Articles

Synthesis of New Mixed Phosphine∼Iminophosphorane Bidentate Ligands and Their Coordination to Group 10 Metal Centers

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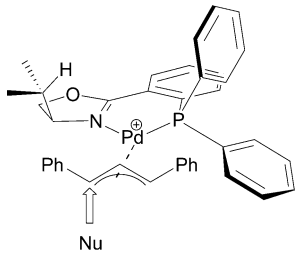
The selective monobromation of a symmetrical bidentate diphosphine (dppm = bis-diphenylphosphinomethane) yielding a highly reactive intermediate, **2** (P∼$PBr^+ \cdot Br^-$), is reported. Two methods of trapping were devised to produce mixed phosphine−aminophosphonium salts **3** (P∼$PNHR^+ \cdot Br^-$). The first method relies on the reaction of **2** with 2 equiv of primary amine to give **3a**−**c** (P∼$PNHR^+ \cdot Br^-$, R = p-Me-Bn, p-MeO-Bn, Ph). The second method utilizes 1 equiv of primary amine and DABCO as trapping agent to give **3a**−**e** (P∼$PNHR^+ \cdot Br^-$, R = p-Me-Bn, p-MeO-Bn, Ph, *n*Bu, α(+)-Me-benzyl). These salts were then deprotonated quantitatively to yield the desired new phosphine−iminophosphorane ligands **4a**−**e** (P∼PNR). This simple strategy allows for a wide variation of the R substituent at the nitrogen donor group (R = alkyl, aryl, benzyl). In particular, the optically pure ligand **4e** (R = α(+)-Me-benzyl) was obtained in one pot from commercially available α(+)-Me-benzylamine. Reaction of **4** with $Pd(COD)Cl_2$ affords the complexes **5** via coordination to Pd(II) centers and revealed the chelating behavior of these ligands. X-ray crystal structures of **5a** (presented in ESI), **5c**, and **5e** are reported. Complexes of platinum(II), **6c** and **6e**, were also synthesized and characterized crystallographically. The complex of nickel(II), **7a**, adopts a tetrahedral geometry as shown by X-ray analysis and consistent with a lack of NMR signal.

Introduction

Mixed P∼N bidentate ligands, such as phosphine−imine[1] or phosphine−oxazoline,[2] have found numerous applications in coordination chemistry and catalysis. In particular, Pfaltz and co-workers have had excellent results in the palladium-catalyzed enantioselective nucleophilic substitution of allylic acetates using chiral enantiopure phosphine−oxazolines. [2,3] In this system, only one stereocenter is present on the bidentate ligand, on the carbon α to the nitrogen atom, as shown in Scheme 1. Following studies have rationalized the results in terms of electronic differentiation of the two allylic termini: *trans* to the phosphorus atom and *trans* to the nitrogen atom. They have shown that nucleophilic attack occurred preferentially *trans* to the phosphorus atom, and thus *cis* to the sterically biased nitrogen atom.[4] Hence, only the chiral center α to the nitrogen atom was necessary.

Scheme 1



From another standpoint, iminophosphoranes (nitrogen analogues of phosphorus ylides) are seldom used as ligands, probably because the P=N bond is usually reactive toward many media. Indeed, it is well known in organic chemistry that iminophosphoranes are readily transformed into amines upon hydrolysis. However, few examples of the utilization of chiral bidentate bis-iminophosphorane complexes in catalysis have been reported by the groups of Réau and Reetz in the late 1990s.[5,6] These groups have thus shown that the imi-

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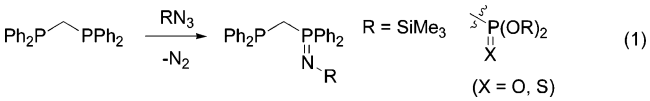
nophosphorane moiety, once coordinated, could withstand conditions that decompose the free ligand. Because of the intrinsic electronic differences between iminophosphorane, imine, and oxazoline, we felt that it was worthwile developing the synthesis of new mixed bidentate P∼N ligands incorporating an iminophosphorane moiety. Only a handful of examples have been reported of such ligands,[7−9] whose coordination chemistry has been investigated.[10,11] These groups used some of the complexes in catalysis.[9,12]

Another important goal of our study was to develop an easy, straightforward synthesis using any available starting diphosphine (commercially or not) that could be amenable to larger scale if needed and allowing for the preparation of optically pure derivatives. In this article, we selected the diphosphine dppm (1,2-bis-diphenylphosphinomethane) as starting material and present our results on the synthesis of such P∼N bidentate ligands and their coordinating behavior toward group 10 metal centers (Ni(II), Pd(II), Pt(II)).

Results and Discussion

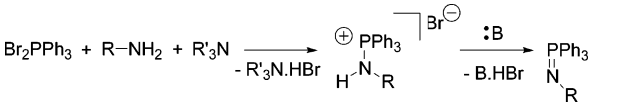
Three methods can be used, a priori, for the synthesis of the iminophosphorane (which can also be called phosphinimine) moiety of the mixed P∼N ligands we set out to develop. The first one is the Staudinger reaction,[13,14] which relies on the addition of an azide to a phosphine (eq 1). This method has been used with great success by Cavell et al. (R = $SiMe_3$)[7,11,15] and more recently by Gimeno et al. (R = $P(X)(OR)_2$).[9] Indeed, with 1 equiv of azide, the mixed ligands are obtained in high yields. The significant drawback of this method is the use of azides, which are usually difficult to prepare or hazardous, and in fact the two above-mentioned groups use commercially available azides.



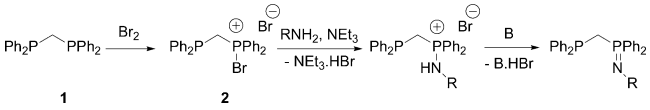
(1)

The second method relies on the reactivity of phosphines with DEAD (DEAD = diethylazodicarboxylate)

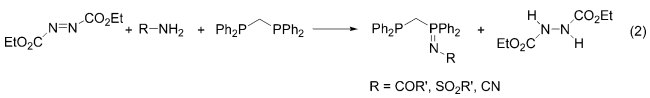
Scheme 2



Scheme 3



followed by trapping with activated RNH_2, such as amides, cyanides, or sulfonamides (eq 2).[16]

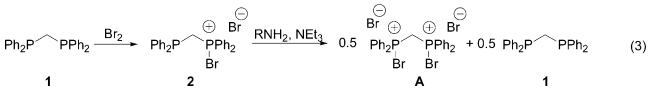


(2)

This second method suffers from the low yields obtained for the mono-iminophosphorane derivatives and is limited to very peculiar activated amine derivatives.

The third method toward iminophosphoranes was developed by Kirsanov et al. in 1950.[14,17] It relies on the bromination of a phosphine followed by trapping with primary amines in the presence of an amine to trap released HBr (Scheme 2). The intermediate salt can be isolated and subsequently treated with a base to yield the desired iminophosphorane. The enormous advantage of this method is the potential use of any commercially available amine and, in particular, optically pure ones. Its major drawback is the use of toxic bromine. This quite powerful method has been used recently to synthesize bidentate N∼N chiral ligands,[5] which were subsequently tested in asymmetric catalysis.[6] However, prior to our work, the Kirsanov approach had not been used to obtain mixed P∼N ligands. The overall strategy is presented in Scheme 3.

The clean formation of the monobromo adduct of dppm is essential for the success of the overall synthesis as a mixture of compounds would not be separable or purified. The first experiments were indeed very encouraging, as the addition of 1 equiv of bromine to a cooled solution (−78 °C) of dppm in methylene chloride followed by warming to room temperature yielded a yellow solution whose ^{31}P NMR spectrum consisted of two sets of doublets at −22.8 ppm ($^2J_{PP}$ = 84.0 Hz) and +58.5 ppm. These signals are consistent with PPh_2 and "PPh_2Br_2" moieties, respectively. Then, following the initial procedures, the solution was cooled to −78 °C, and both *p*-methoxybenzylamine and triethylamine were added in a first attempt. The bath was then removed and the mixture warmed back to room temperature. After 15 min a ^{31}P NMR spectrum was recorded that showed the clean dismutation of the intermediate **2** into starting dppm, **1** (singlet at −23 ppm), and the bis-bromo adduct **A** (singlet at + 48 ppm) (eq 3).



