Reaction of $HP(OC_6H_4NH)_2$ with *n*-BuLi and then with EX (E = Me, $SiMe_3$, $GeMe_3$, $SnMe_3$, $Cp(CO)_2Fe$, Cp(CO)ICo; X = Cl, I), Leading to Selective Deprotonation and Substitution

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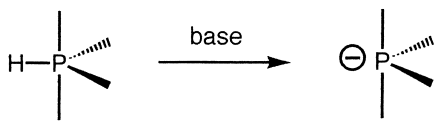
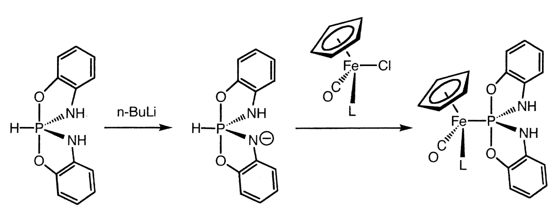
The reaction of $HP(OC_6H_4NH)_2$ with *n*-BuLi yielded the amide anion, $HP(OC_6H_4NH)(OC_6H_4N^-)$, with selective deprotonation at the nitrogen atom. Subsequent treatment of the anion with MeI yielded P-methylated phosphoranes: $MeP(OC_6H_4NH)_2$ and $MeP(OC_6H_4NH)(OC_6H_4NMe)$. In contrast, the reaction of the amide with ECl (E = $SiMe_3$, $GeMe_3$, $SnMe_3$) led exclusively to *N*-substituted phosphoranes: $HP(OC_6H_4NH)(OC_6H_4NE)$ and $HP(OC_6H_4NE)_2$. In the corresponding reaction with $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$, the anion was converted into a P-metalated phosphorane, $(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(OC_6H_4NH)_2\}$, whereas the reaction with $(\eta^5\text{-}C_5H_5)(CO)CoI_2$ yielded an N-metalated phosphorane, $HP(OC_6H_4NH)(OC_6H_4N\{Co(\eta^5\text{-}C_5H_5)(CO)I\})$. The reason for such selectivity was discussed.

An anionic tetracoordinate phosphorus compound, i.e., a phosphoranide, is a member of hypervalent phosphorus compounds which are of interest because of violating the octet rule. One of the often-used preparative methods of phosphoranides is deprotonation of phosphoranes bearing a P-H bond (Eq. 1).[1]



(1)

From a viewpoint of synthesis of transition-metal–phosphorane complexes (P-metalated phosphoranes, referred to as metallaphosphoranes hereafter), a phosphoranide has attracted attention as a precursor.[2] During the course of our investigation of metallaphosphoranes, we encountered unexpected deprotonation of $HP(OC_6H_4NH)_2$ (**1**) (Although the compound should be described as $HP(OC_6H_4NH)_2$, the tie lines are often omitted in this paper for clarity) in the reaction with *n*-BuLi to give only an amide, $HP(OC_6H_4NH)(OC_6H_4N^-)$, but not a phosphoranide $^-P(OC_6H_4NH)_2$, as a detectable species.



