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Facile Synthesis of Bifunctional Ligands using $LiCH_2PPh_2{=}NPh$ Obtained from $[PhNH{-}PPh_3^+][Br^-]$

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The $LiCH_2PPh_2{=}NPh$ derivative **2** was cleanly prepared from the aminophosphonium salt $[PhNH{-}PPh_3^+][Br^-]$ (**1**) and MeLi. After formation of the iminophosphorane $PPh_3{=}NPh$, nucleophilic displacement of one phenyl ring of the P atom by a methyl group occurred. This sequence was demonstrated to highly depend on the experimental conditions and on the substituent pattern at the nitrogen atom. Then, **2** was reacted with various electrophiles, among which phosphine chlorides, silyl chloride, stannyl chloride, and cyanophosphole, leading to bifunctional ligands. Depending on the electrophiles, the products were isolated either as the aminophosphonium salts or the iminophosphorane derivatives. All of these products were characterized by multinuclear NMR spectrocopy and in two cases by X-ray analysis. In particular, reaction of **2** with S_8 gave rise to the thiolate derivative ($LiSCH_2PPh_2{=}NPh$) (**9**), which was subsequently coordinated to Pd(II) and Ru(II) metal centers to give respectively $[(PhNPPh_2CH_2S)Pd(PPh_3)Cl]$ and $[(PhNPPh_2CH_2S)Ru(p\text{-cymene})Cl]$.

During the past decade iminophosphorane-based ligands have attracted the attention of different research groups, and now their potential in coordination chemistry is well recognized.[1] In addition, they have been successfully used for the elaboration of different catalytic systems able to perform, for example, ethylene polymerization[2] or oligomerization,[3] ring-opening lactide polymerization,[4] hydroamination,[5] and transfer hydrogenation reactions.[6] Importantly, the electronic properties of the iminophosphorane (P=N) function differs greatly from those of its carbon counterpart. In contrast to imines, iminophosphoranes do not possess any π system and thus have no π-accepting ability. On the other hand, as the nitrogen atom bears two lone pairs, they behave as strong σ and π donors. Generally these ligands are prepared by the Staudinger reaction, requiring the condensation of an azide on a tertiary phosphine.[7] This methodology is very clean (N_2 being the only

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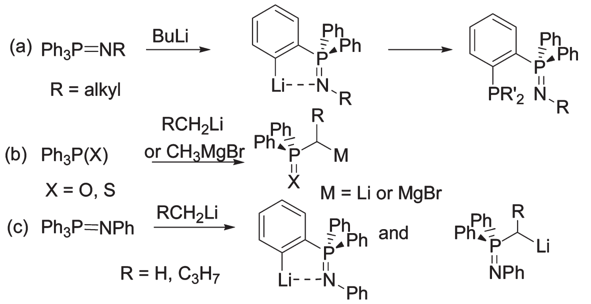
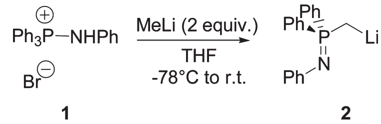
Scheme 1. Metalation of $PPh_3(X)$ Derivatives