(3)

This very deceiving and puzzling result prompted us to explore several other approaches. First, as P−Cl derivatives are usually less reactive than their P−Br

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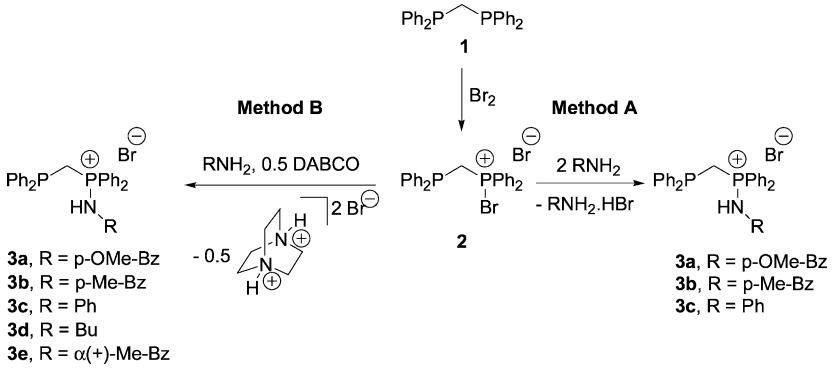
Scheme 4



analogues, the synthesis of the compound resulting from the monoaddition of "Cl_2" was attempted. However, using the usual chlorinating agents such as PCl_5, CCl_4, or C_2Cl_6 in CH_2Cl_2,[18] several products resulting from partial (or total) P−C bond cleavage in dppm were observed (as evidenced by the formation of Ph_2PCl at 82 ppm by ^{31}P NMR). Being stuck working with the monobromo adduct **2**, variation of the tertiary amine was attempted. In fact, a clue to the understanding of the mechanism of the reaction was brought by the reaction of the intermediate **2** with NEt_3 alone. Again the dismutation reaction was observed, which clearly indicated that the amine can serve as bromine transfer agent. Two reactions were therefore in competition: dismutation and nucleophilic substitution. To favor the nucleophilic substitution, conditions that limited to a minimum the presence of "bromine transfer agent" in solution were required, namely, precipitating the amine·HBr salt. Several amines whose ammonium salts could be insoluble were then tested without success: pyridine, (2,2′)-bipy, triphenylamine, (*N*,*N*)-dimethylbenzylamine, etc. We then envisioned the use of 2 equiv of primary amine: one as nucleophile and the second as proton trap. This method proved very successful in several cases (for which the ammonium salts fell rapidly from the solution mixture) and led to the isolation of the desired phosphino-phosphiniminium salt in good yields (72−90%) (method A, Scheme 4). The same dismutation reaction occurred when the ammonium salt did not precipitate, in particular when using the chiral α-(+)-methylbenzylamine. A convenient, reliable method was eventually devised (method B, Scheme 4), using 0.5 equiv of DABCO (DABCO = diazabicyclooctane), whose bis-HBr salt does precipitate from CH_2Cl_2. This allowed us to prepare the above mentioned derivatives **3a**−**c** in slightly lower yields than with method A, and the new derivatives **3d**−**e**.

This second method, B, seems therefore general and, more importantly, allowed for the preparation of the optically pure derivative **3e** in one pot from commercially available dppm. These five new derivatives

Table 1. ^{31}P NMR and ^{1}H NMR Data for Compounds 3 and 4

	^{31}P NMR			^{1}H NMR (bridging CH_2)	
compound	$\delta_{P(III)}$ in ppm	$^2J_{PP}$ in Hz	$\delta_{P(V)}$ in ppm	δ in ppm	$^2J_{H-P(V)}$ in Hz
3a	−30.7	73	41.5	3.96	14.0
3b	−30.4	73	41.8	3.92	15.6
3c	−30.8	73	34.5	4.21	16.5
3d	−30.6	73	40.7	4.08	16.4
3e	−30.1	71	39.7	4.06	63.5[a]
4a	−28.9	51	4.8	3.25	12.4
4b	−29.1	51	5.2	3.30	12.0
4c	−27.2	52	0.4	3.08	12.2
4d	−28.4	56	0.5	3.02	broad
4e	−28.7	49	0.8	3.12	66.4[a]

[a] $\sum J_{H-P(V)}$.

are all air and water stable, crystalline salts that can be stored indefinitely. They have been fully characterized by classical NMR techniques and elemental analyses. In ^{31}P NMR, they are characterized by two sets of doublets at about −30 ppm ($^2J_{PP} \approx 70$ Hz) for the PPh_2 moiety and at about +40 ppm for the iminophosphonium moiety (Table 1). In the ^{1}H NMR, the signal for the bridging methylene is observed at about 4.0 ppm as a surprising doublet only for **3b** and **3c** instead of the expected doublet of doublets (coupling with two different phosphorus atoms) (Table 1). HETCOR $^{1}H-^{31}P$ experiments were carried out and revealed that in these two cases the bridging methylene hydrogens do not couple with the PPh_2 moiety but with the PPh_2═NR moiety. In the case of **3e** the signal of the diastereotopic methylenic protons appears as expected as a complex ABXY spin system. In the ^{13}C NMR the signal of the bridging carbon atom for all compounds **3** is observed as a doublet of doublets with a large ($^1J_{CP} \approx 66$ Hz) and a smaller ($^1J_{CP} \approx 34$ Hz) coupling constant, because of the coupling with two inequivalent P atoms.

These salts could then be deprotonated in quantitative yield with 1 equiv of *n*BuLi in THF at low temperature to give the expected phosphine−iminophosphorane ligands **4a**−**e** (eq 4). The isolated yields of the ligands, after extraction in toluene and filtration of the LiBr salts, are very good (80 to 85%). As expected, and consistent with the known chemical behavior of iminophosphoranes, the ligands **4** are very sensitive. In particular, they react with ketones, aldehydes, protic

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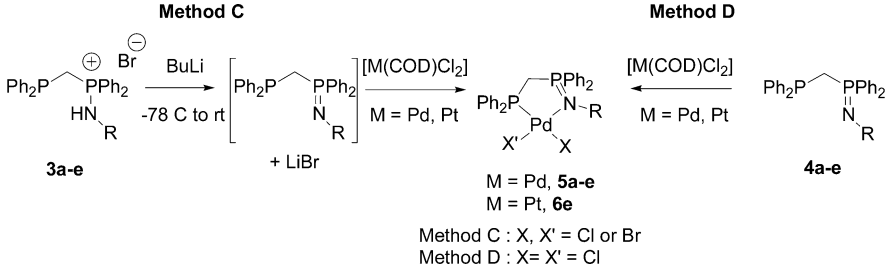
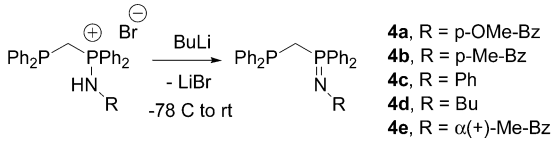
Scheme 5



solvents, and even traces of acid in chlorinated solvents. Thus, in practice they were manipulated in THF or toluene.



(4)

These compounds are characterized by two sets of doublets at about −29 ppm ($^2J_{PP} \approx 50$ Hz) and about 0 ppm in the ^{31}P NMR. As observed in Table 1, there is only a minor change in the chemical shift of the PPh_2 moiety, whereas there is a significant upfield shift going from the salt to the neutral iminophosphorane moiety ($\Delta\delta \approx -40$ ppm). A decrease in the magnitude of the coupling constant is also observed (from about 73 Hz in **3** to about 51 Hz in **4**). In the ^{1}H NMR (see Table 1), the most significant modification is found for the bridging methylene group, whose signal is upfield shifted (from about 4.0 ppm in **3** to about 3.1 ppm in **4**). This seems natural, as the positive charge at phosphorus decreases going from **3** to **4**. As in the case of **3e**, the two protons in **4e** are diastereotopic and thus give rise to a complex signal that is consistent with a classical phosphorus coupled AB spin system pattern.

Having in hands five salts each representing a class of substituents at the nitrogen—aromatic, alkyl, benzyl (chiral or not)—we then studied their coordinating behavior toward group 10 metal centers. Two approaches were utilized. The first one, method C, starts from the salt that is deprotonated in situ, then reacted with the appropriate precursor. This method presents both advantages of using water- and air-stable salt **3** and minimizes the loss of product via extraction of the ligand (**4**) as explained above. The palladium complexes **5** starting with ligand **3** were thus synthesized as well as a representative platinum complex **6e** starting from **3e** (Scheme 5).

Following the progress of the reaction by ^{31}P NMR spectroscopy revealed that several sets of doublets corresponding to different complexes were formed. However these products were very similar in terms of chemical shifts and therefore electronic environments. Clearly, this pointed toward statistical methatetical reactions of LiBr salts with Pd−Cl or Pt−Cl bonds. In some instances the four potential isomers were observed in the ^{31}P NMR spectrum. However, ^{1}H NMR spectra of the crude mixture revealed every time the formation of a "single" product. In practice then, replacement of Cl by Br on the metal center does not influence the electronic environment of the various protons of the bidentate ligand. To check on this hypothesis, method D, starting from the isolated ligands **4a**−**e** freed from LiBr, was tested. As expected, only two sets of doublets were observed in the crude ^{31}P NMR spectrum, corresponding to the major species obtained by method C. The complexes were then characterized by the usual NMR techniques and elemental analyses. In the ^{31}P NMR, a significant downfield shift ($\Delta\delta \approx 50$ ppm) for each phosphorus center was observed showing the coordination of both PPh_2 and N−R moieties to the palladium center of **5a**−**e** (Table 2). Typically, unbound PPh_2 resonates at about −30 ppm in **3** or **4** and at +23 ppm in **5**, and unbound PPh_2═NR resonates at around 0 ppm in **4** and +49 ppm in **5**. For platinum complex **6e**, coupling of the two phosphorus atoms with the ^{195}Pt nucleus was observed as expected. The magnitude of $^1J_{Pt-P}$ of 3845 Hz corresponds to a rather high s character for the P(III) phosphorus center and is also consistent with a structure in which the two halogens are in "*cis*" position. The $^2J_{Pt-P}$ of 275 Hz between the platinum and the P(V) center also clearly indicated the coordination of the nitrogen atom to the platinum center. Each complex **5** precipitated out from the crude THF solution within 15 min stirring at room temperature and was thus obtained by simple filtration. The platinum complex **6e** was synthesized according to method C, and it also precipitated out from solution within 10 min as pale yellow microcrystals. In this last case only one isomer was observed in the ^{31}P NMR spectrum of the crude mixture. These complexes have been fully characterized by usual NMR techniques and elemental analyses. As a test to their robustness, and therefore potential use in catalysis, all the complexes were dissolved in CH_2Cl_2, and large amounts (over 10 equiv) of alcohol, water, or acetone were added. Importantly, in each case no decomposition occurred, suggesting that coordination efficiently stabilizes the phosphinoiminophosphorane ligands. Crystals were obtained for complexes synthesized by either method: **5c** (method D) and **5e** (method D), and **6e** (method C) by slow diffusion of hexanes in a CH_2Cl_2 solution of the complex. Views of molecular structures of complexes **5c**, **5e**, and **6e** are presented in Figures 1, 2, and 3, respectively. Pertinent bond distances and bond angles are presented below the structures. We also obtained crystals of the complex **5e** synthesized according to method C: **5′e**. In this complex, a 16% exchange of the Cl *trans* to the N