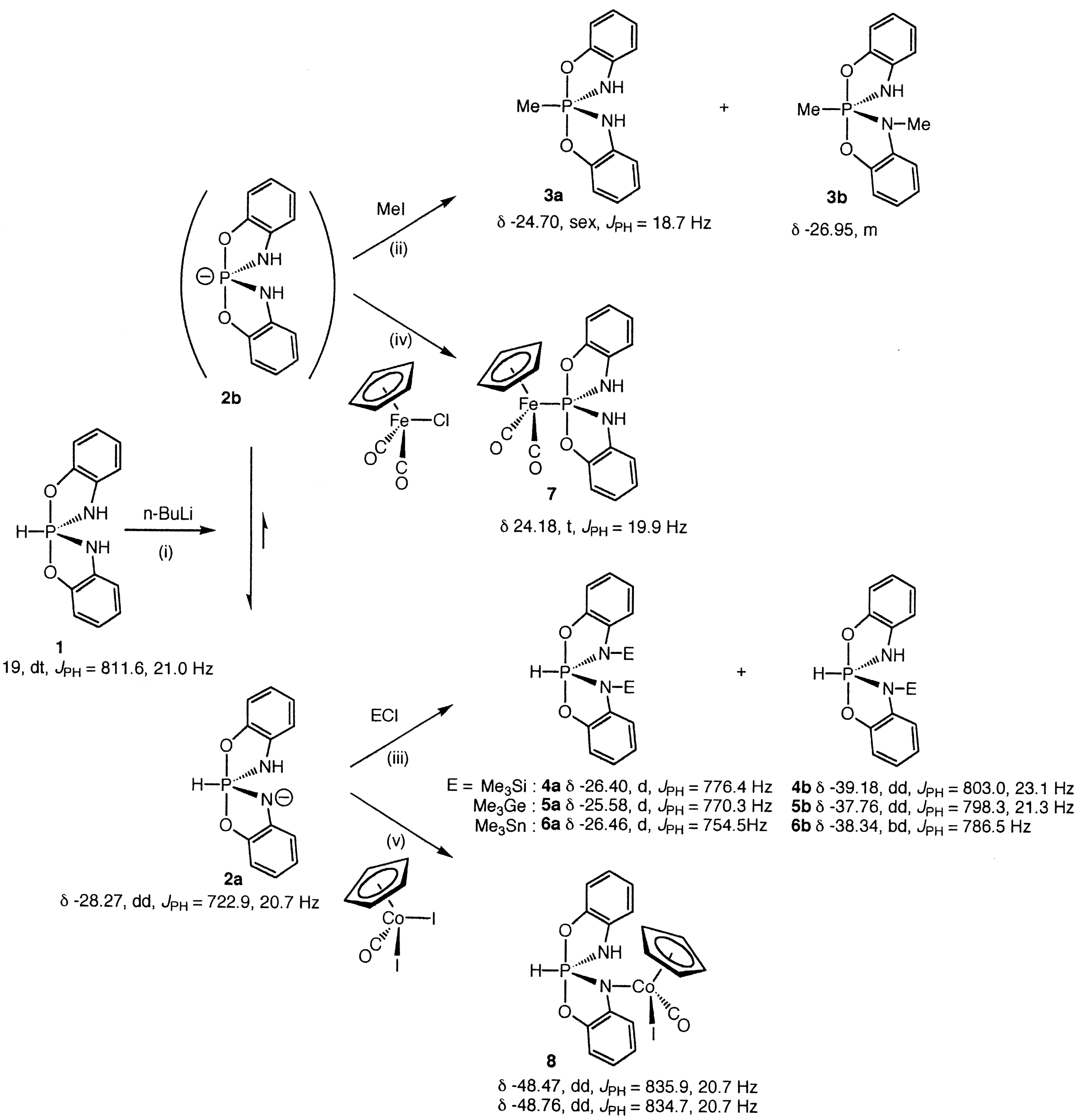
(2)

In addition, the reaction of the resulting amide with Cp(CO)LFeCl (Cp = η^5-C_5H_5, L = phosphine, phosphite) unexpectedly yielded a metallaphosphorane, Cp(CO)LFe{P-$(OC_6H_4NH)_2$} (Eq. 2), but not an N-metalated $HP(OC_6H_4NH)$-$[OC_6H_4N\{FeCp(CO)\text{-}L\}]$.[2c,3]

In this paper, we report the results of our naive extension of the reaction of **1** with *n*-BuLi and then Cp(CO)LFeCl to those with *n*-BuLi and then EX, i.e., a series of group 14 element halides (MeI, Me_3SiCl, Me_3GeCl, Me_3SnCl) and transition-metal–halido complexes ($Cp(CO)_2FeCl$ and $Cp(CO)CoI_2$). A part of the results has already been communicated.[3]