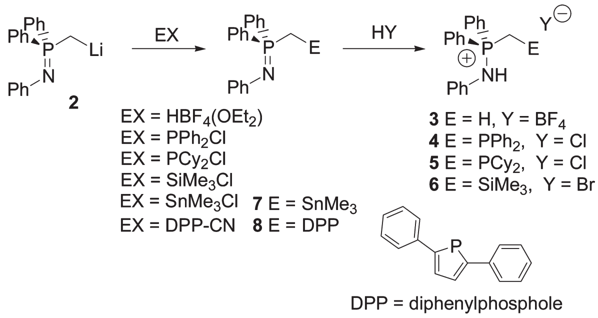


byproduct) but necessitates the handling of azides which are usually difficult to prepare or hazardous, explaining why most research groups employ commercially available azides. Alternatively, we and others prefer a methodology based on the Kirsanov reaction,[3,8] which allows the preparation of iminophosphorane by deprotonation of an aminophosphonium species. These are obtained by addition of a primary amine onto a phosphonium bromide, thus enabling an easy modification of the substitution pattern at the nitrogen atom. We also recently showed that selective ortho lithiation of $PPh_3{=}NR$ (R = alkyl) derivatives can be another synthetic option, which gives access after trapping with a phosphorus-based electrophile to bidentate (P, PN) ligands (Scheme 1a).[9] This behavior markedly differs from the reactivity of thiophosphines and phosphine oxides toward alkyllithium or Grignard reagents reported by Seyferth et al. in the early 1960s.[10] Indeed, as described in Scheme 1b, they have shown that such reactions led to the formation of the diphenylphosphinylalkyl organometallic reagent $(MCH_2)P(X)Ph_2$ (M = MgBr, Li; X = O, S), which could be then reacted with chlorophosphines.[11] Direct coordination of $(MCH_2)P(X)Ph_2$ (X = O, S) anions to different metal centers, such as Au(I) and Hg(II), was also later described.[12] To the best of our knowledge, no such transformation has been reported for iminophosphoranes. Nevertheless, Stuckwisch[13] mentioned that a competitive reaction takes place when performing the ortho lithiation of $PPh_3{=}NPh$ (Scheme 1c); metalated diphenylalkylphosphine *N*-phenylimide was indeed observed as a byproduct. Here, we wish to present a reliable and facile preparation of $LiCH_2PPh_2{=}NPh$ from $[PhNH{-}PPh_3^+][Br^-]$ and its trapping with different electrophiles. The coordination of $LiSCH_2PPh_2{=}NPh$ (obtained by reaction with S_8) to Pd(II) and Ru(II) centers is also described.

Scheme 2. Formation of $(LiCH_2PPh_2NPh)$



Scheme 3. Electrophilic Trapping of 2



Results and Discussion

The lithiation (Scheme 2) was carried out by adding 2 equiv of MeLi (1.6 M in diethyl ether) to a suspension of the triphenylphosphonium bromide adduct **1** in THF (the first equivalent generating the iminophosphorane). This induced a marked color change; the white suspension disappeared to give an orange-red solution. The $^{31}P\{^1H\}$ NMR spectrum of the crude mixture showed a singlet at δ (THF) 24.2 ppm, which is in the range of the chemical shift observed for ortho-lithiated derivatives obtained from $PPh_3{=}NR$ (R = $CH(CH_3)CH(CH_3)_2$, CH_2-*t*-Bu, *i*-Pr)[9,14] in diethyl ether. Nevertheless, ^1H NMR spectroscopy of the crude mixture in d_8-THF shows a broad singlet at δ (THF) −0.11 ppm integrating for two protons and the presence of only two phenyl rings on the phosphorus atom. These observations point toward the displacement of one phenyl ring of the P atom by a methyl group followed by α-metalation (performed by in situ generated phenyllithium) leading to **2**. NMR characterization was achieved in THF, and data were similar to those described by Davidson and Lopez-Ortiz et al., who synthesized this anion from $CH_3PPh_2{=}NPh$ and characterized it in solution and in the solid state.[15]

Importantly, the formation of **2** from $PPh_3{=}NPh$ highly depends on the reaction conditions. When *n*-BuLi was used instead of MeLi in THF, two different products were obtained, one coming from ortho lithiation and the other from a phenyl displacement followed by α-metalation (see Scheme 1c). This can be ascribed to the better nucleophilic properties of MeLi. Moreover, the lithiation carried out with MeLi (1.6 M in diethyl ether) in toluene leads also to a mixture of two anions: **2** and the ortho-lithiated derivative characterized by a singlet at δ (toluene) 16.9 ppm in $^{31}P\{^1H\}$

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NMR. The latter can also be obtained as the sole product by using *n*-BuLi in toluene.

The course of the reaction is also very sensitive to the nature of the nitrogen substituent. Indeed, with an alkyl substituent at the nitrogen, whatever the nature of the base or solvent used, only ortho lithiation was observed as we described earlier (see Scheme 1a).[9]

After having determined the experimental conditions enabling a clean preparation of **2**, this anion was trapped with various electrophiles (Scheme 3). First, **2** was reacted with tetrafluoroboric acid; the protonation induces a rapid fading of the color of the solution which is accompanied by a net shielding of the phosphorus signal (δ (THF) +36.6 ppm). The aminophosphonium salt **3** was isolated in 70% yield as a white solid (Scheme 3). The presence of the methyl group is indicated by a doublet at δ ($CDCl_3$) 2.44 ppm ($^2J_{P,H}$ = 13.5 Hz) in the ^1H NMR spectrum. **3** was characterized by multinuclear NMR spectroscopy, by elemental analysis, as all other trapping products, and by X-ray crystallography (see the Supporting Information).