Table 2. ^{31}P NMR Data for Complexes 5 and 6

compound	$\delta_{P(III)}$ in ppm	$^2J_{PP}$ in Hz	$\delta_{P(V)}$ in ppm
5b	21.3	33	49.9
5c	20.1	32	44.9
5d	23.0	34	49.8
5e	17.2	35	42.8
6c	10.7	12	46.0
6e	−5.3	23	46.0

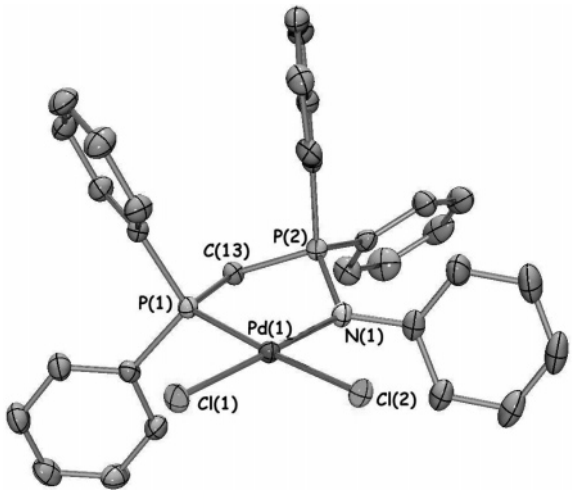


Figure 1. Molecular structure of complex **5c**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg). Pd(1)−N(1) = 2.076(2); Pd(1)−P(1) = 2.2135(6); P(2)−N(1) = 1.619(2); P(1)−C(13) = 1.842(2); P(2)−C(13) = 1.800(2); Pd(1)−Cl(1) = 2.3035(6); Pd(1)−Cl(2) = 2.3668(5); N(1)−Pd(1)−P(1) = 88.90(5); P(1)−Pd-(1)−Cl(1) = 87.25(2); N(1)−Pd(1)−Cl(2) = 92.39(5); Cl(1)−Pd(1)−Cl(2) = 91.67(2); Pd(1)−P(1)−C(1) = 117.25(7); C(13)−P(1)−Pd(1) = 106.03(7); P(1)−C(13)−P(2) = 107.1-(1); N(1)−P(2)−C(13) = 104.2(1).

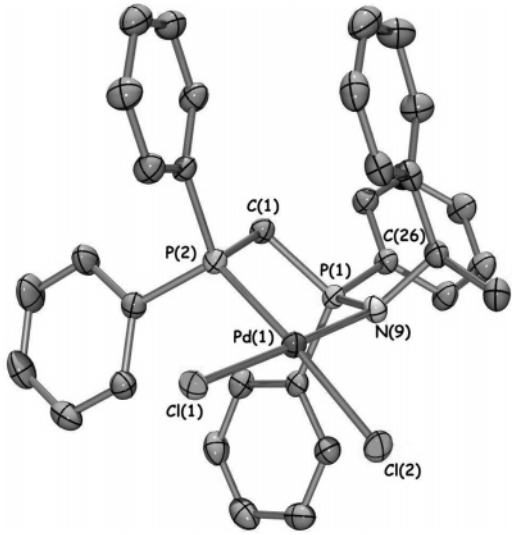


Figure 2. Molecular structure of complex **5e**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pd(1)−N(9) = 2.094(2); Pd(1)−P(2) = 2.2425(6); P(1)−N(9) = 1.601(2); P(1)−C(1) = 1.805(3); P(2)−C(1) = 1.834(2); N(9)−C(26) = 1.499(3); Pd(1)−Cl(1) = 2.3265(6); Pd(1)−Cl(2) = 2.3687(7); N(9)−Pd(1)−P(2) = 89.35(6); N(9)−Pd(1)−Cl(2) = 91.37(6); Cl(1)−Pd(1)−P(2) = 89.04(2); Cl(1)−Pd(1)−Cl(2) = 90.23(2); Pd(1)−N(9)−P(1) = 106.4(1); C(1)−P(2)-Pd(1) = 106.14(8); P(1)−C(1)−P(2) = 104.1(1); N(9)−P(1)−C(1) = 108.6(1).

atom by Br was found by X-ray analysis. This structure is presented in the ESI.

These X-ray structures are in full accord with the structures proposed based on NMR experiments. As expected for a d^8 metal center, the palladium and platinum complexes are square planar. The PN bond distance is normal at about 1.600 Å. Apparent from the structures is the fact that the two PC bond distances

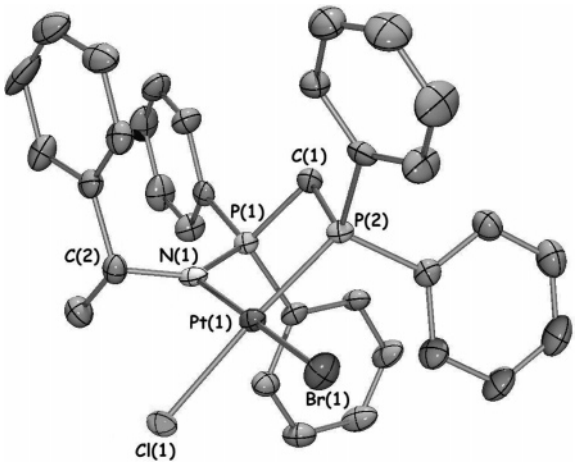


Figure 3. Molecular structure of complex **6e**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pt(1)−N(1) = 2.090(4); Pt(1)−P(2) = 2.203(1); P(1)−N(1) = 1.599(4); P(1)−C(1) = 1.815(5); P(2)−C(1) = 1.842(5); Pt(1)−Cl(1) = 2.364(1); Pt(1)−Br(1) = 2.4400(6); N(1)−Pt(1)−P(2) = 89.9(1); N(1)−Pt(1)−Cl-(1) = 89.8(1); Br(1)−Pt(1)−P(2) = 91.29(4); Cl(1)−Pt(1)−Br(1) = 89.35(4); Pt(1)−N(1)−P(1) = 110.6(2); C(1)−P(2)−Pt(1) = 107.1(2); P(1)−C(1)−P(2) = 104.6(3); N(1)−P(1)−C(1) = 107.8(3).

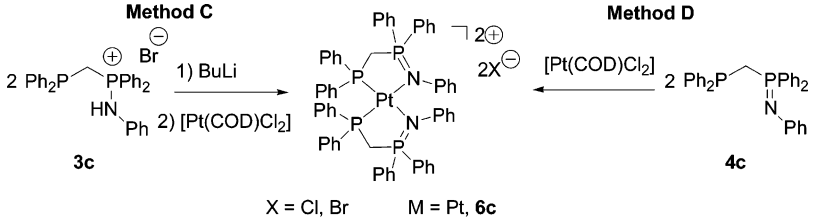
are very different: 1.842 Å (average) for P(III)−C compared to 1.807 Å (average) for P(V)−C. The first one is quite long for a single P−C bond, and usually this bond length is found when very bulky groups (such as *t*Bu) are bound to the phosphorus atom.[19] The Pd−P of 2.228 Å (average) and Pd−N of 2.085 Å (average) are typical values for Pd(II). The same stands for the platinum complexes: Pt−P(III) of 2.203 Å and Pt−N of 2.090 Å. In the case of **5e**, we obtained crystals using the two methods (the X-ray structure of complex **5′e** in which a 16% exchange of the Cl *trans* to the N atom by Br is presented in the ESI), and no significant change in the bond distance for either Pd−P(III) or Pd−N was observed. In the structure of **6e**, in accordance with the ^{31}P NMR spectrum, a single isomer was observed, in which the Cl atom *trans* to the nitrogen atom is replaced by a Br atom. This fact is in full accord with the known *trans* effect and shows that the imino-phosphorane is both a better σ and π donor than the phosphine.

Quite surprisingly, in only one case was the outcome of the reaction different. When the reaction between **3c**/BuLi (method C, Scheme 6) (or **4c**, method D, Scheme 6) and [Pt(COD)Cl_2] was carried out, the expected two sets of doublets, corresponding to a 1:1 ratio of ligand to metal, were quickly replaced by two sets of triplets (with platinum satellites) in the ^{31}P NMR spectrum at +10 ppm ($^1J_{Pt-P}$ = 3433 Hz) and +46 ppm ($^2J_{Pt-P}$ = 198 Hz), respectively. This pointed toward the formation of a complex with a ligand-to-metal ratio of 2:1. This complex rapidly precipitated out from solution and was thus isolated by simple filtration in 45% yield (method D, X = Cl). In a second attempt, the ligand-to-metal ratio of 2:1 was used and conducted to the formation of complex **6c** in 91% yield.

This complex was fully characterized by usual NMR techniques (Table 2) and elemental analysis.

(19) Moores, A.; Ricard, L.; Le Floch, P.; Mézailles, N. *Organometallics* **2003**, *22*, 1960.

Scheme 6



In **6c**, the chemical shift of the PPh_2 moiety was observed at lower field compared to **6e**, and the magnitude of the coupling constant $^2J_{P-P}$ was divided by a factor of 2. The different NMR spectra did not allow for the discrimination between the two isomers (*cis* and *trans*), but fortunately crystals were obtained by slow diffusion of hexanes in a CH_2Cl_2 solution of the complex (method C). X-ray crystal analysis definitely showed the complex to have a *cis* arrangement between the two ligands. The molecular structure is presented below. Significant bond distances and angles are reported below it.