Results and Discussion

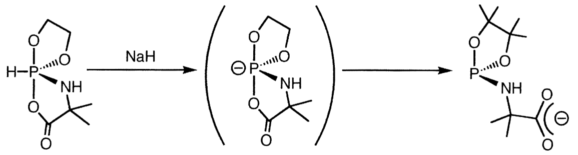
All reactions were carried out under an atmosphere of dry nitrogen by using dry solvents. Through the reactions examined in this paper, we attempted to isolate the products, but considerable difficulty was encountered due to the instability and/or separation problems, except for complex **7** (vide infra). However, the products could be identified by the ^{31}P NMR spectra of the reaction mixtures. Their chemical shifts and coupling constants with hydrogen(s) were informative enough to identify them correctly. For example, the starting phosphorane compound **1** shows a singlet at −47.19 ppm in the $^{31}P\{^1H\}$ NMR spectrum, which becomes a doublet of triplets without proton irradiation. The doublet is due to the coupling with the PH proton (J_{PH} = 811.6 Hz) and the triplets are due to the coupling with the two identical PNH protons (J_{PH} = 21.0 Hz). These ^{31}P NMR data are diagnostic of the TBP structure adopted around the phosphorus with one hydrogen and two NH groups in equatorial positions.[4] The approximate yield of each product mentioned below was obtained from the proton-non-decoupled ^{31}P NMR spectrum of the reaction mixture.



Scheme 1.

Reaction of $HP(OC_6H_4NH)_2$ with *n*-BuLi. The hydridophosphorane **1** was treated with an equimolar amount of *n*-BuLi at −78 °C and then stirred at room temperature for 20 minutes (Scheme 1-i). The ^{31}P NMR spectrum of the mixture showed a broad doublet at −27.0 ppm with a coupling constant of J_{PH} = 710 Hz at room temperature. Since such a large coupling constant indicates the presence of a direct P–H bond, it can be concluded that the proton abstraction does not occur on the phosphorus atom. At −80 °C, this signal was sharpened and split into two; a major signal (≈ 84%) appearing as a doublet of doublets at −28.27 ppm (J_{PH} = 722.9 and 20.7 Hz) and a minor one (≈ 16%) as a slightly broad doublet at −47.06 ppm (J_{PH} = 810.4 Hz). Considering the PH coupling pattern, the doublet of doublets can be reasonably attributed to an amide **2a**, resulting from deprotonation at the nitrogen atom, but not at the phosphorus atom. These observations indicate that the acidity of the NH proton is higher than that of the PH proton. The minor doublet at −47.06 ppm might be due to the starting hydridophosphorane **1**, though the small coupling expected with NH protons was not discernible. Hydrolysis of *n*-BuLi before the reaction with **1** and/or that of **2a** may be responsible for the observation of a small amount of **1** in the reaction mixture. The temperature-dependent ^{31}P NMR spectra may be explained on the basis of the proton exchange between **1** and **2a**, that is, the NH proton exchange takes place readily at room temperature, whereas at −80 °C it does not occur or is very slow on the NMR time scale. There is no spectroscopic evidence for the formation of other species such as **2b**.

Munoz et al.[5] reported the reaction of a closely related hydridophosphorane,$HP(OCH_2CH_2O)\{OC(O)C(CH_3)_2NH\}$, having a PNH group with NaH (Eq. 3). In this reaction, proton abstraction on the phosphorus has been proposed to give a phosphoranide as an intermediate, which then converted into an isolable open-form tricoordinate phosphorus compound. On the other hand, in the reaction of **1** with *n*-BuLi shown in Scheme 1-i, neither an open-form tricoordinate phosphorus compound, $P(OC_6H_4NH)(NHC_6H_4O^-)$, nor any phosphoranide was detected, but the amide anion **2a** was formed. This constitutes, to our knowledge, the first amide formation from hydridophosphorane.



(3)

Reaction with MeI. MeI was added to a solution containing the amide **2a** at −78 °C and then the solution was allowed to warm to room temperature (Scheme 1-ii). The ^{31}P NMR spectrum of the mixture revealed the formation of two new phosphorus compounds in the intensity ratio of 3 : 1. The formation of **1** (≈ 25%) was also observed, though it was not a major product. The main product resonated at −24.70 ppm as a formal sextet (J_{PH} = 18.7 Hz) without proton irradiation. Comparison of the ^{31}P NMR data with those of an authentic sample[6] established that the main product is a P-methylated phosphorane, $MeP(OC_6H_4NH)_2$ (**3a**) (≈ 57%).