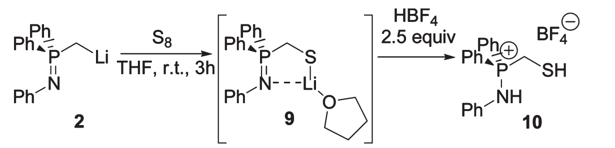
Then, anion **2** was trapped with various chlorophosphines to give mixed phosphine−iminophosphorane ligands. Reaction with 1 equiv of PPh_2Cl induced the formation of the (P, PN) adduct, as indicated by the presence of two doublets at δ (THF) 0.80 and −26.6 ppm ($^2J_{P,P}$ = 51.5 Hz) in the $^{31}P\{^1H\}$ NMR of the crude mixture. After protonation the aminophosphonium salt can be isolated. The NMR data were identical with those we have already described.[10] More interestingly, using chlorophosphines other than diphenylphosphine chloride gave rise to mixed phosphine−iminophosphorane ligands, in which the two phosphorus atoms do not bear the same substituents. Such derivatives cannot be prepared by the monobromation−Kirsanov sequence we developed earlier. By reaction with PCy_2PCl, a mixed phosphine−iminophosphorane adduct was formed, as evidenced by two doublets at δ (THF) −11.2 and 27.1 ppm ($^2J_{P,P}$ = 101.5 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of the crude mixture. Even if the ligand could be directly isolated, we preferred to isolate it as an aminophosphonium salt for storage convenience. Therefore, **5** was obtained after acidic workup. It exhibits in $^{31}P\{^1H\}$ NMR spectroscopy two doublets at δ (CD_2Cl_2) −22.2 and 34.80 ppm ($^2J_{P,P}$ = 87.5 Hz) corresponding respectively to the P(III) and P(V) atoms. The bridging methylene appears as a doublet at δ (CD_2Cl_2) 3.22 ppm ($^2J_{P,H}$ = 16.5 Hz) and a doublet of doublets at δ (CD_2Cl_2) 18.7 ppm ($^2J_{P,C}$ = 39.0 and 68.0 Hz) in the ^1H and ^{13}C NMR spectra, respectively. In the same manner, reaction with trimethylsilyl chloride also proceeded cleanly, leading after acidic workup to the aminophosphonium salt **6**, which was characterized by multinuclear (^{31}P, ^1H, ^{13}C) NMR spectroscopy as well as X-ray analysis (see the Supporting Information).

The intermediate iminophosphosphorane can be alternatively, equally well, isolated (Scheme 3).

Thus, reaction of anion **2** with trimethyltin chloride gave, after removal of lithium salt, **7** as a white solid in 75% yield. In $^{31}P\{^1H\}$ NMR spectroscopy **7** exhibited a singlet at δ (C_6D_6) 7.40 ppm and satellites due to tin isotope ($^2J_{P,Sn}$ = 60.0 Hz). In ^1H NMR the methylene protons appears as a doublet with tin satellites centered at δ (C_6D_6) 2.71 ppm ($^2J_{Sn,H}$ = 52.0 Hz, $^2J_{P,H}$ = 11.0 Hz).

Moreover, trapping **2** with 1-cyano-2,5-diphenylphosphole gave access to **8** in 85% yield. This mixed bidentate ligand is very promising, since it features coordination sites with very different electronic properties. As mentioned earlier, the iminophosphorane is a strong σ and π donor whereas the phosphole ring is a phosphine with greater accepting ability. The formation of **8** was ascertained by NMR spectroscopy.[16] The $^{31}P\{^1H\}$ NMR spectrum is very diagnostic, showing a doublet at δ (C_6D_6) −23.7 ppm for the phosphole P atom and 0.8 ppm for the P(V) atom ($^2J_{P,P}$ = 48.5 Hz).