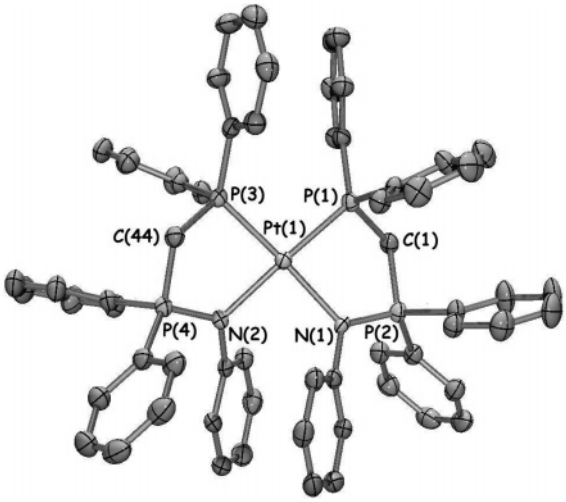
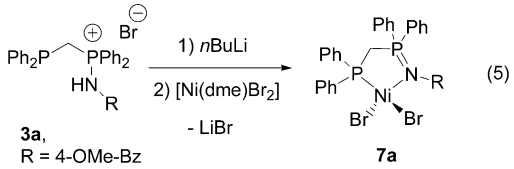


Figure 4. Molecular structure of complex **6c**.Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pt(1)−N(1) = 2.135(2); Pt(1)−N(2) = 2.118(2); Pt(1)−P(1) = 2.2191(7); Pt(1)−P(3) = 2.2251-(8); P(2)−N(1) = 1.614(2); P(4)−N(2) = 1.616(3); P(1)−C(1) = 1.834(3); P(2)−C(1) = 1.808(3); P(3)−C(44) = 1.837(3); P(4)−C(44) = 1.799(3); N(1)−Pt(1)-N(2) = 92.9(1); N(1)−Pt(1)−P(1) = 84.55(7); N(1)−Pt(1)−P(1) = 83.47(7); P(1)−Pt(1)−P(3) = 99.75(3); N(1)−P(2)−C(1) = 103.2(1); N(2)−P(4)−C(44) = 103.1(1); Pt(1)−N(1)−P(2) = 121.5(1); Pt(1)−N(2)−P(4) = 121.8(1); C(1)−P(1)−Pt(1) = 101.8(1); C(44)−P(3)−Pt(1) = 100.9(1); P(1)−C(1)−P(2) = 107.6(3); P(3)−C(44)−P(4) = 107.2(2).

First one can note a very minor inequivalency in the two ligands in the structure that is obviously not retained in solution. The Pt(1)−N(1) and Pt(1)−N(2) bond distances (average = 2.1265 Å) are slightly longer than in complex **6e** (2.090 Å). The same is observed in the Pt(1)−P(2) and Pt(1)−P(3) bond distances (average = 2.2221 Å) compared to 2.203 Å in **6e**. The complex deviates significantly from the expected square planar geometry, as shown by the N(1)−Pt(1)−N(2) (92.9(1)°) and P(1)−Pt(1)−P(3) (99.75(3)°) bond angles. Moreover, the five-membered rings defined by the ligand and the metal are not planar. The bridging carbon atom of the ligand escapes from the plane, as evidenced by the dihedral angles N(2)−Pt(1)−P(3)−C(44) of +38.4° and N(1)−Pt(1)−P(1)−C(1) of −35.0°. This leads to the potential formation of diastereomers in which the two carbon atoms adopt either a *cis* or a *trans* position relative to the plane of the molecule. In the crystal structure, only the *trans* isomer is observed. DFT calculations are being carried out in order to gain information on the relative energies of the several possible isomers.

Finally, the synthesis of a representative nickel complex was attempted according to a similar strategy using the salt **3a** and $[Ni(dme)Br_2]$ as precursor (method C).



After in situ formation of the iminophosphorane−phosphine **4a** by deprotonation of **3a**, the metal salt was added, which resulted in instantaneous color change from colorless to blue. Disappearance of the ^{31}P NMR signals pointed toward a tetrahedral geometry at the

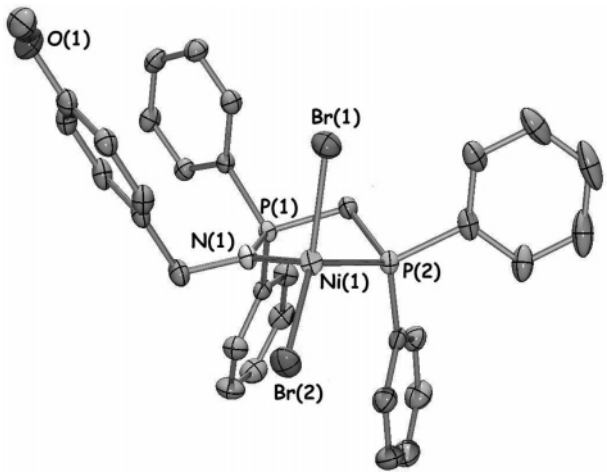


Figure 5. Molecular structure of complex **7a**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ni(1)−N(1) = 1.987(2); Ni(1)−P(2) = 2.3010(7); P(1)−N(1) = 1.596(2); P(1)−C(1) = 1.809(2); P(2)−C(1) = 1.838(3); Ni(1)−Br(1) = 2.3743(5); Ni(1)−Br-(2) = 2.3545(4); N(1)−Ni(1)−P(2) = 88.35(6); N(1)−Ni(1)−Br(1) = 106.44(7); N(1)−Ni(1)−Br(2) = 108.68(6); Br(2)−Ni(1)−P(2) = 123.83(2); Br(1)−Ni(1)−P(2) = 98.21(2); Br(1)−Ni(1)−Br(2) = 124.71(2); Ni(1)−N(1)−P(1) = 121.1-(1); C(1)−P(2)−Ni(1) = 96.70(8); P(1)−C(1)−P(2) = 109.2-(1); N(1)−P(1)−C(1) = 105.5(1).

nickel center (paramagnetic d^8 center). As for the Pd and Pt analogues, the complex precipitated out from solution. It was thus collected by simple filtration, followed by washing first with THF then hexanes. Elemental analysis confirmed the composition of the complex. X-ray quality crystals were obtained by heating a THF suspension of the complex followed by slow cooling. These were subjected to X-ray diffraction analysis. A view of the molecular structure of **7a** is presented in Figure 5 together with significant bond distances and angles.

As expected from the lack of NMR spectra for **7a** the geometry at the nickel center is tetrahedral (bond angles N(1)−Ni(1)−Br of 106.44(7)° and 108.68(6)°). One can note that the Ni(1)−N(1) (1.987 Å) is slightly shorter than the other M−N bond distances (M = Pd or Pt), and the Ni(1)−P(2) is in turn slightly longer than the other M−P. Otherwise, the metric parameters compare with those of the Pd and Pt and do not deserve further comment.

Conclusion

We have developed a simple method for the monobromation of a bisphosphine ligand. From this very reactive intermediate, **2**, two methods were devised to obtain mixed P∼N salts. The first one, method A, gives higher yields and relies on the reaction of the intermediate with 2 equiv of a primary amine. This method is successful only if the ammonium salt precipitates from the solution. If not, a second method, B, can be used that depends on DABCO to trap released HBr. Either one or the other method allowed us to prepare five representative mixed P∼N salts, **3a**−**e**. Starting from these, the corresponding phosphine−iminophosphoranes **4a**−**e** could be synthesized in good isolated yields by simple deprotonation. The versatility of the method allowed for the preparation of P∼NR ligands with R varying from alkyl, aromatic, or benzyl. Moreover, introduction of chirality at R was easily achieved using commercially available α-Me-benzylamine. The coordination of these ligands with group 10 metal centers (M = Ni, Pd, Pt) was then studied and revealed that the complexes are quite robust (unlike the free ligands), which is a prerequisite to their use in catalysis. Alternatively, a one-pot method starting from the water- and air-stable salts, **3**, to the complexes was devised. It was higher yielding, but metathesis between halogen ligands was observed. Altogether we have devised a straightforward, and amenable to large scale, new approach to mixed P∼N bidentate ligands starting from commercially available products. We are currently studying the behavior of our Ni, Pd, and Pt (II) complexes in catalysis, and results will be presented in due course.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethyl ether, hexanes), from Na (toluene), or from P_2O_5 (dichloromethane, $CDCl_3$, NEt_3). Dppm, α-(+)-methylbenzylamine, *p*-methoxybenzylamine, *p*-methylbenzylamine, *n*-butylamine, and aniline were obtained from Aldrich and used without further purification. $[Pd(COD)Cl_2]$,[20] $[Pt(COD)Cl_2]$,[21] and $[Ni(DME)Br_2]$[22] were prepared according to literature procedures. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; v, virtual.

Crystallography. Orange needles of complex **5c** were obtained by slow diffusion of THF into a solution of the complex in dichloromethane at RT. Orange plates of complex **5e** were obtained by slow diffusion of hexanes into a solution of the complex in dichloromethane at RT. Colorless blocks of complex **6c** were obtained by slow diffusion of hexanes into a solution of the complex in dichloromethane at RT. Yellow plates of complex **6e** were obtained by slow diffusion of THF into a solution of the complex in dichloromethane at RT. Blue plates of complex **7a** were obtained by slow diffusion of THF into a solution of the complex in dichloromethane at RT. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Experimental details are described in Tables 1 and 3. The crystal structure was solved using SIR 97 and SHELXL-97. Molecular drawings were made using ORTEP III for Windows, then POV-Ray. CCDC-262280 to -262286 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Preparation of Phosphine−Aminophosphonium Bromide 3a−e. Preparation of $DPPMBr_2$ **2**: Bromine (40 μL, 0.78 mmol) was added dropwise to a solution of dppm (0.30 g, 0.78 mmol) in 20 mL of dichloromethane cooled at −78 °C. The cold bath was removed, and the solution was allowed to warm to room temperature. $^{31}P\{^1H\}$ (CH_2Cl_2): δ −22.8 (d, $^2J_{PP}$ = 84 Hz), 58.5 (d, $^2J_{PP}$ = 84 Hz). This very sensitive derivative was used without further purification.