Although **2a** is the only anionic species present in the starting solution, the main product in the reaction with MeI is not the N-methylated compound, $HP(OC_6H_4NH)(OC_6H_4NMe)$, but the P-methylated compound **3a**. Two reaction routes to **3a** seem to be possible. (a) $HP(OC_6H_4NH)(OC_6H_4NMe)$ is first formed, and then an H on the phosphorus and an Me on the nitrogen exchange their positions in some way. (b) Although only the amide **2a** is detected, the phosphoranide **2b** also exists in solution as a minor equilibrium species. If **2b** is much more reactive than **2a** toward MeI, then **2b** selectively reacts to give eventually **3a** as a main product. Since we confirmed that the H–Me exchange assumed in the route (a) has not been observed for $HP(OC_6H_4NMe)_2$, the route (b) seems more pertinent.

The minor product in the reaction (ii), which exhibited a multiplet at −26.95 ppm, could be reasonably assigned to $MeP(OC_6H_4NH)(OC_6H_4NMe)$ (**3b**) (≈ 18%).[7] Neither $HP(OC_6H_4NMe)_2$ nor $HP(OC_6H_4NH)(OC_6H_4NMe)$ nor an open-form tricoordinate phosphorus compound, $HP(OC_6H_4NH)(NHC_6H_4OMe)$, was formed. Since no N-methylated compound, $HP(OC_6H_4NH)(OC_6H_4NMe)$, was detected, **3b** can be thought to be derived from **3a** in the following sequences: the NH proton in **3a** is abstracted by **2a** still present in solution to give $MeP(OC_6H_4NH)(OC_6H_4N^-)$ and **1**, and then the former reacts with MeI to give **3b**. Although the yield of **1** somewhat fluctuated, presumably due to incomplete conversion of **1** into **2a**, it was almost equal to or slightly greater than that of **3b**. This is consistent with the above reaction sequences.

Reaction with Me_3SiCl, Me_3GeCl, or Me_3SnCl. The reaction of a solution containing **2** with Me_3SiCl was examined in a manner similar to that of the reaction with MeI. The ^{31}P NMR spectrum indicated two products and **1** (≈ 33%) (Scheme 1-iii). A doublet at −26.40 ppm due to the main product has a coupling constant of J_{PH} = 776.4 Hz, suggesting the presence of a PH proton and absence of NH protons. Therefore, this product is reasonably assignable to $HP(OC_6H_4NSiMe_3)_2$ (**4a**) (≈ 40%), in which the two N atoms are both silylated. The signal at −39.18 ppm due to the minor product was observed as a doublet of doublets (J_{PH} = 803.0 and 23.1 Hz), which has the coupling pattern expected for $HP(OC_6H_4NH)(OC_6H_4NSiMe_3)$ (**4b**) (≈ 13%). In this case, no P-silylated compounds were observed at all. In addition, it should be noted that an O-silylated tricoordinate phosphorus compound, $P(OC_6H_4NH)(NHC_6H_4OSiMe_3)$, also could not be detected. This observation indicates that the open-form species, $P(OC_6H_4NH)(NHC_6H_4O^-)$, is practically absent even in equilibrium (see Eq. 4, which will be mentioned below).

Me_3GeCl and Me_3SnCl reacted similarly to Me_3SiCl. That is, $HP(OC_6H_4NGeMe_3)_2$ (**5a**) (−25.58 ppm, d, J_{PH} = 770.3 Hz) (≈ 17%) and $HP(OC_6H_4NH)(OC_6H_4NGeMe_3)$ (**5b**) (−37.76 ppm, dd, J_{PH} = 798.3 and 21.3 Hz) (≈ 43 %) together with **1** (≈ 34 %) were formed in the reaction with Me_3GeCl, and $HP(OC_6H_4NSnMe_3)_2$ (**6a**) (−26.46 ppm, d, J_{PH} = 754.5 Hz) (≈ 31%) and $HP(OC_6H_4NH)(OC_6H_4NSnMe_3)$ (**6b**) (−38.34 ppm, broad d, J_{PH} = 786.5 Hz) (≈ 40 %) together with **1** (≈ 11 %) were formed in the reaction with Me_3SnCl.

Reaction with $Cp(CO)_2FeCl$. Metallaphosphoranes have recently been synthesized in several manners.[2,3,8–14] In some cases, a substitution reaction has been employed with a phosphoranide for a good leaving ligand on a transition-metal complex.[2] The results described in the previous sections reveal that the anionic species derived from **1** can act as both an amide **2a** and a phosphoranide **2b** toward electrophiles, even though the population of the phosphoranide **2b** is quite low in equilibrium. Therefore, when the anion **2** is treated with transition-metal complexes, the two products (an amide complex and a metallaphosphorane) are conceivable.