Scheme 4. Trapping with S_8



If bidentate iminophosphorane−phosphine ligands are well-known, the combination of iminophosphorane with other donors based on different heteroatoms remains scarce.[17] With this in mind, we achieved the synthesis of thiolate **9** and thiol **10** (Scheme 4). Indeed, reaction with S_8 in THF at room temperature induced the precipitation of **9**, which was isolated by filtration in 55% yield. This anion could be solubilized in pyridine and characterized by multinuclear NMR in this solvent. The ^1H NMR data reveal the coordination of one THF molecule per ligand, which allows us to propose the structure presented in Scheme 4. Furthermore, **9** can be protonated by addition of 2.5 equiv of HBF_4 in ether, yielding the aminophosphonium salt **10**, which was also fully characterized.

In the first coordination experiments, anion **9** was coordinated to Pd(II) and Ru(II) centers. Due to the low solubility of **9** in THF, reactions were carried out by addition of THF onto a mixture of isolated **9** and the metal precursor. With *trans*-$PdCl_2(PPh_3)_2$, after 4 h at room temperature, the yellow slurry had turned to an orange solution. The $^{31}P\{^1H\}$ NMR spectrum of the crude mixture showed the presence of 1 equiv of free triphenylphosphine (δ (THF) −5.1 ppm) and an AB signal pattern evidencing the coordination of the ligand to the palladium center. The complex [$(PhNPPh_2CH_2S)Pd(PPh_3)Cl$] (**11**) exhibited a doublet ($^3J_{PP}$ = 6.5 Hz) at δ (THF) 34.2 and 45.0 ppm corresponding respectively to the coordinated triphenylphosphine and iminophosphorane functions. This complex was isolated in 87% yield by evaporation of THF and removal of lithium salt after precipitation in dichloromethane, followed by washing of the solid obtained after evaporation of the solvent with *n*-hexanes. It was characterized by multinuclear NMR, elemental analysis, and X-ray diffraction analysis. Single crystals were obtained by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution of **11**. An Ortep plot of **11** is depicted in Figure 1 together with the most relevant metric and angular parameters. It is a neutral square-planar complex where the iminophosphorane and the phosphine are located trans to each other (this comes from the trans arrangement of the phosphine ligands in the palladium precursor). The deviation from planarity was found to be 16.70(9)°. The P−N bond distance is normal at 1.597(3) Å, and the P3−C1 bond is shortened compared to the P−C bond in [$(Ph_2PCH_2PPh_2NPh)PdCl_2$] featuring a bidentate phosphine−iminophosphorane ligand: 1.801(3) vs 1.842(2) Å.[8b] In contrast, both the N−Pd (2.100(2) Å) and the Pd−Cl bond lengths (2.3869(7) Å) are elongated in comparison to the same reference (N−Pd = 2.076(2) Å and Pd−Cl = 2.3668(5) Å, 2.3035(6) Å).

(16) For **7** and **8**, which proved to be air and moisture sensitive, satisfactory elemental analyses could not be obtained.

(17) For an example of an iminophosphorane−thioether ligand see: Alajarín, M.; López-Leonardo, C.; Llamas-Lorente, P.; Bautista, D.; Jones, P. G. *Dalton Trans.* **2003**, 426–434.

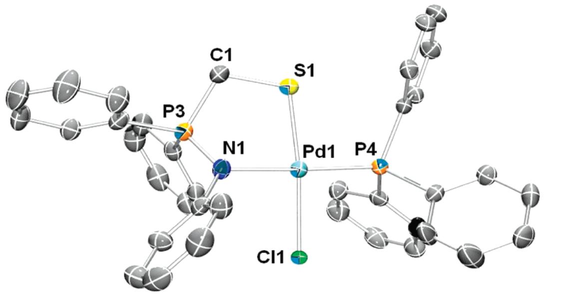
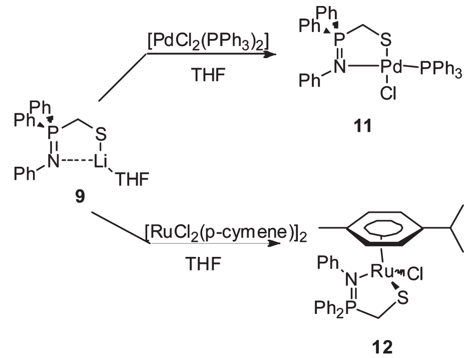


Figure 1. ORTEP view of complex **11**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (deg): Pd1−N1 = 2.100(2), N1−P3 = 1.597(3), P3−C1 = 1.801(3), C1−S1 = 1.824(3), S1−Pd1 = 2.289(1), Pd1−P4 = 2.2528(8), Pd1−Cl1 = 2.3869(7); N1−Pd1−S1 = 88.52(7), P4−Pd1−S = 189.87(3), N1−Pd1−Cl1 = 92.45(7), P4−Pd1−Cl1 = 89.73(3), P3−C1−S1 = 109.5(2), N1−P3−C1 = 104.9(2), C1−S1−Pd1 = 103.6(1), S1−Pd1−N1−Cl1 = 16.70(9).