Method A. The amine (1.48 mmol) was added dropwise to a solution of $dppmBr_2$ (0.78 mmol) in 20 mL of dichloromethane cooled at −78 °C. The resulting mixture became immediatly cloudy, and the cold bath was removed. After 2 h of stirring at room temperature, the solution was washed twice with water, the organic layer was dried over $MgSO_4$, and solvent was removed under vacuum. The residue was washed with diethyl ether, and each derivative **3a**−**c** was obtained as a white solid.

3a: Yield 90% (421 mg). $^{31}P\{^1H\}$ ($CDCl_3$): δ −30.7 (d, $^2J_{PP}$ = 73 Hz, $P^{(III)}$), 41.5 (d, $^2J_{PP}$ = 73 Hz, $P^{(V)}$). ^1H ($CDCl_3$): δ 3.72 (s, 3H, MeO), 3.89 (dd, 2H, $^1J_{HP(V)}$ = 16.3 Hz, $^1J_{HP(III)}$ = 0.7 Hz, PCH_2P), 3.96 (dd, 2H, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 7.2 Hz, CH_2N), 6.68 (d, 2H, $^3J_{HH}$ = 8.7 Hz, m-H (p-MeOPh)), 7.10 (d, 2H, $^3J_{HH}$ = 8.7 Hz, o-H (p-MeOPh)), 7.15−7.31 (m, 10H, $Ph_2P^{(V)}$), 7.43 (vtd, 4H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 3.5 Hz, m-H ($Ph_2P^{(III)}$), 7.61 (vdtt, 2H, $^3J_{HH}$ = 7.5 Hz, $^5J_{HP}$ = 1.8 Hz, p-H ($Ph_2P^{(III)}$), 7.66−7.77 (m, 4H, o-H ($Ph_2P^{(III)}$), 8.10 (dt, 1H, $^3J_{HH}$ = $^2J_{HP}$ = 7.2 Hz, NH). $^{13}C\{^1H\}$ ($CDCl_3$): δ 24.9 (dd, $^1J_{CP}$ = 65.3 Hz, $^1J_{CP}$ = 33.6 Hz, PCH_2P), 45.2 (d, $^2J_{CP}$ = 2.4 Hz, CNH), 55.2 (s, OMe), 113.8 (s, m-CH (p-MeOPh)), 120.2 (d, $^1J_{CP}$ = 98.6 Hz, C^{IV}-$P^{(III)}$), 128.8 (d, $^4J_{CP}$ = 7.9 Hz, p-CH ($Ph_2P^{(V)}$)), 129.3 (d, $^3J_{CP}$ = 12.5 Hz, m-CH ($Ph_2P^{(V)}$)), 129.4 (s, m-CH ($Ph_2P^{(III)}$)), 129.5 (s, o-CH (p-MeOPh)), 129.7 (d, $^1J_{CP}$ = 5.3 Hz, C^{IV} (p-MeOPh)), 132.7 (d, $^2J_{CP}$ = 21.4 Hz, o-CH ($Ph_2P^{(V)}$), 133.3

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(21) McDermott, J. X.; White, J. F.; Whitesides, J. F. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(22) King, R. B. *Organometallic Syntheses Academic* **1965**, Vol. 1, 71.

Table 3. Crystal Data and Structural Refinement Details for 5c and 5e

	5c	5e
formula	$C_{31}H_{27}Cl_2NP_2Pd$	$C_{33}H_{31}Cl_2NP_2Pd$
M_r	652.78	680.83
T [K]	150.0(1)	150.0(1)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a [Å]	11.3600(10)	12.3350(10)
b [Å]	14.8220(10)	13.6480(10)
c [Å]	17.0950(10)	17.6430(10)
α [deg]	90.00	90.00
β [deg]	105.1700(10)	90.00
γ [deg]	90.00	90.00
V [Å^3]	2778.1(3)	2970.2(4)
Z	4	4
ρ [g cm^{-3}]	1.561	1.523
μ [cm^{-1}]	0.998	0.937
cryst size [mm]	0.22 × 0.16 × 0.14	0.20 × 0.16 × 0.05
F(000)	1320	1384
index ranges	−15 15; −19 20; −24 24	−17 17; −19 19; −24 24
scan type	phi and omega scans	phi and omega scans
$2\theta_{max}$ [deg]/criterion	29.99/$I > 2\sigma I$	30.02/$I > 2\sigma I$
no. of params refined; data/param	334; 18	354; 20
reflections collected	14300	8575
no. of indep reflns	8054	8575
no. of reflns used	6288	7398
wR2	0.0939	0.0819
R1	0.0341	0.0337
goodness of fit	1.019	1.008
largest diff peak/hole [e Å^{-3}]	1.096(0.092)/ −1.123(0.092)	0.857(0.087)/ −0.923(0.087)

Table 4. Crystal Data and Structural Refinement Details for 6c, 6e, and 7a

	6c	6e[a]	7a
formula	$C_{62}H_{54}N_2P_4Pt$,2.5 (CH_2Cl_2), (Br), (Cl)	$C_{33}H_{31}BrClNP_2Pt$,C_4H_8O, CH_2Cl_2	$C_{33}H_{31}Br_2NNiOP_2$, C_4H_8O
M_r	1473.72	971.01	810.16
T [K]	150.0(1)	150.0(1)	150.0(1)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/c$
a [Å]	12.4100(10)	8.5010(10)	19.9970(10)
b [Å]	12.6440(10)	16.3370(10)	9.7900(10)
c [Å]	21.6810(10)	13.5450(10)	17.6700(10)
α [deg]	75.6000(10)	90.00	90.00
β [deg]	75.8500(10)	94.0500(10)	95.4000(10)
γ [deg]	81.0400(10)	90.00	90.00
V[Å^3]	3178.8(4)	1876.4(3)	3443.9(4)
Z	2	2	4
ρ [g cm^{-3}]	1.540	1.719	1.563
μ [cm^{-1}]	3.229	5.134	3.011
cryst size [mm]	0.20 × 0.20 × 0.20	0.20 × 0.18 × 0.05	0.22 × 0.18 × 0.03
F(000)	1470	956	1648
index ranges	−17 12; −17 17; −30 29	−11 11; −22 20; −19 19	−25 25; −10 12; −22 22
scan type	phi and omega scans	phi and omega scans	phi and omega scans
$2\theta_{max}$ [deg]/criterion	30.03/$I > 2\sigma I$	30.02/$I > 2\sigma I$	27.47/$I > 2\sigma I$
no. of params refined; data/param	722; 21	400; 22	407; 14
no. of reflns collected	25 128	10 110	14 102
no. of indep reflns	18 447	10 110	7871
no. of reflns used	15 385	9116	5916
wR2	0.1012	0.1001	0.0903
R1	0.0379	0.0390	0.0350
goodness of fit	1.058	1.005	1.039
largest diff peak/hole [e Å^{-3}]	1.985(0.118)/ −1.871(0.118)	1.405(0.157)/ −2.506(0.157)	0.907(0.079)/ −0.669(0.079)

[a] Note for structure **6e**, a highly disordered half CH_2Cl_2 molecule was accounted for using the Platon SQUEEZE function.

(dd, $^2J_{CP}$ = 10.6 Hz, $^4J_{CP}$ = 3.1 Hz, o-CH ($Ph_2P^{(III)}$)), 134.4 (d, $^4J_{CP}$ = 2.9 Hz, p-CH ($Ph_2P^{(III)}$)), 135.1 (dd, $^1J_{CP}$ = 12.1 Hz, $^3J_{CP}$ = 8.7 Hz, C^{IV}-$P^{(V)}$), 158.9 (s, C^{IV}−OMe). Anal. Calcd for $C_{33}H_{32}BrNOP_2$: C, 66.01; H, 5.37. Found: C, 65.89; H, 5.62.

3b: Yield 86% (390 mg). $^{31}P\{^1H\}$ ($CDCl_3$): δ −30.4 (d, $^2J_{PP}$ = 73 Hz, $P^{(III)}$), 41.8 (d, $^2J_{PP}$ = 73 Hz, $P^{(V)}$). ^1H ($CDCl_3$): δ 2.24 (s, 3H, CH_3), 3.92 (d, A_2XY, 2H, $^2J_{P(V)H}$ = 15.6 Hz, $^3J_{P(III)H}$ = 0 Hz, PCH_2P), 3.97 (dd, A_2MX, 2H, $^3J_{HH}$ = 7.1 Hz, $^3J_{P(V)H}$ = 13.7 Hz, CH_2NH), 6.96 (d, 2H, $^3J_{HH}$ = 7.9 Hz, m-H (p-Me-Ph)), 7.07 (d, 2H, $^3J_{HH}$ = 7.9 Hz, o-H (p-Me-Ph)), 7.15−7.81 (m, 20H, Ph_2-P), 8.08 (dd, 1H, $^3J_{HH}$ = 7.1 Hz, $^2J_{P(V)H}$ = 15.6 Hz, NH). $^{13}C\{^1H\}$ ($CDCl_3$): δ 21.0 (s, CH_3), 24.8 (dd, AXY, $^1J_{CP}$ = 66.5 Hz, $^1J_{CP}$ = 31.5 Hz, PCH_2P), 45.4 (s, CNH), 120.3 (d, $^1J_{CP}$ = 98.6 Hz, C^{IV}-$P^{(III)}$), 128.0 (s, o-CH (p-Me-Ph)), 128.8 (d, J_{CP} = 7.9 Hz, CH, Ph_2P), 129.1 (s, m-CH (p-Me-Ph)), 129.3 (d, J_{CP} = 13 Hz, CH, Ph_2P), 129.5 (s, CH, Ph_2P), 130.9 (dd, J_{CP} = 9.6 Hz, J_{CP} = 1.5 Hz, CH, Ph_2P), 132.7 (d, J_{CP} = 21.4 Hz, CH, Ph_2P), 133.3 (dd, J_{CP} = 10.6 Hz, J_{CP} = 1.0 Hz, CH, Ph_2P), 134.4 (d, $^3J_{CP}$ = 2.9 Hz, C^{IV} (p-Me-Ph)), 135.1 (dd, $^1J_{CP}$ = 11.4 Hz, $^3J_{CP}$ = 8.9 Hz, C^{IV}-$P^{(V)}$), 137.2 (s, C^{IV}-CH_3). Anal. Calcd for $C_{33}H_{32}BrNP_2$: C, 67.81; H, 5.52. Found: C, 67.49; H, 5.59.