The iron-chloro complex, $Cp(CO)_2FeCl$, was added to the THF solution containing **2** at −78 °C, and the mixture was stirred for 3 h at ambient temperature (Scheme 1-iv). The ^{31}P NMR spectrum showed a triplet (J_{PH} = 19.9 Hz) at 24.18 ppm, together with weak signals due to unidentified compounds and the starting compound **1**. The chemical shift (24.18 ppm) which is at a much lower magnetic field than that for hydridophosphorane **1** (−47.19 ppm) and its coupling pattern strongly suggest the formation of a P-substituted compound. After removal of volatile components from the mixture, the product was extracted with ether, and then dried under reduced pressure to give a yellow powder. The spectroscopic data (IR spectrum and ^{1}H, ^{13}C and ^{31}P NMR spectra) and the elemental analysis data revealed that the product is an iron phosphorane complex **7** (76%).[3] $Cp(CO)_2RuCl$ showed a similar reactivity.[2c]

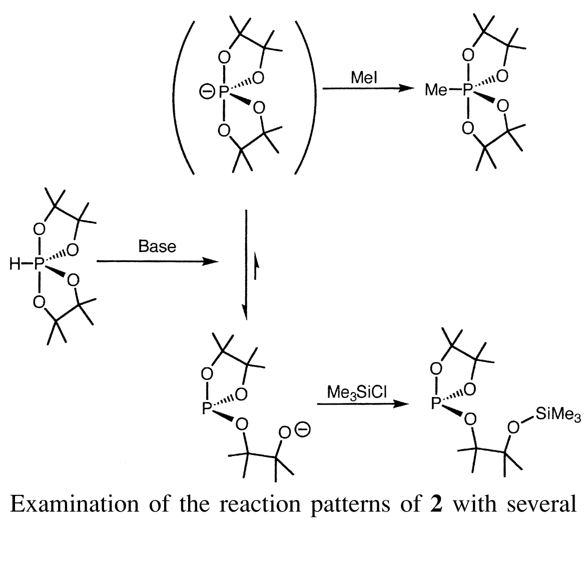
Reaction with $Cp(CO)CoI_2$. We examined the reactions of **2** with transition-metal–halido complexes other than group 8 transition metals. In most cases, complicated reactions took place involving a redox, so that the phosphorus-containing products would not be identified. However, in the reaction with $Cp(CO)CoI_2$, we found that the main product is an N-metalated phosphorane.

After addition of $Cp(CO)CoI_2$ to a solution containing **2** at −78 °C, the mixture was stirred for 1 h at room temperature (Scheme 1-v). The ^{31}P NMR spectrum of the mixture displayed two doublets of doublets in almost equal intensity at −48.47 ppm (J_{PH} = 835.9 and 20.7 Hz) and at −48.76 ppm

(J_{PH} = 834.7 and 20.7 Hz), together with the signal due to **1** (≈ 62%). These two products were thermally unstable, and additional stirring of the mixture led to the decomposition. In contrast to the above iron case, the chemical shifts of these signals are in a magnetic field close to that of the starting organophosphorane **1**. The coupling patterns of the signals strongly suggest the formation of the N-substituted hydridophosphoranes. Therefore, it could be concluded that the product is $HP(OC_6H_4NH)[OC_6H_4N\{Co(\eta^5\text{-}C_5H_5)(CO)I\}]$ (**8**) (≈ 38 %), in which the cobalt atom is bonded to a nitrogen atom. The observation of the two products having almost the same chemical shifts and the same coupling constants in the ^{31}P NMR spectra is consistent with the formation of **8**, because **8** has the phosphorus and the cobalt atoms which are both chiral. That is, they are diastereomers to each other.

