligands and have been used in the preparation of a wide number of metal complexes through Li−metal exchange reactions.[3b,c,f,9] We describe here the regioselective deprotonation of *N*-benzoyliminophosphoranes at the *ortho* position of the phosphorus and carbonyl group as evidenced from trapping reactions with methyl iodide, an improved method for generating *ortho*-lithiated species **I** (Scheme 2) via halogen−lithium exchange, the structural characterization of the intermediate anion formed based on multinuclear magnetic resonance studies, and the application of this anion in the synthesis of new derivatives through electrophilic quench with alkyl, phosphorus, silyl, tin, and mercury halides, aldehydes, and iodinating reagents.

Results and Discussion

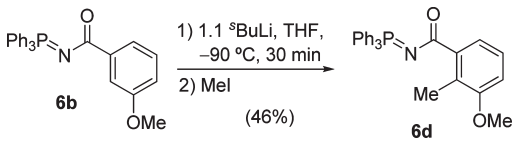
Deprotonation of CH Bonds As Synthetic Strategy. Iminophosphoranes **6a** ($R^1 = R^2 = H$), **6b** (R^1 = 3-OMe, $R^2 = H$), and **6c** ($R^1 = H$, R^2 = 2-Br) have been prepared through methods described in the literature.[10] To ascertain the relative strength of the functional groups presents in **6** as directors of *ortho* metalations (D*o*M), compound **6a** was lithiated under standard deprotonation conditions previously applied to similar iminophosphoranes.[8c,e] However, the reaction of **6a** with an organolithium base (*n*-BuLi, *s*-BuLi, *t*-BuLi; 1:1.1 molar ratio) in THF or toluene at −90 °C did not promote observable deprotonation since, after quenching with methyl iodide and usual aqueous workup, the crude reaction mixture did not show the incorporation of methyl groups into the aryl rings. When the mixture of **6a** and *t*-BuLi (1:1.1 molar ratio) was allowed to react at −30 °C, the compound **7** was isolated in 30% yield (Scheme 3), together with the starting iminophosphorane **6a**.

Compound **7** was characterized through spectroscopic methods. The ^{13}C NMR spectrum shows a very deshielded peak at δ 196.68 ppm, assignable to the carbonyl carbon of the benzophenone-like fragment. On the other hand, the ^{31}P NMR spectrum shows a signal at δ 31.32 ppm, characteristic of tri(aryl)phosphine oxides. It is reasonable to assume that the synthesis of **7** from **6a** occurs through *ortho* deprotonation of one *P*-C_6H_5 ring by the lithium reagent. The resulting carbanion may undergo intramolecular attack to the carbonyl carbon, generating a heterocyclic alkoxide. This intermediate would be hydrolyzed during the workup leading to **7**.

SCHEME 3. ***Ortho*-PN Deprotonation of 6a and Intramolecular Quench**



SCHEME 4. ***Ortho*-CO Deprotonation of 6b and Subsequent Methylation**



Deprotonation of **6** occurred at the unwanted *ortho* position with respect to the PN linkage, suggesting that the acidity and/or directing strength of the PN is higher than that of the CO group. Moreover, intermolecular electrophilic trapping of the anion failed due to the favored anionic cyclization reaction with the nearby carbonyl group. We reasoned that *ortho*-CO deprotonation could be promoted by using iminophosphorane derivatives of **6** containing an additional D*o*M group in the benzamide ring that could cooperate with the CO in directing the lithiation reaction. A good candidate is iminophosphorane **6b**, bearing a methoxy substituent at the *meta* position of the CO group. In fact, the treatment of **6b** with *s*-BuLi (1:1.1 molar ratio) in THF at −90 °C for 30 min results in the synthesis of **6d** in 46% isolated yield (Scheme 4). The variation of the reaction conditions (alkyllithium reagents, temperature, and reaction times) did not improve the yield.

The results aforementioned show that although regioselective *ortho* deprotonation of iminophosphoranes **6** at either side of the PNCO moiety is feasible, the synthetic usefulness of these anions is rather limited due to the intramolecular quench observed for the *ortho*-PN anion of the parent compound **6a** and the poor performance in the case of the *ortho*-CO anion arising from the methoxy derivative **6b**. Owing to these drawbacks, we turned our attention to halogen−lithium exchange reactions[11] as a method for accessing *ortho*-lithiated iminophosphoranes **6** in high yield. Compound **6c**,

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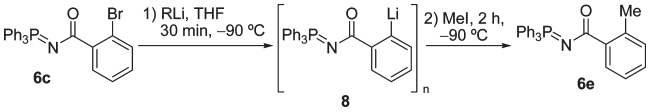
TABLE 1. Transmetalation−Methylation of Stabilized Iminophosphorane 6c[a]



entry	RLi	ratio **6c**:RLi:MeI	**6a** (%)	**6e** (%)
1	*n*-BuLi	1:1.1:2.0[b]	32	68
2	*s*-BuLi	1:1.1:2.0	22	78
3	*t*-BuLi	1:1.1:2.0	36	64
4	*t*-BuLi	1:1.1:2.0[b]	40	60
5	*t*-BuLi	1:1.5:2.5	13	87
6	*s*-BuLi	1:1.2:5.0[c]	86	0
7	*s*-BuLi	1:1.5:2.5	8	92
8	*s*-BuLi	1:2.2:3.0	6	94

[a]In all cases 0.11 M solutions of **6c** were employed. Conversions were established on the basis of $^{31}P\{^1H\}$ NMR spectra. A 2−8% yield of $Ph_3P(O)$ was always observed. [b]3 h 30 min of contact time between the Li base and **6c**. [c]H_2O as electrophile, time of contact 0.5 h.

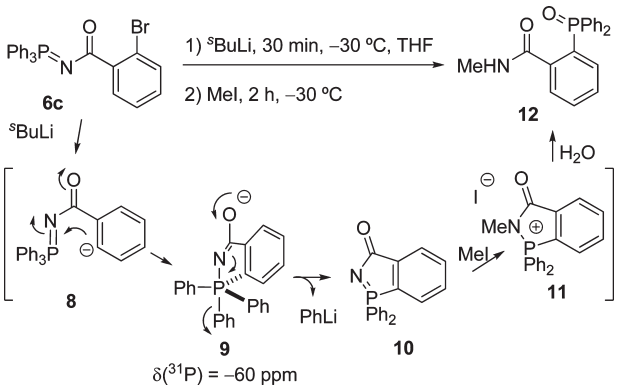
brominated at the *ortho* position of the benzoyl fragment, is readily available.[10a]

Halogen−Lithium Exchange as Synthetic Strategy. First, optimized reaction conditions for Br/Li exchange in **6c** were investigated by analyzing the effect of the alkyllithium base used, stoichiometry, temperature, and time of contact of the anion with the reference electrophile, MeI. The results are summarized in Table 1. Of the three bases assayed, *s*-BuLi afforded the best results (entries 1−3) in 30 min at −90 °C. *n*-BuLi needs a longer reaction time (3 h 30 min) with substrate **6c** to afford similar conversions (entry 1). In the case of *t*-BuLi the increase of the lithiation time produces a decrease in the yield of the methylated species **6e** (entry 4). Better yields were obtained only at the expense of the increase of the amounts of *t*-BuLi and methylating reagent (1:1.5:2.5; entry 5). Gratifyingly, the use of the same or slightly higher molar ratios of *s*-BuLi and MeI (with respect to entry 5: entries 7, 8) produced the highest conversions of **6e**, allowing the use of the less hazardous *s*-BuLi instead of *t*-BuLi. Thus, **6e** was almost quantitatively obtained when the Br/Li exchange was performed with 2.2 equivalents of *s*-BuLi at −90 °C in THF during 30 min, and the anion formed (**8**) was quenched with MeI.[12] In most studied cases significant amounts of the debrominated compound **6a** were formed, which suggests that the trapping reaction with MeI proceeds slowly and the anion **8** remaining in solution is protonated during aqueous workup to give **6a**. This hypothesis was demonstrated by using water as electrophile (entry 6). In this case the anion was instantaneously quenched, affording **6a** in 86% yield. It must be pointed out that this experiment does not exclude that a small amount of **8** undergoes quenching through proton abstraction from the solvent.