3c: Yield 92% (m). $^{31}P\{^1H\}$ (CD_2Cl_2): δ −30.8 (d, $^2J_{PP}$ = 73 Hz, $P^{(III)}$), 34.5 (d, $^2J_{PP}$ = 73 Hz, $P^{(V)}$). ^1H (CD_2Cl_2): δ 4.21 (d, $^2J_{HP}$ = 16.5 Hz, 2H, PCH_2P), 6.87−7.46 (m, 19H, Ph), 7.48−7.60 (m, 2H, Ph), 7.69−7.86 (m, 4H, Ph). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 25.7 (dd, $^1J_{CP}$ = 66 Hz, $^1J_{CP}$ = 34 Hz, PCH_2P), 119.4 (s, C^{IV}-$P^{(III)}$), 120.1, 123.2, 128.7 (d, J_{CP} = 8 Hz), 128.9, 129.4, 129.5 (d, J_{CP} = 9 Hz), 132.7 (d, J_{CP} = 21 Hz), 133.1 (dd, J_{CP} = 4 Hz, J_{CP} = 11 Hz), 134.6 (d, J_{CP} = 3 Hz), 134.9 (m, C^{IV}-$P^{(V)}$), 138.2

(d, $^2J_{CP}$ = 3 Hz, C_{ipso} of PhNH). Anal. Calcd for $C_{31}H_{28}BrNP_2$: C, 66.92; H, 5.07. Found: C, 66.52; H, 5.22.

Method B. A solution of DABCO (43 mg, 0.39 mmol) and the amine (0.78 mmol) in 5 mL of dichloromethane was added via a cannula to the solution of $DPPMBr_2$ **2** (0.78 mmol) cooled at −78 °C. The resulting mixture became immediatly cloudy, and the cold bath was removed. After 2 h of stirring at room temperature, the solution was washed twice with water, the organic layer was dried over $MgSO_4$, and solvent was removed under vacuum. The residue was washed with diethyl ether, and each derivative **3d**−**e** was obtained as a white solid.

3d: Yield 55% (256 mg). $^{31}P\{^1H\}$ ($CDCl_3$): δ −30.6 (d, $^2J_{PP}$ = 73 Hz, $P^{(III)}$), 40.7 (d, $^2J_{PP}$ = 73 Hz, $P^{(V)}$). ^1H ($CDCl_3$): δ 0.73 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3 of *n*Bu), 1.19 (vsext, Σ*J* = 36.8 Hz, 2H, C*H*$_2$−CH_3 of *n*Bu), 1.54 (vq, Σ*J* = 29.8 Hz, 2H, C*H*$_2$-CH_2-CH_3 of *n*Bu), 2.71 (vq, Σ*J* = 30.5 Hz, 2H, C*H*$_2$-NH), 4.08 (d, $^2J_{HP}$ = 16.4, 2H, PCH_2P), 7.16−7.88 (m, 20H, Ph_2P). $^{13}C\{^1H\}$ ($CDCl_3$): δ 13.5 (s, CH_3), 19.8 (s, *C*H_2-CH_3), 24.1 (dd, $^1J_{CP}$ = 66 Hz, $^1J_{CP}$ = 33 Hz, PCH_2P), 32.8 (d, $^4J_{CP}$ = 8 Hz, *C*H_2-CH_2-CH_3), 42.0 (d, $^3J_{CP}$ = 3 Hz, *C*H_2NH), 120.3 (d, $^1J_{CP}$ = 98 Hz, C^{IV}-$P^{(III)}$), 128.7 (d, $^4J_{CP}$ = 8 Hz, p-CH ($Ph_2P^{(V)}$), 129.4 (d, $^3J_{CP}$ = 13 Hz, m-CH ($Ph_2P^{(V)}$), 130.9 (dd, $^3J_{CP}$ = 9 Hz, $^5J_{CP}$ = 2 Hz, m-CH ($Ph_2P^{(III)}$), 132.8 (d, $^2J_{CP}$ = 21 Hz, o-CH ($Ph_2P^{(V)}$), 133.2 (dd, $^2J_{CP}$ = 10 Hz, $^4J_{CP}$ = 3 Hz, o-CH ($Ph_2P^{(III)}$), 134.4 (d, $^4J_{CP}$ = 3 Hz, p-CH ($Ph_2P^{(III)}$), 135.1 (dd, $^1J_{CP}$ = 12 Hz, $^3J_{CP}$ = 9 Hz, C^{IV}-$P^{(V)}$). Anal. Calcd for $C_{29}H_{32}BrNP_2$: C, 64.93; H, 6.01. Found: C, 64.41; H, 6.06.

3e: Yield 65% (296 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ −30.1 (d, $^2J_{PP}$ = 71 Hz), 39.7 (d, $^2J_{PP}$ = 71 Hz). ^1H (CD_2Cl_2): δ 1.55 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 4.06 (ABXY, 2H, Σ*J* = 63.5 Hz, PCH_2P), 4.05 (vt, 1H, CHN), 7.09−7.56 (m, 23H), 7.75−7.88 (m, 2H), 8.21 (vt, 1H, $^3J_{HH}$ = $^3J_{HP}$ = 9.1 Hz, NH). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 24.5 (dd, $^1J_{CP}$ = 66 Hz, $^1J_{CP}$ = 34 Hz, PCH_2P), 25.7 (d, $^3J_{CP}$ = 8 Hz, CH_3), 54.7 (s, CNH), 120.5 (dd, $^3J_{CP}$ = 55 Hz, $^1J_{CP}$ = 97 Hz, C^{IV}-$P^{(III)}$), 126.7 (s, o-CH (PhCHN)), 127.5 and 128.7 (s, m-CH, p-CH (PhCHN)), 128.9 and 129.0 (d, J_{CP} = 8 Hz), 129.3 (d, J_{CP} =13 Hz), 129.7, 132.0 (d, J_{CP} = 21 Hz), 133.5 and 133.6 (d, J_{CP} = 3 Hz), 134.5 and 134.8 (d, J_{CP} = 3 Hz), 135.8 (dd, $^1J_{CP}$ = 9 Hz, $^3J_{CP}$ = 6 Hz, C^{IV}-$P^{(V)}$), 144.0 (d, $^3J_{CP}$ = 3 Hz, C_i (PhCHN)). Anal. Calcd for $C_{33}H_{32}BrNP_2$: C, 67.81; H, 5.52. Found: C, 67.63; H, 5.66.

General Procedure for the Preparation of Iminophosphoranes 4a−e. *n*-Butyllithium (1 equiv) was added dropwise to a solution of aminophosphonium bromide **3a**−**e** (100 mg, 1 equiv) in 5 mL of THF cooled at −78 °C. After 5 min, the cold bath was removed and the solution was allowed to warm to RT. The solvent was removed under vacuum and the residue dissolved in toluene. The resulting cloudy solution was filtered and the solvent removed under vacuum.

4a: Yield 96% (166 mg). $^{31}P\{^1H\}$ (THF-d_8): δ −28.9 (d, $^2J_{PP}$ = 51 Hz, $P^{(III)}$), 4.8 Hz (d, $^2J_{PP}$ = 51 Hz, $P^{(V)}$). ^1H (THF-d_8): δ 3.25 (d, 2H, $^2J_{HP}$ = 12.4 Hz, PCH_2P), 3.71 (s, 3H, MeO), 4.13 (d, 2H, $^3J_{HP}$ = 16.6 Hz, CH_2Ph), 6.73 (d, 2H, $^3J_{HH}$ = 8.7 Hz, m-H (p-MeOPh)), 7.04−7.51 (m, 16H, PPh_2), 7.26 (d, 2H, $^3J_{HH}$ = 8.7 Hz, o-H (p-MeOPh)), 7.69−7.80 (m, 4H). $^{13}C\{^1H\}$ (THF-d_8): δ 30.8 (dd, $^1J_{CP}$ = 66 Hz, $^1J_{CP}$ = 32 Hz, PCH_2P), 48.8 (s, CNH), 55.4 (s, OMe), 113.6 (s, m-CH (p-MeOPh)), 126.0 (s, C^{IV}-$P^{(III)}$), 128.9 (d, $^4J_{CP}$ = 5 Hz, p-CH ($Ph_2P^{(V)}$)), 129.0 (s, m-CH ($Ph_2P^{(V)}$)), 129.7 (s, m-CH ($Ph_2P^{(III)}$)), 131.5 (d, $^4J_{CP}$ = 3 Hz, o-CH (p-MeOPh)), 132.7 (dd, $^2J_{CP}$ = 11 Hz, $^4J_{CP}$ = 3 Hz, o-CH ($Ph_2P^{(III)}$)), 133.9 (d, $^2J_{CP}$ = 21 Hz, o-CH ($Ph_2P^{(V)}$)), 139.5 (d, J_{CP} = 22 Hz, C^{IV}), 140.7 (dd, $^1J_{CP}$ = 16 Hz, $^3J_{CP}$ = 7 Hz, C^{IV}-$P^{(V)}$), 158.7 (s, C^{IV}-OMe). Anal. Calcd for $C_{33}H_{31}NOP_2$: C, 76.29; H, 6.01. Found: C, 75.87; H, 6.24.