Selectivity. In the reaction with *n*-BuLi of phosphorane **1** having one H and two NHR groups in equatorial positions, only an amide **2a** was detected, whereas the reaction of a similar hydridophosphorane, $HP(OCH_2CH_2O)\{OC(O)C(CH_3)_2NH\}$, with NaH gave initially a phosphoranide as an intermediate (Eq. 3).[5] Although in the reaction of **1** the possibility of PH deprotonation, which induces subsequent proton migration from N to P to give a thermodynamically stable amide **2a**, can not be ruled out, it is highly likely that direct NH proton abstraction takes place. This is because an electron-withdrawing aromatic ring bonded to the amide nitrogen renders the NH group more acidic than the PH group in **1**, while the NH group is less acidic than the PH group in $HP(OCH_2CH_2O)\{OC(O)C(CH_3)_2NH\}$ having no such electron-withdrawing group. The amide **2a** is proposed to be in equilibrium with a phosphoranide **2b** though the equilibrium is so heavily shifted toward **2a** that **2b** can not be detected spectroscopically.

It has been reported that $HP(OCMe_2CMe_2O)_2$, as well as $HP(OCH_2CH_2O)\{OC(O)C(CH_3)_2NH\}$, reacts with a Lewis base to give an anionic tricoordinate phosphorus compound (Eqs. 3 and 4).[5,15] Since similar reactions have been reported in many cases,[1] it seems often the case that a Lewis base converts a hydridophosphorane into a tricoordinate phosphorus compound. Thus, the amide formation reported here is unique in that the phosphorus keeps its pentacoordinate framework, the stability of which is attributed to the rigid chelate structure of the substituents on the phosphorus atom.[16]



(4)

Examination of the reaction patterns of **2** with several halides presented above points to the presence of selectivity. In the reaction with halides of group 14 elements, methyl iodide reacts with **2b** to give a P-substituted phosphorane, whereas trimethyl-silyl, -germyl, and -stannyl chlorides react with **2a** to yield N-substituted phosphoranes. Although the reaction of $P(OCMe_2CMe_2O)(OCMe_2CMe_2O^-)$ with MeI similarly yields a P-methylated phosphorane, the reaction with Me_3SiCl does not form a phosphorane but does form an O-silylated phosphite (Eq. 4).[15]

Since the P- and N-substituted products prepared in this paper except **8** do not change further, the selectivity mentioned above may be explained by the difference in thermodynamic stability between E–P and E–N bonds. It is well-known that a P–C bond is more stable than P–Si, P–Ge, and P–Sn bonds,[17] so that an alkyl group tends to bond to a phosphorus atom. In contrast, Si, Ge, and Sn fragments would more preferably bond to a nitrogen atom, because the third and subsequent row main group elements in the periodic table can use empty d and/or σ^* orbital(s) to make π bonds with lone pair electrons on the N atom. These bonding abilities may cause the selectivity mentioned above.

The selectivity in the reaction of **2** with transition-metal–halido complexes can be understood in terms of π donacity from a transition-metal fragment to a phosphorane phosphorus. It has been demonstrated that a phosphorane fragment accepts π electrons into its empty σ^* orbital of the 3-center-4-electron bond from a filled d orbital of Cp(CO)LFe (L = CO, phosphine, phosphite) fragments, making the P–M bond strong.[2a,3] In $Cp(CO)_2FeCl$, the formal oxidation state of Fe is 2+, whereas that of Co in $Cp(CO)CoI_2$ is 3+. Therefore, the π electron donacity of the Cp(CO)CoI fragment is expected to be poorer than that of the $Cp(CO)_2Fe$ fragment. Indeed, in the ^1H NMR spectra, a signal due to the Cp ligand is observed at a lower magnetic field in the cobalt complex (5.96 ppm) than in the iron complex (5.05 ppm). In addition, it is highly likely that σ electron donacity of the Cp(CO)CoI fragment is weaker than that of H. Therefore, the Cp(CO)CoI fragment may prefer to make a bond with a nitrogen atom, which does not require π-back donation at all.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. THF was distilled from sodium benzophenone ketyl, and then stored under a nitrogen atmosphere. MeI, Me_3SiCl, Me_3GeCl, Me_3SnCl and a hexane solution of *n*-BuLi (1.6 M) were obtained from common commercial sources, and used without further purification. $HP(OC_6H_4NH)_2$,[16] $Cp(CO)_2FeCl$[18] and $Cp(CO)CoI_2$[19] were prepared according to the literature.