Increasing the temperature of the lithiation−methylation process to −30 °C lead to a mixture of compounds. Column chromatography allowed isolating the major product *N*-methylated carboxamide **12**, bearing a diphenylphosphinoyl group at the *ortho* position, in 41% yield (Scheme 5). The formation of **12** may be explained by assuming that the *ortho* anion arising from the Br/Li exchange reaction undergoes intramolecular attack to the phosphorus atom of the

(12) In all cases, small amounts of $Ph_3P(O)$ were observed in the ^{31}P NMR spectra of the crude reaction mixtures most probably due to hydrolysis of the P=N linkage of the respective iminophosphoranes during workup.

SCHEME 5. Synthesis and Suggested Reaction Mechanism for the Formation of 12



polar PN linkage, leading to the hypervalent phosphorus intermediate **9**.[13] This species evolves through elimination of PhLi to give the cyclic iminophosphorane **10**,[14] which is *N*-methylated by the MeI present in the reaction medium. Hydrolysis of the resulting phosphonium salt **11** during aqueous workup furnishes **12**,[15] characterized on the basis of the NMR spectra as a mixture of two rotamers due to restricted rotation around the C−N bond (Supporting Information).

^{31}P NMR monitoring of the reaction showed the presence of a signal at δ −60 ppm appropriate for pentacoordinated phosphorane **9**.[16] *Ortho* functionalization of aromatic rings with P-containing groups involving D*o*M reactions and P−X−Ar (X = N, O, S) to P−C_{Ar} migration rearrangement has been described in a number of cases.[17] To the best of our knowledge, there is no precedent of the participation of iminophosphoranes in this type of transformations.

Reactivity of the Lithiated Species 8. Once optimized reaction conditions for the Br−Li exchange and methylation of **6c** were available (entry 8, Table 1), we sought to extend the process to other electrophiles. To evaluate the scope of the method, the quench reagents selected involve C−C and

(13) Formation of pentacoordinated phosphoranes through intramolecular addition of XH groups (X = O, NH, NHPh) to iminophosphoranes has been described. (a) Sánchez, M.; Brazier, J.-F.; Houalla, D.; Munoz, A.; Wolf, R. *J. Chem. Soc., Chem. Commun.* **1976**, 730. (b) Cadogan, J. I. G.; Gosney, I.; Henry, E.; Naisby, T.; Nay, B.; Stewart, N. J.; Tweddle, N. J. *J. Chem. Soc., Chem. Commun.* **1979**, 189.

(14) This PhLi elimination is analogous to the displacement of PhLi by organolithium bases observed in Ph_3P=O. (a) Seyferth, D.; Welch, D. E.; Heeren, J. K. *J. Am. Chem. Soc.* **1963**, *85*, 642. (b) Seyferth, D.; Welch, D. E.; Heeren, J. K. *J. Am. Chem. Soc.* **1964**, *86*, 1100. (c) Wittig, G.; Cristau, H. J. *Bull. Soc. Chim. Fr.* **1969**, 1293.

(15) Briggs, E. M.; Brown, G. W.; Jiricny, J.; Meidine, M. F. *Synthesis* **1980**, 295.

(16) Pentacoordinated phosphoranes are characterized by large negative ^{31}P chemical shifts. (a) Chesnut, D. B.; Quin, L. D. *Tetrahedron* **2005**, *61*, 12343, and references therein. (b) For related phosphoranes see also: García-López, J.; Peralta-Pérez, E.; Forcén-Acebal, A.; García-Granda, S.; López-Ortiz, F. *Chem. Commun.* **2003**, 856.

(17) Selected references: (a) Melvin, N. S. *Tetrahedron Lett.* **1981**, *22*, 3375. (b) Heinicke, J.; Nietzschmann, E.; Tzschach, A. *J. Organomet. Chem.* **1983**, *243*, 1. (c) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1984**, *49*, 4018. (d) Jardine, A. M.; Vather, S. M.; Modro, T. A. *J. Org. Chem.* **1988**, *53*, 3983. (e) Masson, S.; Saint-Clair, J.-F.; Saquet, M. *Tetrahedron Lett.* **1994**, *35*, 3083. (f) Heinicke, J.; Kadyrov, R. *J. Organomet. Chem.* **1996**, *520*, 131. (g) He, Z.; Modro, T. A. *Synthesis* **2000**, 565. (h) Legrand, O.; Brunel, J. M.; Buono, G. *Tetrahedron* **2000**, *56*, 595. (i) Moulin, D.; Bago, S.; Bauduin, C.; Darcel, C.; Jugé, S. *Tetrahedron: Asymmetry* **2000**, *11*, 3939. (j) Mauger, C.; Vazeux, M.; Masson, S. *Tetrahedron Lett.* **2004**, *45*, 3855. (k) Velder, J.; Robert, T.; Weidner, I.; Neudoerfl, J.-M.; Lex, J.; Schmalz, H.-G. *Adv. Synth. Catal.* **2008**, *350*, 1309.

SCHEME 6. Reactivity of Lithiated Species 8 toward Different Electrophiles

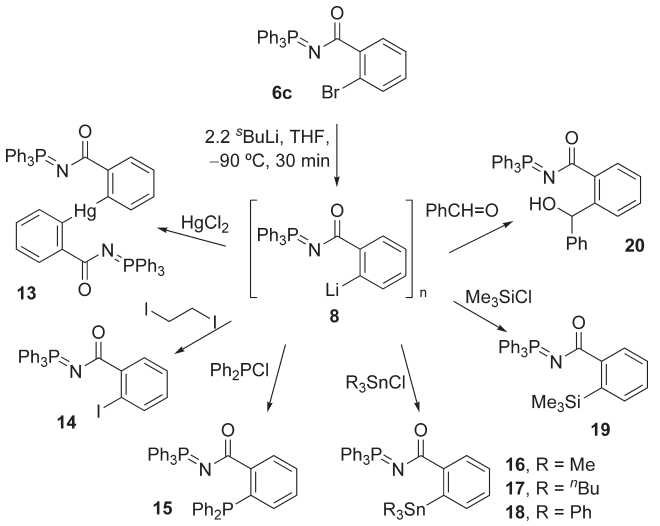
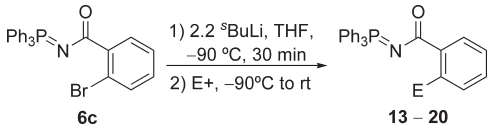


TABLE 2. Regioselective Synthesis of Functionalized Iminophosphoranes by Br/Li-Exchange−Electrophilic Quench



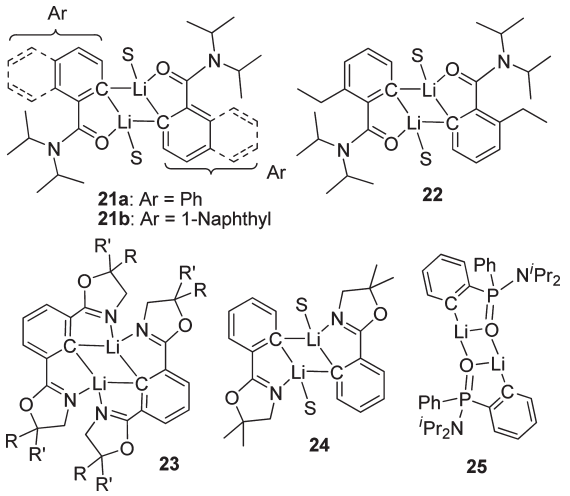
entry	compd	E^+	E	yield (%)
1	**13**	$HgCl_2$	Hg[a]	62
2	**14**	ICH_2CH_2I	I	92
3	**15**	Ph_2PCl	PPh_2	41
4	**16**	Me_3SnCl	$SnMe_3$	87
5	**17**	Bu_3SnCl	$SnBu_3$	49
6	**18**	Ph_3SnCl	$SnPh_3$	44
7	**19**	Me_3SiCl	$SiMe_3$	89
8	**20**	PhCHO	PhCHOH	77

[a]The bis-aryl derivative was obtained (Scheme 6).

C−heteroatom bond-forming reactions. The obtained results are shown in Scheme 6 and Table 2.