4b: Yield 92% (159 mg). $^{31}P\{^1H\}$ (THF-d_8): δ −29.1 (d, $^2J_{PP}$ = 51 Hz, $P^{(III)}$), 5.2 (d, $^2J_{PP}$ = 51 Hz, $P^{(V)}$). ^1H (THF-d_8): δ 2.27 (s, 3H, Me), 3.30 (d, 2H, $^2J_{HP}$ = 12 Hz, PCH_2P), 4.11 (d, 2H, $^3J_{HP}$ = 16 Hz, CH_2N), 6.97 (d, 2H, $^3J_{HH}$ = 7.9 Hz, m-H (p-Me-Ph)), 7.26 (d, 2H, $^3J_{HH}$ = 7.9 Hz, o-H (p-Me-Ph)), 7.15−7.52 (m, 20H, Ph_2P). $^{13}C\{^1H\}$ (THF-d_8): δ 21.3 (s, Me), 30.6 (dd, $^1J_{CP}$ = 65 Hz, $^1J_{CP}$ = 33 Hz, PCH_2P), 49.0 (s, CH_2N), 127.7 (s, o-CH (p-Me-Ph)), 128.8 (s, m-CH (p-Me-Ph)), 129.0, 131.5 (d, J_{CP} = 3 Hz), 132.7 (dd, J_{CP} = 10 Hz, J_{CP} = 9 Hz), 133.5, 133.9 (d, J_{CP} = 20 Hz), 134.1 (d, J_{CP} = 21 Hz), 134.5 (s, C^{IV}-$P^{(V)}$), 134.6 (s, C^{IV}-CH_3), 140.6 (dd, $^3J_{CP}$ = 7 Hz, $^1J_{CP}$ = 16 Hz, C^{IV}-$P^{(III)}$), 144.5 (d, $^3J_{CP}$ = 23 Hz, C^{IV} (p-MePh)). Anal. Calcd for $C_{33}H_{31}NP_2$: C, 78.71; H, 6.21. Found: C, 78.39; H, 5.98.

4c: Yield 97% (166 mg). $^{31}P\{^1H\}$ (C_6D_6): δ −27.2 (d, $^2J_{PP}$ = 52 Hz, $P^{(III)}$), 0.4 (d, $^2J_{PP}$ = 52 Hz, $P^{(V)}$). ^1H (C_6D_6): δ 3.08 (d, 2H, $^2J_{HP}$ = 12.2 Hz, PCH_2P), 6.73−6.82 (m, 1H), 6.90−7.14 (m, 16H), 7.33−7.43 (m, 4H), 7.66−7.77 (m, 4H). $^{13}C\{^1H\}$ (C_6D_6): δ 31.2 (dd, $^1J_{CP}$ = 34 Hz, $^1J_{CP}$ = 74 Hz), 117.9, 124.1 (d, J_{CP} = 19 Hz), 128.7, 128.9 (d, J_{CP} = 6 Hz), 129.0, 129.1, 129.4 (d, J_{CP} = 2 Hz), 131.7 (d, J_{CP} = 3 Hz), 132.6 (dd, J_{CP} = 9 Hz, J_{CP} = 2 Hz, C^{IV}-$P^{(III)}$), 133.7 (d, J_{CP} = 20 Hz), 139.8 (dd, J_{CP} = 16 Hz, J_{CP} = 7 Hz, C^{IV}-$P^{(V)}$), 152.5 (d, J_{CP} = 3 Hz, C_{ipso} of aniline). Anal. Calcd for $C_{31}H_{27}NP_2$: C, 78.30; H, 5.72. Found: C, 78.07; H, 5.71.

4d: Yield 85% (144 mg). $^{31}P\{^1H\}$ (C_6D_6): δ −28.4 (d, $^2J_{PP}$ = 56 Hz, $P^{(III)}$), 0.5 (d, $^2J_{PP}$ = 56 Hz, $P^{(V)}$). ^1H (C_6D_6): δ 0.79 (t, 3H, $^3J_{HH}$ = 7.4 Hz, C*H*$_3$ of *n*Bu), 1.33 (m, 2H, C*H*$_2$-CH_3 of *n*Bu), 1.77 (m, 2H, C*H*$_2$-CH_2-CH_3 of *n*Bu), 3.02 (b, 2H, C*H*$_2$-N), 3.94 (b, 2H, PCH_2P), 6.88−7.13 (m, 12H), 7.57−7.77 (m, 8H). $^{13}C\{^1H\}$ (C_6D_6): δ 14.2 (s, CH_3 of *n*Bu), 20.7 (s, *C*H_2-CH_3 of *n*Bu), 27.1 (b, PCH_2P), 36.1 (s, *C*H_2-CH_2-CH_3 of *n*Bu), 44.5 (s, *C*H_2-NH), 128.6, 128.7, 129.0, 132.2, 133.2 (d, J_{CP} = 9 Hz) 133.8 (d, J_{CP} = 21 Hz), 137.6 (dd, $^1J_{CP}$ = 12 Hz, $^3J_{CP}$ = 7 Hz, C^{IV}-$P^{(V)}$). Anal. Calcd for $C_{29}H_{31}NP_2$: C, 76.47; H, 6.86. Found: C, 77.15; H, 6.94.

4e: Yield 78% (134 mg). $^{31}P\{^1H\}$ (THF-d_8): δ −28.7 (d, $^2J_{PP}$ = 50 Hz, $P^{(III)}$), 0.8 (d, $^2J_{PP}$ = 50 Hz, $P^{(V)}$). ^1H (THF-d_8): δ 1.24 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH_3), 3.12 (ABXY, 2H, $^2J_{HH}$ = 14.5 Hz, Σ*J* = 66.4 Hz, PCH_2P), 4.33 (dq, 1H, $^3J_{HH}$ = 6.5 Hz, $^3J_{HP(V)}$ = 20.1 Hz, CHN), 6.97−7.55 (m, 21H, Ph), 7.57−7.2 (m, 4H, Ph). $^{13}C\{^1H\}$ (THF-d_8): δ 30.8 (s, CH_3), 31.1 (dd, $^1J_{CP}$ = 32 Hz, $^1J_{CP}$ = 69 Hz, PCH_2P), 55.6 (d, $^2J_{CP}$ = 3 Hz, CHN), 125.8, 127.2, 128.1, 128.7, 128.9, 129.6, 131.3, 132.7 (d, J_{CP} = 9 Hz), 133.7 (d, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 21 Hz), 135.2 (d, $^1J_{CP}$ = 90 Hz, C^{IV}-$P^{(V)}$), 135.3 (d, $^1J_{CP}$ = 90 Hz, C'^{IV}-$P^{(V)}$), 140.8 (vdd, ΣJ_{CP} = 25 Hz, C^{IV}-$P^{(III)}$), 152.8 (d, $^3J_{CP}$ = 12 Hz, C^{IV} (Ph)). Anal. Calcd for $C_{33}H_{31}NP_2$: C, 78.71; H, 6.21. Found: C, 79.09; H, 6.28.

General Procedure for the Preparation of Palladium and Platinum Complexes 5a−e. Method C. To a solution of **3a**−**e** (100 mg, 1 equiv) in 5 mL of THF cooled at −78 °C was added dropwise *n*-butyllithium (1 equiv). The cold bath was removed, and the solution allowed to warm back to room temperature. $[Pd(COD)Cl_2]$ (1 equiv) was added, and the solution turned immediately from colorless to orange. After 10 min of stirring, the product precipitated as an orange solid. The latter was isolated by filtration, washed with THF then hexanes, and dried under vacuum.

Method D. To a solution of freshly prepared **4a**−**e** (0.171 mmol) in 5 mL of THF was added $[Pd(COD)Cl_2]$ (49 mg, 0.171 mmol). The solution turned immediately from colorless to orange, and after 10 min of stirring, the product precipitated as an orange solid. The latter was isolated by filtration, washed with hexanes, and dried under vacuum.

5a: Yield 95% (113 mg). The complex obtained was too poorly soluble to obtain NMR spectra. Crystals suitable for X-ray diffraction were obtained by heating the powder **5a** with THF at 90 °C in a sealed tube over 2 days. Elemental analysis was carried out on the complex synthesized via method D. Anal. Calcd for $C_{33}H_{31}Cl_2NOP_2Pd$: C, 56.88; H, 4.48. Found: C, 57.13; H, 4.66.