Scheme 5. Coordination of the Thiolate−Iminophosphorane Ligand to Pd(II) and Ru(II)



The iminophosphorane−thiolate anion was also easily coordinated to a Ru(II) center. Addition of THF to a mixture of **9** and dichloro(p-cymene)ruthenium(II) dimer in the solid state led rapidly to a red solution. The disappearance of the precipitated anion was a good sign of coordination, which was confirmed by $^{31}P\{^1H\}$ NMR of the crude mixture showing the formation of a unique product exhibiting a singlet at δ (THF) 36.9 ppm. After 3 h at room temperature, the solvent was evaporated, the lithium salt was filtered off after precipitation in dichloromethane, and **12** was isolated as a red solid in 76% yield. This complex was characterized by multinuclear NMR and elemental analysis. In the ^1H NMR spectrum the methylene protons appear as two doublets at 2.67 and 4.12 ppm; this accounts for the chirality of the Ru center, which bears four different substituents. In the same manner the protons of the coordinated p-cymene ring are differentiated, giving three doublets at 4.64, 4.76, and 4.90 ppm integrating respectively for 1, 2, and 1 proton. In the aromatic area, the differentiation of the protons of the phenyl rings on the phosphorus atom can also be seen. In the ^{13}C spectrum most of the carbons of both the p-cymene and phenyl rings (on P) are differentiated. All these data lead us to propose the structure depicted in Scheme 5 for complex **12**.

In conclusion, the clean preparation of $LiCH_2PPh_2{=}NPh$ anion from $[PhNH{-}PPh_3^+][Br^-]$ was realized, which has opened the way to an easy synthesis of new bidentate ligands. First, electrophilic trapping gave access to mixed iminophosphorane−phosphine, −silyl, −stannyl, or −thiolate derivatives, which were often isolated as aminophosphonium derivatives after acidic workup. All these products were characterized by multinuclear NMR techniques and elemental analyses and in some cases by X-ray analysis. Then, the coordination chemistry of the iminophosphorane−thiolate anion **9** to Pd(II) and Ru(II) centers was studied, yielding $[(SCH_2PPh_2NPh)Pd(PPh_3)Cl]$ (**11**) and $[(SCH_2PPh_2NPh)(p\text{-cymene})RuCl]$ (**12**), respectively. These complexes were fully characterized, including X-ray analysis for **11**. Following these first results, the coordination chemistry of the new bidentate ligands, which are easily available via the described methodology, is currently under investigation in our laboratory.

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethyl ether, petroleum ether) and from P_2O_5 (dichloromethane). The aminophosphonium compound **1**[18] and $[Ru(p\text{-cymene})Cl_2]_2$[19] were prepared according to literature procedures. All other reagents and chemicals were obtained commercially and used without further purification. 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. Solvent peaks were used as internal references for ^1H and ^{13}C chemical shifts (ppm). ^{31}P peaks were referenced to external 85% H_3PO_4. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France, or at the elemental analysis service of the London Metropolitan University (United Kingdom).

Preparation of 2. MeLi (1.6 M, 0.46 mmol, 287 μL) was added dropwise to a suspension of **1** (0.23 mmol, 0.1 g) in THF (2.5 mL) at −78 °C. The cold bath was removed, and stirring was pursued at room temperature for 30 min to give an orange-red solution. The formation of **2** was indicated by in situ NMR data similar to those previously described.[15] $^{31}P\{^1H\}$ NMR (d_8-THF): δ 24.18 (s). ^1H NMR (d_8-THF): δ −0.11 (2H, br. s, CH_2), 6.27 (1H, t, $^2J_{H,H}$ = 7.5 Hz, p-CH(NPh)), 6.44 (2H, d, $^3J_{H,H}$ = 7.5 Hz, o-CH(NPh)), 6.70 (2H, $^3J_{HH}$ = 7.5 Hz, m-CH(NPh)), 7.27 (6H, m, m-and p- CH(PPh_2), 7.68 (4H, m, o- CH(PPh_2)).