The reaction of a THF solution of **8** with $HgCl_2$ (2:1 molar ratio) proceeded under very mild experimental conditions, affording bis-aryl derivative **13**. After the addition of the mercury salt at −90 °C, stirring was maintained at this temperature for an additional 30 min, and subsequently it was allowed to reach room temperature overnight. Then, simple extraction with CH_2Cl_2 in order to eliminate the lithium salts and further evaporation of the organic extracts gave pure **13** in moderate yield. The *ortho*-regioselective introduction of heteroatoms other than bromine in the benzamide skeleton also occurs under smooth conditions. The treatment of **8** with di-iodoethane (ICH_2CH_2I as synthetic equivalent of I^+) and Ph_2PCl (as a source of Ph_2P^+) afforded excellent yields of **14** and moderate yields of **15**, respectively (entries 2, 3). Compound **14** represents a valuable starting material for accessing new iminophosphoranes

SCHEME 7. Examples of *o*-Lithiated Dimers Bearing Amide or Amide-like Functional Groups



via C−C metal-catalyzed cross-coupling reactions.[18] Compound **15** can also be viewed as an interesting alternative to known P,N (or even P,O) chelating ligands.[19] Using the same strategy the novel stannanes **16**−**18** and silane **19** (Scheme 6) have been obtained by reaction of **8** with R_3SnCl (R = Me, ^{n}Bu, Ph) or Me_3SiCl, respectively. The organotin derivatives were isolated as air-stable white solids in high (**16**) to moderate (**17**, **18**) yields, while the organosilicon species **19** was isolated as large colorless needles in high yield. Products **16**−**19** are interesting reagents for participating in, for instance, Stille (Sn) and/or Hiyama (Si) Pd-catalyzed C−C couplings processes. This wide prospect of C−heteroatom couplings (C−Hg, C−I, C−P, C−Sn, and C−Si), which shows the high synthetic potential of lithiated species **8**, can be complemented with the formation of new carbon−carbon bonds, other than the methylation reactions previously described. Thus, addition of benzaldehyde to a solution of **8** led after the usual workup to the hydroxyalkyl derivative **20**. A brief discussion of the structural characterization of products **13**−**20** is included in the Supporting Information.

Structural Characterization of Anionic Species 8. NMR samples of **8** were prepared in 5 mm tubes, in nondeuterated THF, under conditions analogous to those used in the bulk (see Supporting Information for experimental details).[20] The stoichiometry selected corresponded to a ratio of **6c**:*s*-BuLi of 1:1.2 (Table 1, entry 6). We used an amount of base lower than the optimum value (entry 8) to avoid possible complications derived from the formation of mixed aggregates between the base and **8** when the bromine−lithium exchange is performed in the presence of a larger excess of *s*-BuLi. The samples prepared at −90 °C were transferred to the magnet precooled at the same temperature. After a short time interval (2−5 min) for temperature and homogeneity adjustment a series of ^{7}Li, ^{31}P, and ^{13}C NMR spectra were acquired

(18) For reviews see: (a) Hartung, C. G.; Snieckus, V. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, FRG, 2002; p 330. (b) Anctil, E. J. G.; Snieckus, V. *J. Organomet. Chem.* **2002**, *653*, 150. (c) Anctil, E. J. G.; Snieckus, V. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F., Eds.; Wiley-VCH: Weinheim, FRG, 2004; Chapter 14, p 761.

(19) (a) Pfeiffer, J.; Kickelbick, G.; Schubert, U. *Organometallics* **2000**, *19*, 62. (b) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (c) Chen, H.-P.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2003**, *22*, 4893. (d) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784. (e) Peloso, R.; Pattacini, R.; Cazin, C. S. J.; Braunstein, P. *Inorg. Chem.* **2009**, *48*, 11415.

(20) About 5−10 samples were examined. They gave consistent and reproducible results. Among the variables analyzed we evaluated the effect of concentration, starting temperature, and time of metalation.

to unravel the solution structure of **8**. ^{1}H NMR proved to be useless due to the appearance of all aromatic protons in a narrow spectral region.

Extensive structural studies of lithiated aromatic species have provided a general picture about the privileged structures that *ortho*-lithiated compounds may adopt.[21] In noncoordinating or ethereal solvents, they tend to form aggregates by assembling monomeric units through electron-deficient C−Li−C bridges. In dimers, this binding mode leads to characteristics Li_2C_2 cores in which the deprotonated carbon is bound to two lithium atoms and the lithiums attain the favorite 4-fold coordination by chelation with the *ortho* functional group and/or through bonding to solvent molecules. *Ortho*-lithiated carboxamides **21**[22] and **22**[23] and oxazolidines **23**[24] and **24**[25] are examples structurally related to *ortho* lithium species **8**, showing this self-aggregation mode (Scheme 7). Very recently, some of us have reported the formation of Li−O−Li−O four-membered rings in the dimerization of *ortho*-lithiated *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinic amide **25**.[26] This structural motif in which dimers show only one C_{ipso}−lithium contact was unprecedented in aryllithium chemistry.

Phosphorus-31 NMR constitutes a sensitive and easy probe for monitoring *in situ* NMR reactions,[8e,27] and this nucleus was our first choice for obtaining structural information of **8**. At −80 °C four singlets located at δ_P 15.4 (**A**), 16.1 (**B**), 17.0 (**6c**), and 17.5 (**6a**) ppm in a ratio 1:1:0.6:0.6, respectively, were observed. The signals of starting material **6c** and the protonated derivative **6a** were readily assigned on the basis of their corresponding ^{31}P chemical shifts.[28] Although the concentration of these compounds is relatively high, they do not intervene in the structure of **8** (see below). Increasing the temperature of the sample produced two simultaneous effects on the ^{31}P NMR spectra: the exchange between the signals **A** and **B** (coalescence temperature $T_c \approx -40$ °C) and the progressive disappearance of these two signals in parallel with a significant growth of the resonance of **6a** (Figure S34). At −20 °C signals **A** and **B** vanished. Quenching the NMR sample with water and subsequent aqueous workup afforded a crude mixture, which ^{31}P NMR spectrum showed exclusively the presence of **6a** and **6c**. Interestingly, the slight shielding of the phosphorus signals for lithiated species **A** and **B** as compared to the nonlithiated ones **6a** and **6c** suggests that the P═N bond is weakly or not coordinated at all to the lithium cation (see below). All these NMR data are consistent with the existence in solution of two separated lithium species differing in the aggregation state. ^{31}P NMR measurements in the concentration range 0.04−0.150 M revealed that the variations of the integrals of the high-field ^{31}P signals **A** and **B** at −80 °C correlate reasonably well with an equilibrium monomer−dimer. From the log[dimer] versus log[monomer] plot (Figure 2), a slope of 1.85 and an apparent equilibrium constant K_{MD} of 15.6 M^{-1} at this temperature was calculated, assuming that the major species in the most diluted sample (0.04 M) is the monomer **A**. In the following, monomeric species **A** will be also represented as **M** and dimers **B** will be denoted as **D*n***, where the label $n = 1, 2$, etc., refers to isomers arising from different arrangements of the interacting monomers.

To further prove the exchange between phosphorus **A** and **B**, we performed a 2D exchange spectroscopy, ^{31}P{^{1}H} EXSY, experiment. Using a mixing time τ_m of 50 ms the expected correlations indicative of exchange between species **A** and **B** were clearly observed (Figure 3), and, what may be more significant, the absence of any correlation for the signals corresponding to **6a** and **6c** indicates that these neutral compounds do not participate in a dynamic process involving lithiated species **A** and **B**.