A JEOL EX-400 and LA-300 spectrometers were used to obtain ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra. ^1H and ^{13}C resonances were measured relative to $SiMe_4$, as an internal standard. The ^{31}P resonances were measured relative to 85% H_3PO_4 as an external standard. A Shimadzu FTIR-8100A spectrometer was used to obtain an IR spectrum. Elemental analysis data were obtained on a Perkin–Elmer 2400 CHN elemental analyzer.

General Procedure. Since the procedures in the reactions of **2** with MeI, Me_3SiCl, Me_3GeCl, Me_3SnCl or $Cp(CO)CoI_2$ are basically similar, the reaction with MeI is described as a typical example. A hexane solution of n-BuLi (1.6 M, 0.52 mL, 0.83 mmol) was added to a THF solution (10 mL) containing **1** (190 mg, 0.77 mmol) at −78 °C. After 20 min stirring at room temperature, the mixture was re-cooled to −78 °C, and then MeI (67 μL, 1.54 mmol) was added. The reaction mixture was stirred overnight at room temperature, and then subjected to the ^{31}P NMR measurements.

Reaction with $Cp(CO)_2FeCl$. A THF solution (15 mL) of **1** (1.667 g, 6.77 mmol) was cooled at −78 °C, then a hexane solution of n-BuLi (1.6 M, 4.3 mL, 6.88 mmol) was added. After the cooling bath was removed and the solution was stirred for 20 min, it was cooled again to −78 °C, and then a solution of $Cp(CO)_2FeCl$ (1.460 g, 6.87 mmol) in THF (10 mL) was added dropwise. The solution was allowed to warm to room temperature and then stirred for 3 h. After removal of the solvents under reduced pressure, soluble compounds were extracted with ether (130 mL). The ether solution was concentrated to 3 mL and hexane (6 mL) was added to give a yellow powder, which was then washed with hexane (4 × 10 mL) to give **7** (2.206 g, 5.23 mmol, 76% yield). When the product has greenish color, the powder should be washed with a small amount of ether several times, though substantial yield loss will occur. Anal. Found: C, 53.84; H, 3.38; N, 6.44%. Calcd for $C_{19}H_{15}FeN_2O_4P$: C, 54.05; H, 3.58; N, 6.64%. IR (THF) ν_{CO} 2026, 1977 cm^{-1}. ^{31}P NMR (THF) δ 24.18 (t, J_{PH} = 19.9 Hz). ^{1}H NMR ($CDCl_3$) δ 4.94 (d, J_{PH} = 1.1 Hz, 5H, C_5H_5), 5.20 (d, J_{PH} = 17.2 Hz, 2H, NH), 6.60–6.66 (m, 8H, OC_6H_4N). ^{13}C NMR ($CDCl_3$) δ 85.31 (s, C_5H_5), 108.55 (d, J_{PC} = 12.9 Hz, OC_6H_4N), 108.69 (s, OC_6H_4N), 118.73 (s, OC_6H_4N), 119.27 (s, OC_6H_4N), 132.46 (d, J_{PC} = 11.0 Hz, OC_6H_4N), 149.55 (d, J_{PC} = 5.5 Hz, OC_6H_4N), 210.96 (d, J_{PC} = 42.3 Hz, CO), 212.62 (d, J_{PC} = 44.1 Hz, CO).

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6 A reaction mixture of $HOC_6H_4NH_2$ (519 mg, 4.76 mmol) with n-BuLi (1.61 M in hexane, 1.45 mL, 2.33 mmol) in THF was added to a solution of $[MeP(OPh)_3]I$ (1.06 g, 2.35 mmol) at −78 °C. After the mixture was stirred at room temperature for 3.5 h, the volatile components were removed under vacuum. The residue was dissolved in $CHCl_3$ and filtered, and then the solvent was removed under reduced pressure from the filtrate. The product was then extracted with ether/hexane = 2 mL/5 mL for six times. The solvents were removed under vacuum to give a white powder of $MeP(OC_6H_4NH)_2$ (461 mg, 1.77 mmol, 75% yield). ^{1}H NMR ($CDCl_3$) δ 1.96 (d, J_{PH} = 17.9 Hz, 3H, CH_3), 5.02 (broad d, J_{PH} = 17.6 Hz, 2H, NH), 6.50–6.90 (m, 8H, C_6H_4). ^{31}P NMR (THF) δ −25.78 (sex, J_{PH} = 18.3 Hz).

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