Electrophilic Trapping. Synthesis of 3. $HBF_4(Et_2O)_2$ (0.46 mmol, 63 μL) was added to a solution of **2** (0.23 mmol, 0.1 g) in THF, inducing a rapid fading of the initial orange solution. After $^1/_2$ h of stirring at room temperature, the solvent was removed in vacuo, dichloromethane (5 mL) was added, and the lithium salts were filtered off. Then evaporation of the solvent yielded **3** as a white solid (61 mg, 70%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.6 (s). ^1H NMR ($CDCl_3$): δ 2.44 (3H, d, $^2J_{P,H}$ = 13.5 Hz, CH_3), 6.78 (2H, d, $^3J_{H,H}$ = 7.5 Hz, o-CH(NPh)), 6.86 (1H, d, $^3J_{H,H}$ = 7.5 Hz, p-CH(NPh)) 6.99 (2H, $^3J_{H,H}$ = 7.5 Hz, m-CH(NPh)), 7.53 (4H, m, o- CH(PPh_2), 7.68 (6H, m, m and p- CH(PPh_2)). ^{13}C NMR ($CDCl_3$): δ 12.7 (d, $^1J_{P,C}$ = 69.5 Hz, CH_3), 120.2 (d, $^3J_{P,C}$ = 6.5 Hz, o-CH(NPh)), 120.4 (d, $^1J_{P,C}$ = 100 Hz, C^{IV}-(PPh_2)), 124.0 (s, p-CH(NPh)), 129.5 (s, m-CH(NPh)), 130.1 (d, $^2J_{P,C}$ = 13.5 Hz, o-CH(PPh_2)), 132.4 (d, $^3J_{P,C}$ = 11.5 Hz, m-CH(PPh_2)), 135.2 (d, $^4J_{P,C}$ = 3.0 Hz, p-CH(PPh_2)), 137.5 (d, $^2J_{P,C}$ = 2.5 Hz, C^{IV}-(NPh)). Anal. Calcd for $C_{19}H_{19}BF_4NP$: C, 60.19; H, 5.05; N, 3.69. Found: C, 59.74; H, 4.82; N, 4.03.

(18) Albright, T. A.; Freeman, W. A.; Schweizer, E. E. *J. Org. Chem.* **1976**, *41*, 2716–2720.
(19) Bennet, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74–78.

Synthesis of 5. Dicyclohexylphosphine chloride (0.58 mmol, 128 μL) was added to a solution of **2** (0.58 mmol, 0.25 g) in THF to give a clear yellow solution, which was stirred for $^1/_2$ h at room temperature. Then, the volatiles were evaporated in vacuo and dichloromethane (12 mL) was added. The reaction mixture was washed with 2 M aqueous HCl solution (2×7 mL); the organic phase was then dried on Na_2SO_4 and filtered under N_2. After evaporation of the solvent and precipitation with hexanes, **5** was obtained as a white solid (228 mg, 75%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.2 (d, $^2J_{P,P}$ = 87.5 Hz, PCy_2), 34.8 (d, $^2J_{P,P}$ = 87.5 Hz, P^VPh_2). ^1H NMR (CD_2Cl_2): δ 0.80−1.52 (22H, m, Cy), 3.22 (2H, d, $^2J_{P,H}$ = 16.5 Hz, PCH_2), 6.82 (1H, t, $^3J_{H,H}$ = 7.5 Hz, *p*-C*H*(NPh)), 6.90 (2H, d, $^3J_{H,H}$ = 7.5 Hz, *o*-C*H*(NPh)), 6.99 (2H, t, $^3J_{H,H}$ = 7.5 Hz, *m*-C*H*(NPh)), 7.57 (6H, m, *m*- and *p*-C*H*(PPh_2)), 8.01 (4H, dd, $^3J_{H,H}$ = 8.0 Hz and $^3J_{P,H}$ = 12.5 Hz, *o*-C*H*(PPh_2)). ^{13}C NMR (CD_2Cl_2): δ 18.7 (dd, $^1J_{P,C}$ = 39.0 Hz and $^1J_{P,C}$ = 68.0 Hz, PCH_2), 25.2 (s, CH_2(Cy)), 26.2 (d, $J_{P,C}$ = 12.0 Hz, CH_2(Cy)), 28.2 (t, $J_{P,C}$ = 13.0 Hz, CH_2(Cy)), 33.1 (dd, $^3J_{P,C}$ = 8.0 Hz and $^1J_{P,C}$ = 15.0 Hz, *C*H(Cy)), 119.3 (d, $^3J_{P,C}$ = 7.5 Hz, *o*-*C*H(NPh)), 119.7 (d, $^1J_{P,C}$ = 97.5 Hz, C^{IV}-(PPh_2)), 122.0 (s, *p*-*CH*(NPh)), 128.2 (s, *m*-*C*H(NPh)), 128.7 (d, $^2J_{P,C}$ = 13.0 Hz, *m*-*C*H(PPh_2)), 133.04 (dd, $^3J_{P,C}$ = 10.1 Hz and $^3J_{P,C}$ = 4.5 Hz, *o*-*C*H(PPh_2)), 133.8 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-*C*H(PPh_2)), 138.5 (d, $^2J_{P,C}$ = 3.0 Hz, C^{IV}-(NPh)). Anal. Calcd for $C_{31}H_{40}ClNP_2$: C, 71.05; H, 7.69; N, 2.67. Found: C, 71.28; H, 7.47; N, 2.36.