Direct evidence on the aggregation state of aryllithiums can be derived from ^{13}C NMR data through the well-known correlation of multiplicity and chemical shift of the *ipso* carbon with the degree of aggregation. Increasing aggregation causes a shielding of the C_{ipso} due to the existence of a larger number of C−Li contacts.[29,30] A recent example

(21) For recent references see: (a) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Tzschucke, C. C. *Org. Lett.* **2001**, *3*, 33. (b) Reich, H. J.; Goldenberg, W. S.; Gudmundsson, B. Ö.; Sanders, A. W.; Kulicke, K. J.; Simon, K.; Guzui, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 8067. (c) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Jantzi, K. L.; Tzschucke, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 3509. (d) Vestergren, M.; Eriksson, J.; Hilmersson, G.; Hakansson, M. *J. Organomet. Chem.* **2003**, *682*, 172. (e) Kronenburg, C. M. P.; Rijnberg, E.; Jastrzebski, J. T. B. H.; Kooijman, H.; Lutz, M.; Spek, A. L.; Gossage, R. A.; van Koten, G. *Chem.—Eur. J.* **2004**, *11*, 253. (f) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W. *Arkivok* **2004**, 97. (g) Kronenburg, C. M. P.; Rijnberg, E.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Eur. J. Org. Chem.* **2004**, 153. (h) Arink, A. M.; Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Lutz, M.; Spek, A. L.; Gossage, R. A.; van Koten, G. *J. Am. Chem. Soc.* **2004**, *126*, 16249. (i) Linnert, M.; Bruhn, C.; Rüffer, T.; Schmidt, H.; Steinborn, D. *Organometallics* **2004**, *23*, 3668. (j) Jantzi, K. L.; Puckett, C. L.; Guzei, I. A.; Reich, H. J. *J. Org. Chem.* **2005**, *70*, 7520. (k) Jambor, R.; Dostal, L.; Cisarova, I.; Rouzicka, A.; Holecek, J. *Inorg. Chim. Acta* **2005**, *358*, 2422. (l) Singh, K. J.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 13753. (m) Kawachi, A.; Tani, A.; Machida, K.; Yamamoto, Y. *Organometallics* **2007**, *26*, 4697. (n) Riggs, J. C.; Singh, K. J.; Yun, M.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 13709. (o) Chase, P. A.; Lutz, M.; Spek, A. L.; Gossage, R. A.; van Koten, G. *Dalton Trans.* **2008**, 5783. (p) Singh, K. J.; Hoepker, A. C.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 18008. (q) Konrad, T. M.; Gruenwald, K. R.; Belaj, F.; Moesch-Zanetti, N. C. *Inorg. Chem.* **2009**, *48*, 369. (r) Neshat, A.; Seambos, C. L.; Beck, J. F.; Schmidt, J. A. R. *Dalton Trans.* **2009**, 4987. (s) Petrov, A. R.; Rufanov, K. A.; Harms, K.; Sundermeyer, J. *J. Organomet. Chem.* **2009**, *694*, 1212.

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(28) In all samples prepared with a ratio of **6c**:*s*-BuLi of 1:1.2 variable amounts of unreacted **6c** and protonated **6a** were detected, in agreement with the reactions performed in laboratory scale. Entry 6 of Table 1 shows that lithiation is not complete. In addition, the absence of stirring in the NMR tube, possible difusion of air into the sample, and proton abstraction from the solvent may contribute to the partial quench of the anion.

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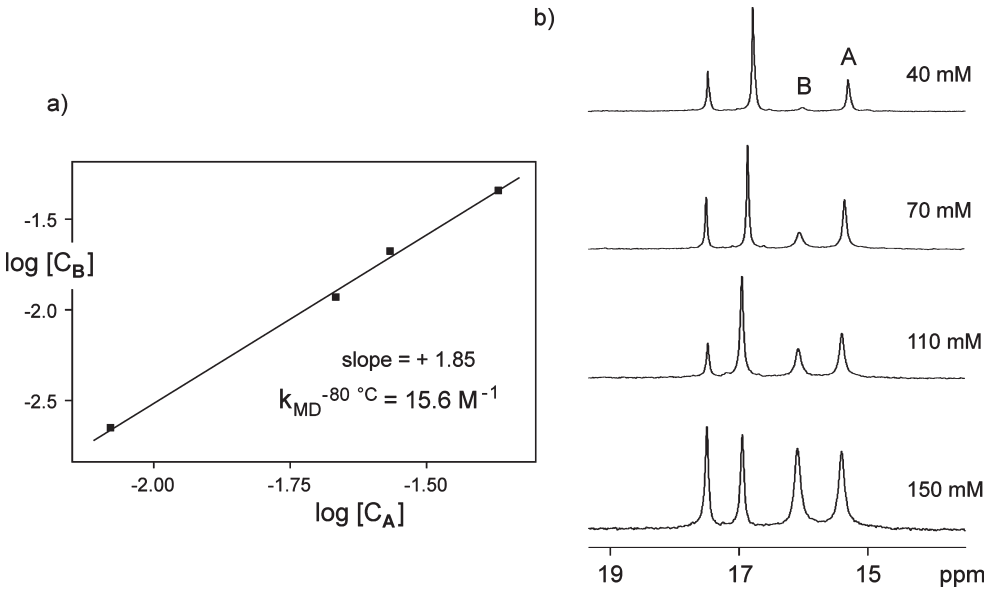

FIGURE 2. (a) Log−log monomer−dimer plot based on variable-concentration ^{31}P NMR (202.46 MHz) spectra of **8** at −80 °C, (b), illustrating the equilibrium between monomer **A** and dimer **B** (see Supporting Information for details).

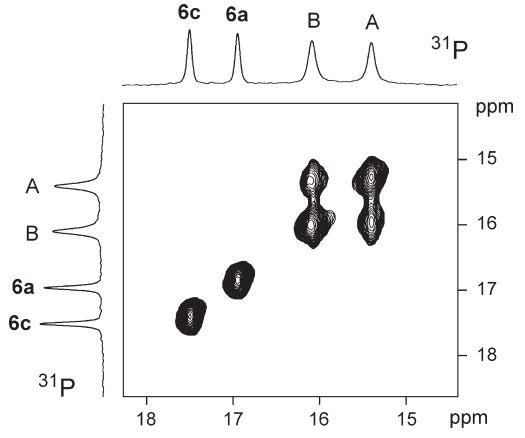

FIGURE 3. ^{31}P{^{1}H} EXSY NMR spectrum (202.46 MHz) of 0.15 M **8** at −80 °C in THF with a mixing time of 50 ms.

closely related to **8** is provided by the solution structure of **24**.[31] In 3:2 THF/Et_2O at −114 °C exists a mixture of a monomer $(\mathbf{24})_1$ and a dimer $(\mathbf{24})_2$. The C_{ipso} of $(\mathbf{24})_1$ appears as a quartet [$^{1}J(^{7}Li,^{13}C)$ = 29.3 Hz] at δ_C 206.6 ppm. The C−Li carbon of dimer $(\mathbf{24})_2$ is characterized by a heptet of $^{1}J(^{7}Li,^{13}C)$ = 19.0 Hz at δ_C 194.6 ppm. Similar values are found for other *ortho*-substituted aryllithiums.[30,31] Although the multiplicity of the C_{ipso} of **8** could not be unraveled in the temperature range investigated (down to −115 °C), the two broad signals located at δ_C 203.9 and 192.9 ppm are a clear indication of the presence of a monomer and a dimer, respectively (Figure S32, Supporting Information). The chemical shift difference of 11 ppm between monomer and dimer C−Li signals is almost identical to that of related well-characterized *ortho*-lithiated phenyloxazolines.[31]

The next relevant source of structural information in lithiated organophosphorus compounds is the lithium nucleus. Since we try to reproduce in the NMR tube the bulk reaction conditions, we use *s*-BuLi containing $^{6/7}$Li isotopes in natural abundance. This implies that ^{7}Li is the nucleus of choice.[29] The ^{7}Li NMR spectrum of a 0.11 M sample of **8** measured at −80 °C exhibits three major lithium signals, at δ_{Li} −1.51 (**I**), 0.19 (**II**), and 0.64 (**III**) ppm, with relative integrals of 1.3:1.1:1, respectively. As in the ^{31}P and ^{13}C NMR spectra, no coupling of these nuclei to ^{7}Li was observed in the range from −80 to −115 °C. In order to shed light on the, somehow surprising, counting of lithium signals, a series of 2D ^{7}Li EXSY experiments were performed (Figure 4).

At the lowest mixing time of 5 ms used, exchange is relatively slow and only correlations of **I** and **III** with **II** were clearly observed (Figure 4a). Increasing the mixing time to 50 ms favors the random exchange among all species in solution, becoming evident the exchange between **I** and **III** (see inset boxes in Figure 4b) together with the previously observed exchange of **I**/**III** with **II**. The results of the NMR study are consistent with complex **8** existing in THF solution as a mixture of one monomer **II** and two different dimers **I** and **III**. In addition, the 2D ^{7}Li EXSY map indicates that dimers **I** and **III** exchange preferably through the monomer **II**; that is, they break up into monomers, which subsequently recombine back to dimers. The lack of cross-peaks between **I** and **III** for τ_m = 5 ms validates this statement.