5b: Yield 72% (84 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 49.9 (d, $^2J_{PP}$ = 33 Hz), 21.3 (d, $^2J_{PP}$ = 33 Hz). ^1H (CD_2Cl_2): δ 2.31 (s, 3H, CH_3), 3.29 (dd, 2H, $^2J_{HP}$ = 20.0 Hz, $^2J_{HP}$ = 10.7 Hz, PCH_2P), 4.29 (d, 2H, $^3J_{HP}$ = 9.3 Hz, CH_2N), 7.00 (d, 2H, $^3J_{HH}$ = 8.3 Hz), 7.15 (d, 2H, $^3J_{HH}$ = 8.3 Hz), 7.29−7.39 (m, 4H, Ph_2P), 7.45−7.72 (m, 16H, Ph_2P). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 21.4 (s, CH_3), 34.5 (broad, PCH_2P), 51.0 (d, J_{CP} = 23 Hz, CH_2N), 125.9 (C^{IV}-$P^{(V)}$), 128.2,

129.2 (d, J_{CP} = 9 Hz), 130.0 (d, J_{CP} = 12 Hz), 132.3, 133.4 (d, J_{CP} = 10 Hz), 134.1 (d, J_{CP} = 12 Hz), 134.3 (d, J_{CP} = 12 Hz), 134.5, 136.5 (C^{IV}-$P^{(III)}$), 140.3 (C^{IV} (p-MePh)). Anal. Calcd for $C_{33}H_{31}Cl_2NP_2Pd$: C, 58.21; H, 4.59. Found: C, 58.59; H, 4.75.

5c: Yield 87% (97 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 20.1 (d, $^2J_{PP}$ = 32 Hz), 44.9 (d, $^2J_{PP}$ = 32 Hz). ^1H (CD_2Cl_2): δ 3.35 (dd, 2H, $^2J_{HP}$ = 11.1 Hz, $^2J_{HP}$ = 8.7 Hz, PCH_2P), 7.34−7.80 (m, 20H, Ph_2P), 6.80−6.87 (m, 1H, aniline), 6.91−6.97 (m, 4H). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 35.3 (dd, $^1J_{CP}$ = 79 Hz, $^1J_{CP}$ = 20 Hz, PCH_2P), 123.7, 124.7 (dd, $^1J_{CP}$ = 93 Hz, $^3J_{CP}$ = 6 Hz, C^{IV}-$P^{(III)}$), 128.2, 128.7 (s, C^{IV}-$P^{(V)}$), 129.1 (d, J_{CP} = 9 Hz), 129.5 (d, J_{CP} = 12 Hz), 130.0 (d, J_{CP} = 12 Hz), 132.5 (d, J_{CP} = 3 Hz), 133.7 (d, J_{CP} = 10 Hz), 134.1 (d, J_{CP} = 12 Hz), 134.6 (d, J_{CP} = 3 Hz), 147.5 (s, C^{IV}-aniline). Anal. Calcd for $C_{31}H_{27}Cl_2NP_2Pd$: C, 57.03; H, 4.17. Found: C, 56.76; H, 4.16.

5d: Yield 89% (96 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 49.8 (d, $^2J_{PP}$ = 34 Hz), 23.0 (d, $^2J_{PP}$ = 34 Hz). ^1H (CD_2Cl_2): δ 0.64 (t, 3H, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$ of *n*Bu), 1.01 (vs, 2H, ΣJ = 37.5 Hz, C*H*$_2$-CH_3 of *n*Bu), 1.58 (vq, 2H, ΣJ = 29.6 Hz, C*H*$_2$-CH_2-CH_3 of *n*Bu), 3.02 (vq, 2H, ΣJ = 22.9 Hz, C*H*$_2$-N), 3.26 (d, 2H, $^2J_{HP}$ = 9.3 Hz, $^2J_{HP'}$ = 0 Hz, PCH_2P), 7.10−7.79 (m, 20H, Ph_2P). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 13.9 (s, *C*H$_3$ of *n*Bu), 19.7 (s, *C*H$_2$-CH_3 of *n*Bu), 33.3 (b, PCH_2P) 37.2 (s, *C*H$_2$-CH_2-CH_3 of *n*Bu), 47.9 (s, *C*H$_2$-N), 125.3, 128.7 (dd, J_{CP} = 8 Hz, J_{CP} = 20 Hz), 129.0, 129.4 (d, J_{CP} = 12), 131.7, 132.7 (dd, J_{CP} = 3 Hz, J_{CP} = 13 Hz), 133.5, 133.8, C^{IV} of Ph_2P not observed. Anal. Calcd for $C_{29}H_{31}Cl_2NP_2Pd$: C, 55.04; H, 4.94. Found: C, 55.32; H, 5.11.

5e: Yield 93% (108 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of THF into a solution of **5e** in dichloromethane at RT. $^{31}P\{^1H\}$ (CD_2Cl_2): δ 42.8 (d, $^2J_{PP}$ = 35 Hz), 17.2 (d, $^2J_{PP}$ = 35 Hz). ^1H (CD_2Cl_2): δ 1.59 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3), 3.21−3.38 (m, 2H, PCH_2P), 5.56 (b, 1H, CHN), 7.00−7.96 (m, 25H, Ph_2P and Ph). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 23.8 (d, $^3J_{CP}$ = 5 Hz, CH_3), 34.7 (b, PCH_2P), 58.9 (s, CHN), 115.1 (C^{IV}-$P^{(III)}$), 126.7, 127.7, 129.2, 129.3, 129.5 (d, J_{CP} = 12 Hz), 129.8 (d, J_{CP} = 12 Hz), 131.3, 132.1, 133.4 (d, J_{CP} = 11 Hz), 133.6 (d, J_{CP} = 11 Hz), 133.7, 133.8, 133.9, 134.0, 134.1, 134.2, 146.4 (d, $^3J_{CP}$ = 3 Hz, C_{ipso} of Ph). Anal. Calcd for $C_{33}H_{31}Cl_2NP_2Pd$: C, 58.21; H, 4.59. Found: C, 58.35; H, 4.75.

Synthesis of Platinum Complexes 6c and 6e. Method C. Platinum complex of aniline **6c**: To a solution of **3c** (100 mg, 0.210 mmol) in 5 mL of THF was added dropwise *n*BuLi (0.210 mmol). The cold bath was removed and the solution allowed to warm to room temperature. $[Pt(COD)Cl_2]$ (40 mg, 0.105 mmol) was added in one portion, and after 10 min the solution turned from yellow to colorless and became cloudy. The solid was filtered and washed with THF then hexanes and dried under vacuum. Yield: 91% (116 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 10.7 (tt, $^2J_{PP}$ = 12 Hz, $^1J_{P-Pt}$ = 3433 Hz), 46.0 (tt, $^2J_{PP}$ = 12 Hz, $^2J_{P-Pt}$ = 198 Hz). ^1H (CD_2Cl_2): δ 4.87 (b, 4H), 6.48−8.12 (m, 50H). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 34.2 (m, PCH_2P), 123.3, 123.8, 126.3, 127.3, 128.9, 129.4, 129.7, 132.9, 133.6, 134.8, 135.4, 146.3 (C of phenyl). Anal. Calcd (method D) for $C_{62}H_{54}Cl_2N_2P_4Pt$: C, 61.19; H, 4.47. Found: C, 61.18; H, 4.56.

Platinum Complex of α-methylbenzylamine 6e. To a solution of **3e** (100 mg, 0.171 mmol) in 5 mL of THF cooled at −78 °C was added dropwise *n*BuLi (107 μL). The cold bath was removed, and the solution allowed to warm back to room temperature. $[Pt(COD)Cl_2]$was added in one portion, and after 10 min, a yellow crystalline solid precipitated. The solid was isolated by filtration and washed with THF then hexanes. Yield: 80% (110 mg). $^{31}P\{^1H\}$ (CD_2Cl_2): δ −5.3 (td, $^2J_{PP}$ = 24 Hz, $^1J_{P-Pt}$ = 3845 Hz), 46.0 (td, $^2J_{PP}$ = 24 Hz, $^2J_{P-Pt}$ = 275 Hz). ^1H (CD_2Cl_2): δ 1.60 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.19 (dd, 2H, $^2J_{HP}$ = 9.3 Hz, $^2J_{HP}$ = 10.6 Hz, PCH_2P), 5.50 (q, 1H, $^3J_{HH}$ = 7.1 Hz, CHN), 6.88−6.98 (m, 2H, m-H (Ph)), 7.00−7.09 (m, 1H, p-H (Ph)), 7.15−7.26 (m, 2H, o-H (Ph)), 7.30−7.79 (m, 20H, Ph_2P). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 23.0 (s, CH_3), 32.9 (dd, $^1J_{CP}$ = 30 Hz, $^1J_{CP}$ = 71, PCH_2P), 58.2 (s, CHN), 126.5 (s, p-CH (Ph)), 127.6 (s, o-CH (Ph)), 128.1 (s, m-CH (Ph)), 128.8 and 128.9 (d, J_{CP} = 12 Hz), 129.3 and 129.6 (d, J_{CP} = 13 Hz), 131.8 (b), 133.3 (d, J_{CP} =11 Hz), 133.5 (dd, J_{CP} = 11 Hz, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 12 Hz), 145.8 (s, C_{ipso}-Ph), C^{IV} (Ph_2P) not observed. Anal. Calcd for $C_{33}H_{31}BrClNP_2Pt$: C, 48.69; H, 3.84. Found: C, 49.02; H, 3.97.

Synthesis of Nickel Complex 7a. To a solution of **3a** (100 mg, 0.167 mmol) in 5 mL of THF cooled at −78 °C was added dropwise *n*BuLi (104 μL, 0.167 mmol). The cold bath was removed, and the solution allowed to warm to room temperature. $[Ni(dme)Br_2]$ (51 mg, 0.167 mmol) was added, the solution turned from colorless to blue immediately, and after 15 min, a blue solid precipitated. Filtration of the solution, followed by solvent removal under vacuum, gave **7a**. Yield: 96% (118 mg). Anal. Calcd for $C_{33}H_{31}Br_2NNiOP_2$: C, 53.70; H, 4.23. Found: C, 54.00; H, 4.39.

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Supporting Information Available: CIF files and tables giving crystallographic data for **5a**, **5c**, **5e**, **5′e**, **6c**, **6e**, and **7e**, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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