Amine- and ether-chelated *ortho* aryllithiums have been shown to exist as an equilibrium mixture of dimeric isomers **26**, **27**, and **28** (Chart 1).[21a−c,f,h,32]

In complex **26** the donating arms are coordinated to the same lithium atom, while in aggregates **27** and **28**, each lithium atom is coordinated to only one side arm either from the same face, **27**, or from the opposite face, **28**, of the C_2Li_2 plane. The ^{7}Li NMR spectra of dimers **26** are characterized by two different lithium signals in the same ratio, whereas the lithium atoms of species **27** and **28** are equivalent and would show only one signal for each structure. Reich and co-workers have elegantly shown that the ratio between

(31) Jantzi, K. L.; Guzei, I. A.; Reich, H. J. *Organometallics* **2006**, *25*, 5390.

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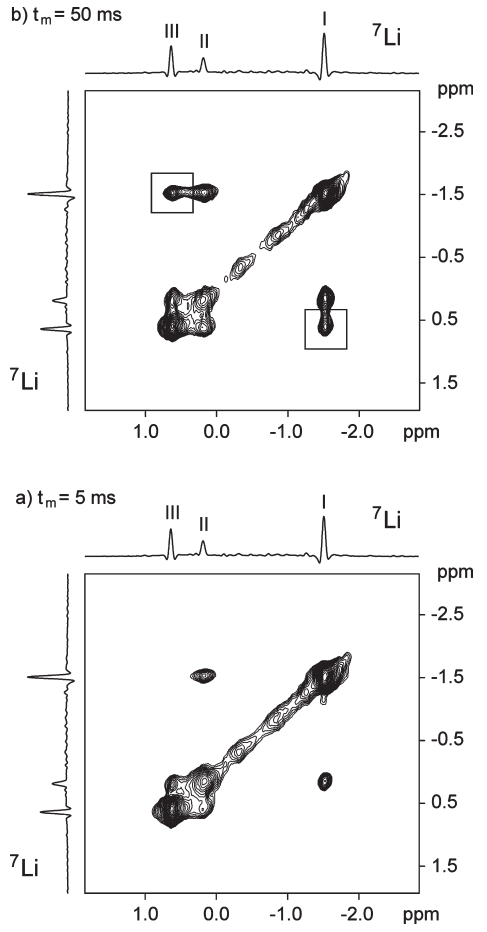
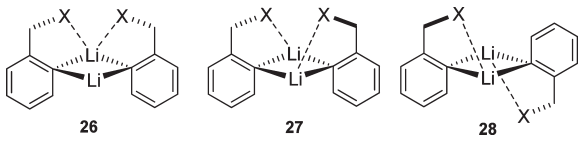


FIGURE 4. ^{7}Li EXSY NMR spectra (194.37 MHz) of a 0.11 M sample of **8** at −80 °C in THF with mixing times of (a) 5 ms and (b) 50 ms.

CHART 1. Structures of Amine- and Ether-Chelated Aryllithiums (X = NR_2, OR)



aggregates **26**, **27**, and **28** depends on the nature of the substituents on NR_2 or OR. For instance, in amine-chelating derivatives, X = NR^1R^2, in which R^1 = R^2 = Me, the ratio **26**:**27**:**28** in 3:2:1 THF/Me_2O/Et_2O at −137 °C is 38:15:47, whereas for R^1 = Me, R^2 = ^{i}Pr in 3:2 THF/ether the major isomer is **27**.[21b] Variable-concentration ^{7}Li NMR spectra of **8** contributed to clarify the solution structure of this organolithium reagent (Figure 5). Lithium **II** (δ_{Li} 0.19 ppm) showed the lowest integral of all signals at the highest concentration assayed (150 mM) and became the dominant signal in the most diluted sample. This concentration-dependent behavior allows assigning lithium **II** to the monomer species (**M**). Since the ^{31}P NMR study evidenced the existence of a monomer−dimer equilibrium, lithium signals **I** and **III** must proceed from dimeric aggregates (**D*n***). Taking into account that lithium **I** is not detected in the 40 mM sample and that the relative amounts of **I** (integral 0.74) and **III** (integral 1) are similar at a concentration 150 mM,

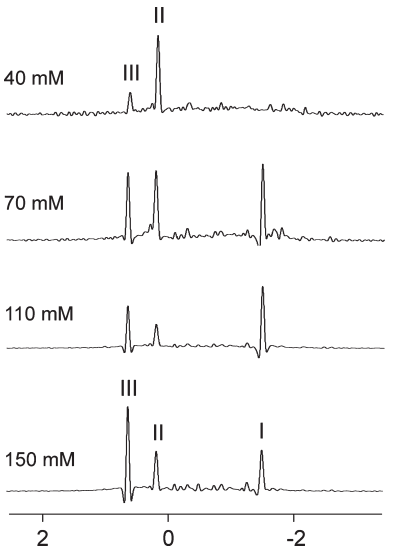
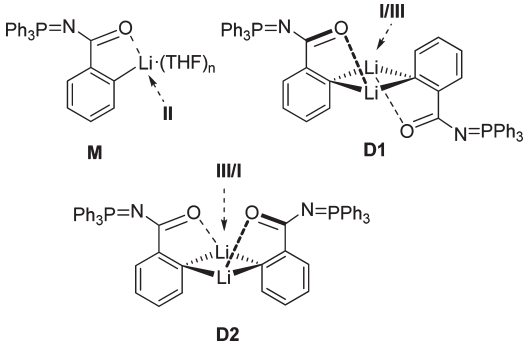


FIGURE 5. Variable-concentration ^{7}Li NMR (194.37 MHz) spectra of **8** in THF at −80 °C. Gaussian multiplication (LB = −20, GB = 0.04) of the FID prior to FT was applied.

CHART 2. Species 8 Characterized in THF Solution



one may conclude that each signal **I**/**III** represents a different dimeric species. Consequently, lithiums **I** and **III** must arise from dimers of **8** analogous to model systems **27** and **28**, given that their population may be different and they show only one lithium signal. To summarize, *ortho*-CO-lithiated iminophosphorane **8** exists as a mixture of monomer **M** and two dimers, **D1** and **D2** (Chart 2). It is not possible to assign unequivocally lithiums **I** and **III** to the corresponding aggregate on the basis of their NMR data.[21b] Significantly, organolithium **8** can be envisaged as a particular type of *ortho*-lithiated carboxamide, and these anions have been characterized in the solid state as dimers of type **D1** (see compounds **21** and **22**, Scheme 7).

Conclusions

In summary, we have shown that *N*-aroyl-*P*,*P*,*P*-triphenyliminophosphoranes **6** can be selectively deprotonated at the *ortho*-CO and *ortho*-PN positions by alkyllithium bases and subsequently methylated to give new iminophosphoranes, albeit in low yields. A more efficient procedure for accessing *ortho*-CO-lithiated derivatives of **6** has been developed making use of Li/Br exchange methodology. The lithiated species **8** proved to be stable at low temperature.

Trapping reactions with a representative series of electrophiles allowed the transformation of the C−Li bond of **8** into a wide variety of C−X (X = I, P, Si, Sn, Hg) and C−C bonds, providing access to new stabilized iminophosphoranes[33] not accessible through other synthetic pathways.

The solution structure of the key intermediate *ortho*-CO-lithiated **8** has been elucidated through multinuclear magnetic resonance studies. In THF **8** exists as a mixture of three species, one monomer, **M**, and two dimers, **D1** and **D2**, in which the monomeric units are self-assembled through C_2Li_2 cores. Each lithium atom is part of a five-membered-ring chelate due to the coordination with the oxygen atom of the carbonyl side arm. Dimers differ in the relative orientation of the two five-membered-ring chelates with respect to the plane defined by the C_2Li_2 core, to the same or opposite sides, leading to a structure with a plane of symmetry, **D2**, or a center of inversion, **D1**, respectively. Further applications of lithiated species **8** and the *ortho*-CO-functionalized iminophosphoranes in organic and organometallic chemistry are under investigation.

Experimental Section

For all compounds, C_1 is assigned to the carbon linked to the CO group. Carbon atoms of the *P*-phenyl rings are labeled as C_i (*ipso*), C_o (*ortho*), C_m (*meta*), and C_p (*para*).

Synthesis of 2-Bromo-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 6c. Compound **6c** has been obtained following the same experimental method as that reported previously for other stabilized iminophosphoranes.[10a] Therefore, PPh_3 (2.402 g, 9.15 mmol) was reacted with di-*tert*-butyl azadicarboxylate (DBAD) (2.109 g, 9.15 mmol) and 2-bromobenzamide (1.832 g, 3.98 mmol) in THF at 0 °C to give **6c** as a white solid in quantitative yield. ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.18 (m, 1H, C_6H_4Br), 7.31 (m, 1H, C_6H_4Br), 7.52 (m, 6H, PPh_3), 7.60 (m, 4H, 1H C_6H_4Br + PPh_3), 7.88 (m, 7H, 1H C_6H_4Br + PPh_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz) δ 120.6 (s, C_6, C_6H_4Br), 126.8 (s, C_6H_4Br), 127.8 (d, C_i, PPh_3, $^1J_{PC}$ = 99.3), 128.7 (d, C_m, PPh_3, $^3J_{PC}$ = 12.4), 129.8 (s, C_6H_4Br), 130.7 (s, C_6H_4Br), 132.4 (d, C_p, PPh_3, $^4J_{PC}$ = 2.9), 133.3 (d, C_o, PPh_3, $^2J_{PC}$ = 10.1), 133.4 (s, C_6H_4Br), 142.0 (d, C_1, C_6H_4Br, $^3J_{PC}$ = 21.2), 177.3 (d, CO, $^2J_{PC}$ = 6.1); ^{31}P NMR ($CDCl_3$, 161.98 MHz) δ 21.0. Anal. Calcd for $C_{25}H_{19}BrNOP$: C, 65.23; H, 4.16; N, 3.04. Found: C, 65.23; H, 4.17; N, 3.13.

Synthesis of 3-Methoxy-2-methyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 6d. To a suspension of **6b** (0.200 g, 0.46 mmol) in dry THF (20 mL) at −90 °C was added 0.36 mL of ^{s}BuLi (1.4 M, 0.51 mmol). The red solution was stirred for 30 min at this temperature. After this time MeI (63.50 μL, 1.02 mmol) was added, and the mixture was further stirred for 2 h at −90 °C. Then, the colorless solution was diluted with CH_2Cl_2 (15 mL) and washed with H_2O (3 × 20 mL). The organic phase was extracted, dried by stirring with anhydrous $MgSO_4$, and evaporated to dryness, affording **6d** as a white solid. Obtained: 0.095 g (46% yield). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 2.23 (s, 3H, CH_3), 3.85 (s, 3H, OMe), 6.87 (d, 1H, H_6, C_6H_3, $^3J_{H6H5}$ = 7.2), 7.17 (t, 1H, H_5, C_6H_3, $^3J_{H5H4}$ = 7.3), 7.45−7.51 (m, 9H, $H_m + H_p$ (PPh_3)), 7.69 (m, 6H, H_o, PPh_3), 7.78 (d, 1H, H_4, C_6H_3, $^3J_{H4H3}$ = 7.7); ^{31}P{^{1}H} NMR ($CDCl_3$, 161.98 MHz) δ 20.8.

Synthesis of {2-[(Triphenyl-λ^5-phosphanylidene)carbamoyl]-phenyl}lithium, 8. To a solution of the iminophosphorane **6c** (0.644 g, 1.40 mmol) in dry THF (25 mL) at −90 °C was slowly added 2.0 mL of ^{s}BuLi (1.4 M, 2.80 mmol) over a period of 1 min. The resulting deep red solution was stirred at −90 °C for 30 min. Quenching the anion with MeI indicated that the yield of $[Li\{C_6H_4(C(O)N{=}PPh_3)\text{-}2\}]_n$ **8** is higher than 95% (see main text). NMR samples of **8** were prepared in nondeuterated THF. The ^{1}H NMR (500.13 MHz) spectrum shows broad signals in the aromatic region arising from species **8** overlapped with **6a** and **6c** and is uninformative. The ^{13}C NMR spectrum show similar features. The relevant signals arise from the C−Li carbons at δ 203.9 and 192.9 ppm (Figure S35). ^{7}Li NMR (THF, 194.37 MHz) δ −1.51, 0.19, 0.64; ^{31}P{^{1}H} NMR (THF, 202.46 MHz) δ 15.4, 16.1.

Synthesis of 2-(Diphenylphosphoryl)-*N*-methylbenzamide, 12. To a solution of **6c** (0.644 g, 1.40 mmol) in 20 mL of dry THF, at −30 °C, was slowly added 2.0 mL of ^{s}BuLi (1.4 M, 2.8 mmol). The red solution obtained was stirred for 30 min at this temperature; then MeI (348.4 μL, 5.60 mmol) was added, and the stirring was maintained at −30 °C during 2 additional hours. After the reaction time, the resulting colorless solution was evaporated to dryness. The treatment of the residue with Et_2O (15 mL) gave impure **12**, which was purified by column chromatography (AcOEt/MeOH, 9:1), affording pure **12** as a mixture of two isomers in 0.4:1 molar ratio. Obtained: 0.193 g (41% yield). *M* and *m* stand for major and minor isomer, respectively. IR (Nujol) ν 3220 (N−H), 1658 (C=O), 1102 (P=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 2.27−2.30 (d overlapped, CH_3 *M* + *m*), 7.13 (ddd, H_6, C_6H_4 *M* + *m*), 7.49−7.60 (m, H_5 (C_6H_4) + H_m + H_p (PPh_2), *M* + *m*), 7.66−7.71 (m, H_o, PPh_2, *M* + *m*), 8.01 (t, H_4, C_6H_4, $^3J_{H4H3}$ = $^3J_{H4H5}$ = 7.5, *m*), 8.09 (t, H_4, C_6H_4, $^3J_{H4H3}$ = $^3J_{H4H5}$ = 7.5, *M*), 8.57 (t, H_3, C_6H_4, $^4J_{HP}$ = 4.8, $^3J_{HH}$ = 7.0, *m*), 8.60 (t, H_3, C_6H_4, $^4J_{PH}$ = 4.4, $^3J_{HH}$ = 7.0, *m*), 8.73 (d, 1H, NH, $^3J_{HH}$ = 4.7, *m*), 8.88 (d, 1H, NH, $^3J_{HH}$ = 4.6, *M*); ^{13}C{^{1}H} NMR ($CDCl_3$, 125.76 MHz) δ 26.1 (s, CH_3, *m*), 26.1 (s, CH_3, *M*), 116.7 (d, C_i, PPh_2, $^1J_{PC}$ = 94.0, *m*), 121.7 (d, C_i, PPh_2, $^1J_{PC}$ = 94.4, *M*), 129.8 (d, C_m, PPh_2, $^3J_{PC}$ = 13.1, *M*), 129.8 (d, C_m, PPh_2, $^3J_{PC}$ = 13.0, *m*), 131.7 (d, C_3, C_6H_4, $^3J_{PC}$ = 13.6, *m*), 131.9 (d, C_3, C_6H_4, $^3J_{PC}$ = 13.4, *M*), 133.8 (d, C_o, PPh_2, $^2J_{PC}$ = 9.9, *M*), 133.7−134.1 (several d overlapped, C_o + C_p (PPh_2) + C_5 (C_6H_4), *M* + *m*), 136.0 (d, C_4, C_6H_4, $^4J_{PC}$ = 2.8, *m*), 136.1 (d, C_4, C_6H_4, $^4J_{PC}$ = 2.8, *M*), 137.0 (d, C_6, C_6H_4, *M* + *m*), 166.3 (d, CO, $^3J_{PC}$ = 2.5, *m*), 166.4 (d, CO, $^3J_{PC}$ = 2.8, *M*); signals corresponding to C_1 and C_2 (C_6H_4) were not observed; ^{31}P{^{1}H} NMR ($CDCl_3$, 202.4 MHz) δ 27.2 (*M*), 27.1 (*m*); MS (MALDI +) 200 (90%) $[O{=}PPh_2]^+$.

Synthesis of Bis{2-[(triphenyl-λ^5-phosphanylidene)carbamoyl]-phenyl}mercury(II), 13. To a solution of the iminophosphorane **6c** (0.644 g, 1.40 mmol) in dry THF (25 mL) at −90 °C was slowly added 2.0 mL of ^{s}BuLi (1.4 M, 2.80 mmol) over a period of 1 min. The resulting deep red solution of **8** was stirred at −90 °C for 30 min. Then $HgCl_2$ (0.190 g, 0.70 mmol) was added in one portion, and the mixture was further stirred for 15 h, allowing it to reach room temperature. Then, the solvent was evaporated to dryness. The white residue was extracted with CH_2Cl_2 (3 × 15 mL), and the combined extracts were concentrated almost to dryness (~1 mL). The oily residue was treated with Et_2O (15 mL). Further stirring gave **13** as a white solid, which was filtered, washed with Et_2O (15 mL), and dried under vacuum. Obtained: 0.414 g (62% yield). IR (Nujol) ν 1648 (C=O), 1284 (P=N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.37−7.39 (m, 2H, H_4 + H_5, C_6H_4), 7.47−7.54 (m, 7H, H_6 (C_6H_4) + H_m (PPh_3)), 7.60 (m, 3H, H_p, PPh_3), 7.80 (m, 6H, H_o, PPh_3), 8.46 (dd, 1H, H_3, C_6H_4, $^3J_{H3H4}$ = 7.8, $^4J_{H3H5}$ = 1.5); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz) δ 127.2 (d, C_i, PPh_3, $^1J_{PC}$ = 100.0), 128.1 (s, C_6H_4), 128.7 (d, C_m, PPh_3, $^3J_{PC}$ = 12.5), 130.5 (d, C_3, C_6H_4, $^4J_{PC}$ = 2.6), 131.3 (s, C_6, C_6H_4), 132.5 (d, C_p, PPh_3, $^4J_{PC}$ = 2.6), 133.2 (d, C_o, PPh_3, $^2J_{PC}$ = 9.5), 135.9 (s, C_6H_4), 142.7 (d, C_2, C_6H_4, $^3J_{PC}$ = 18.1), 171.6 (s, CO),

(33) By analogy with "stabilized phosphorus ylides" (stabilized phosphoranes), stabilized iminophosphoranes are those derivatives in which the negative charge of the nitrogen of the P=N linkage is delocalized through conjugation with electron-withdrawing groups.

signals due to C_1 (C_6H_4) were not observed; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz) δ 25.8; MS (MALDI+) 961 (60%) $[M]^+$. Anal. Calcd for $[C_{50}H_{38}HgN_2O_2P_2]$ (961.40): C, 62.5; H, 3.98; N, 2.91. Found: C, 62.31; H, 3.99; 2.76.

General Procedure for the Preparation of Compounds 14−20. To a solution of **6c** (0.193 g, 0.42 mmol) in 20 mL of dry THF, at −90 °C, was added 0.60 mL of ^{s}BuLi (1.4 M, 0.84 mmol). The resulting red solution of **8** was stirred for 30 min at this temperature, then reacted with the corresponding electrophile (0.46 mmol) and allowed to slowly reach room temperature by stirring for 12 h. The solution obtained was evaporated to dryness. The excess of base was quenched with MeOH, and the reaction was poured into water and extracted with CH_2Cl_2 (3×15 mL). The organic layers were dried over $MgSO_4$ and concentrated under vacuum. The purification method used is indicated for each compound (see below).

Synthesis of 2-Iodo-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 14. The yellow residue obtained was washed with Et_2O (2×10 mL) and recrystallized from a CH_2Cl_2/pentane mixture, furnishing pale yellow crystals of **14**. Obtained: 0.196 g (92% yield). IR (Nujol) ν 1590 (C=O), 1335 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 400.13 MHz) δ 7.02 (m, 1H, C_6H_4I), 7.33 (m, 1H, C_6H_4I), 7.54 (m, 6H, H_m, PPh_3), 7.63 (m, 3H, H_p, PPh_3), 7.83 (m, 1H, C_6H_4I), 7.86−7.91 (m, 7H, C_6H_4I + H_o (PPh_3)); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 93.9 (d, C_6, C_6H_4I, $^4J_{PC}$ = 1.1), 127.6 (s, C_6H_4I), 127.7 (d, C_i, PPh_3, $^1J_{PC}$ = 96.5), 128.7 (d, C_m, PPh_3, $^3J_{PC}$ = 12.3), 130.0 (s, C_6H_4I), 130.1 (s, C_6H_4I), 132.4 (d, C_p, PPh_3, $^4J_{PC}$ = 3.0), 133.3 (d, C_o, PPh_3, $^2J_{PC}$ = 10.0), 140.1 (s, C_6H_4I), 144.90 (d, C_1, C_6H_4I, $^3J_{PC}$ = 20.5), 178.3 (d, CO, $^2J_{PC}$ = 7.9); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz) δ 21.2; MS (ESI^+) 507.9 (M + 1H). Anal. Calcd for $[C_{25}H_{19}INOP]$ (507.41): C, 59.17; H, 3.78; N, 2.76. Found: C, 59.06; H, 3.78; N, 2.41.

Synthesis of 2-Diphenylphosphanyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 15. Purification by column chromatography over silica gel (CH_2Cl_2/MeOH, 98:2) yielded **15** as a white solid. Obtained: 0.197 g (41% yield). IR (Nujol) ν 1590 (C=O), 1329 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 400.13 MHz) δ 6.81 (m, 1H, C_6H_4), 7.23−7.27 (m, 7H, PPh_3 + PPh_2), 7.30−7.38 (m, 8H, PPh_3 + PPh_2), 7.41−7.51 (m, 5H, C_6H_4 + PPh_2), 7.52−7.64 (m, 6H, PPh_3), 7.69 (m, 1H, C_6H_4), 8.29 (m, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz) δ 126.1 (d, C_i, PPh_2, $^1J_{PC}$ = 101.8), 128.1 (d, C_i, PPh_3, $^1J_{PC}$ = 97.8), 128.1−129.0 (3C, C_6H_4 + C_m PPh_3 + C_m PPh_2), 131.9 (d, C_p, PPh_3, $^4J_{PC}$ = 2.9), 132.0 (s, C_6H_4), 132.5 (d, C_p, PPh_2, $^4J_{PC}$ = 0.9) 133.2−133.4 (m, C_o, PPh_2+PPh_3), 133.8 (s, C_6H_4), 134.1 (s, C_6H_4), 137.7 (d, C_6, C_6H_4, $^3J_{PC}$ = 23.1), 140.2 (d, C_1, C_6H_4, $^2J_{PC}$ = 14.2), 177.4 (d, CO, $^2J_{PC}$ = 9.1); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz) δ −6.0 (d, PPh_2, $^5J_{PP}$ = 5.1), 22.6 (d, N=PPh_3); MS (ESI^+) 566.1 (M + 1H). Anal. Calcd for $[C_{37}H_{29}NOP_2]$ (565.6): C, 78.57; H, 5.17; N, 2.48. Found: C, 78.19; H, 5.02; N, 2.33.

Synthesis of 2-Trimethylstannyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 16. White solid. Obtained: 0.199 g (87% yield). IR (Nujol) ν 1540 (C=O), 1336 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 500.13 MHz) δ 0.00 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 55), 7.43−7.49 (m, 8H, PPh_3 + C_6H_4), 7.54−7.59 (m, 3H, PPh_3), 7.67 (m, 1H, C_6H_4), 7.80−7.87 (m, 6H, PPh_3), 8.70 (m, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.76 MHz) δ −6.7 (s, $SnMe_3$, $^1J_{SnC}$ 378.5), 127.4 (s, C_6H_4), 128.0 (d, C_i, PPh_3, $^1J_{PC}$ = 98.9), 128.1 (d, C_m, PPh_3, $^3J_{PC}$ = 12.2), 129.35 (s, C_6H_4), 129.63 (s, C_6H_4), 131.8 (d, C_p, PPh_3, $^4J_{PC}$ = 2.5), 133.0 (d, C_o, PPh_3, $^2J_{PC}$ = 10.0), 135.3 (s, C_6H_4), 141.9 (d, C_1 C_6H_4, $^3J_{PC}$ = 20.1), 145.8 (d, C_6 C_6H_4, $^4J_{PC}$ = 4.1), 178.6 (d, CO, $^2J_{PC}$ = 8.6); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.4 MHz) δ 22.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 186.50 MHz) δ −59.9; MS (ESI^+) 546.0 (M + 1H). Anal. Calcd for $[C_{28}H_{28}NOPSn]\cdot CH_2Cl_2$ (629.16): C, 55.36; H, 4.81; N, 2.23. Found: C, 55.33; H, 4.97; N, 2.22.

Synthesis of 2-Tri-*n*-butylstannyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 17. White solid. Obtained: 0.138 g (49% yield). IR (Nujol) ν 1541 (C=O), 1340 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 500.13 MHz) δ 0.80−0.97 (m, 15H, CH_3CH_2, $SnBu_3$), 1.19−1.25 (m, 6H, CH_2, $SnBu_3$), 1.35−1.41 (m, 6H, CH_2, $SnBu_3$), 7.43−7.51 (m, 8H, PPh_3 + C_6H_4), 7.58 (m, 3H, PPh_3), 7.67 (m, 1H, C_6H_4), 7.87 (m, 6H, PPh_3), 8.78 (m, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.76 MHz) δ 11.9 (s, CH_2), 12.1 (s, CH_3), 27.7 (s, CH_2), 29.3 (s, CH_2), 127.4 (s, C_6H_4), 128.4 (d, C_i, PPh_3, $^1J_{PC}$ = 91.6), 128.4 (d, C_m, PPh_3, $^3J_{PC}$ = 12.0), 129.6 (s, C_6H_4), 129.7 (s, C_6H_4), 132.0 (d, C_p, PPh_3, $^4J_{PC}$ = 2.7), 133.1 (d, C_o, PPh_3, $^2J_{PC}$ = 9.4), 136.1 (s, C_6H_4), 142.2 (d, C_1, C_6H_4, $^3J_{PC}$ = 19.1), 146.1 (d, C_6, C_6H_4, $^4J_{PC}$ = 3.1), 176.6 (d, CO, $^2J_{PC}$ = 7.5); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.4 MHz) δ 22.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 186.50 MHz) δ −66.9; MS (ESI^+): 672.1 (M + 1H). Anal. Calcd for $[C_{37}H_{46}NOPSn]$ (670.46): C, 66.29; H, 6.92; N, 2.09. Found: C, 66.67; H, 7.24; N, 1.91.

Synthesis of 2-Triphenylstannyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 18. Column chromatography (silica gel, CH_2Cl_2) afforded a white solid that was recrystallized from CH_2Cl_2/pentane. Obtained: 0.135 g (44% yield). IR (Nujol) ν 1530 (C=O), 1358 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.19 (m, 6H, $SnPh_3$), 7.28 (m, 3H, $SnPh_3$), 7.37−7.45 (m, 7H, PPh_3 + C_6H_4), 7.46 (m, 6H, $SnPh_3$), 7.51 (m, 2H, C_6H_4), 7.69 (m, 3H, PPh_3), 7.71−7.73 (m, 6H, PPh_3), 8.83 (m, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.76 MHz) δ 127.1 (s, C_6H_4), 127.9 (d, C_i, PPh_3, $^1J_{PC}$ = 91.1), 127.3 (s, C_m, $SnPh_3$), 128.3 (d, C_m, PPh_3, $^3J_{PC}$ = 12.2), 129.3 (s, C_6H_4), 129.4 (s, C_6H_4), 130.6 (s, C_p, $SnPh_3$), 132.0 (d, C_p, PPh_3, $^4J_{PC}$ = 2.7), 132.9 (d, C_o, PPh_3, $^2J_{PC}$ = 10.0), 137.0 (s, C_6H_4), 137.4 (s, C_o, $SnPh_3$), 141.6 (d, C_1, C_6H_4, $^3J_{PC}$ = 20.1), 142.2 (d, C_6, C_6H_4, $^4J_{PC}$ = 4.4), 144.0 (s, C_i, $SnPh_3$), 175.7 (d, CO, $^2J_{PC}$ = 7.1); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.4 MHz) δ 23.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 186.50 MHz) δ −165.1; MS (ESI^+) 654 (M − Ph). Anal. Calcd for $[C_{43}H_{34}NOPSn]$ (730.43): C, 70.71; H, 4.69; N, 1.92. Found: C, 70.38; H, 4.59; N, 1.98.

Synthesis of 2-Trimethylsilyl-*N*-(triphenyl-λ^5-phosphanylidene)-benzamide 19. White solid. Obtained: 0.169 g (89% yield). Crystals of **19**$\cdot CH_2Cl_2$ were obtained by slow evaporation of a CH_2Cl_2 solution of the crude compound. IR (Nujol) ν 1592 (C=O), 1331 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 400.13 MHz) δ 0.16 (s, 9H, $SiMe_3$), 7.39−7.43 (m, 2H, C_6H_4), 7.47 (m, 6H, PPh_3), 7.57 (m, 3H, PPh_3), 7.63 (m, 1H, C_6H_4), 7.86 (m, 6H, PPh_3), 8.51 (dd, 1H, C_6H_4, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz) δ 0.0 (s, $SiMe_3$), 127.6 (s, C_6H_4), 127.8 (d, C_i, PPh_3, $^1J_{PC}$ = 98.7), 127.7 (d, C_m, PPh_3, $^3J_{PC}$ = 12.2), 128.4 (s, C_6H_4), 129.2 (s, C_6H_4), 131.4 (d, C_p, PPh_3, $^4J_{PC}$ = 2.8), 132.5 (d, C_o, PPh_3, $^2J_{PC}$ = 9.8), 134.1 (d, C_6H_4, J_{PC} = 1.2), 140.2 (d, C_6, C_6H_4, $^4J_{PC}$ = 3.3), 144.2 (d, C_1, C_6H_4, $^3J_{PC}$ = 19.8), 177.6 (d, CO, $^2J_{PC}$ = 8.1); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz) δ 20.8; MS (ESI^+) 454.2 (M+1H). Anal. Calcd for $[C_{28}H_{28}NOPSi]\cdot CH_2Cl_2$ (538.53): C, 64.68; H, 5.61; N, 2.60. Found: C, 64.83; H, 5.88; N, 2.61.

Synthesis of 2-[Hydroxy(phenyl)methyl]-*N*-(triphenyl-λ^5-phosphanylidene)benzamide, 20. Column chromatography (silica gel, CH_2Cl_2) afforded a white solid, which was recrystallized from CH_2Cl_2/pentane. Obtained: 0.135 g (77% yield). IR (Nujol) ν 1580 (C=O), 1343 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$, 400.13 MHz) δ 4.60 (s, 1H, CH), 5.83 (m, 1H, C_6H_4), 7.09−7.84 (m, 22H, PPh_3 + Ph + C_6H_4), 8.14 (m, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz) δ 76.0 (s, C−OH), 126.1 (s, C_6H_4), 126.4 (s, C_m, Ph), 127.1 (d, C_i, PPh_3, $^1J_{PC}$ = 95.2), 127.3 (s, C_p, Ph), 127.6 (s, C_o, Ph), 128.6 (d, C_m, PPh_3, $^3J_{PC}$ = 12.5), 130.1 (s, C_6H_4), 130.2 (s, C_6H_4), 132.2 (s, C_6H_4), 132.3 (d, C_p, PPh_3, $^4J_{PC}$ = 2.9), 132.9 (d, C_o, PPh_3, $^2J_{PC}$ = 10.0), 138.9 (d, C_1, C_6H_4, $^3J_{PC}$ = 19.1), 143.3 (d, C_6, C_6H_4, $^4J_{PC}$ = 1.1), 144.0 (s, C_i, Ph), 179.1 (d, CO, $^2J_{PC}$ = 8.5); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz) δ 23.1; MS (ESI^+) 488.1 (M + 1H). Anal. Calcd for

$[C_{32}H_{26}NO_2P]$ (487.54): C, 78.84; H, 5.38; N, 2.87. Found: C, 78.59; H, 5.17; N, 2.49.

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Supporting Information Available: Details on general experimental methods, structural characterization of compounds **13**−**20**, copies of ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of all new compounds, $^{119}Sn\{^{1}H\}$ NMR spectra of **16**−**18**, variable-temperature ^{31}P NMR spectra of **8**, expansion of the ^{13}C NMR spectrum of **8**, and crystallographic details of **16**. This material is available free of charge via the Internet at http://pubs.acs.org.