Synthesis of 6. 6 (0.139 g, 60%) was obtained by a procedure similar to that used for **5**, employing trimethylsilyl chloride (0.58 mmol, 75 μL) as electrophile and HBr as acid. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.2 (s). ^1H NMR ($CDCl_3$): δ 0.0 (9H, s, CH_3), 2.71 (2H, d, $^2J_{P,H}$ = 18,0 Hz, PCH_2), 6.86 (1H, t, $^3J_{H,H}$ = 7.0 Hz, *p*-C*H*(NPh)), 7.03 (4H, m, $^3J_{H,H}$ = 7.5 Hz, *o*- and *m*-C*H*(NPh)), 7.57 (4H, td, $^3J_{H,H}$ = 7.5 Hz and $^3J_{P,H}$ = 3.5 Hz, *m*-C*H*(PPh_2)), 7.78 (2H, dd, $^3J_{H,H}$ = 7.5 Hz and $^4J_{P,H}$ = 6.0 Hz, *p*-C*H*(PPh_2)), 7.91 (4H, dd, $^3J_{H,H}$ = 7.5 Hz and $^2J_{P,H}$ = 13.0 Hz, *o*-C*H*(PPh_2)). ^{13}C NMR ($CDCl_3$): δ 0.0 (s, CH_3), 14.5 (d, $^1J_{P,C}$ = 58.5 Hz, PCH_2), 120.0 (d, $^3J_{P,C}$ = 6.0 Hz, *o*-*C*H(NPh)), 122.5 (d, $^1J_{P,C}$ = 96.5 Hz, C^{IV}-(PPh_2)), 122.9 (s, *p*-*CH*(NPh)), 129.0 (s, *m*-*C*H(NPh)), 129.7 (d, $^2J_{P,C}$ = 13.0 Hz, *o*-*C*H(PPh_2)), 132.6 (d, $^3J_{P,C}$ = 11.0 Hz, *m*-*C*H(PPh_2)), 134.4 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-*C*H(PPh_2)), 139.0 (d, $^2J_{P,C}$ = 2.5 Hz, C^{IV}-(NPh)). Anal. Calcd for $C_{22}H_{27}BrNPSi$: C, 59.46; H, 6.12; N, 3.50. Found: C, 58.81; H, 5.93; N, 3.40.

Synthesis of 7. A solution of trimethyltin chloride (0.58 mmol, 0.116 g) in THF (2 mL) was added to a THF solution (12 mL) of **2** (0.58 mmol, 0.250 g) to give, after 30 min of stirring, a pale yellow solution. Then, solvent was removed and toluene added to filter off the lithium salts. After evaporation of toluene, iminophosphorane **7** was obtained as a white solid (341 mg, 75%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −6.88 (s + sat, $^2J_{P,Sn}$ = 60.0 Hz). ^1H NMR (C_6D_6): δ 0.10 (9H, s + sat, $^2J_{Sn,H}$ = 50.0 Hz, Sn(CH_3)$_3$), 1.55 (2H, d + sat, $^2J_{P,H}$ = 11.0 Hz, $^2J_{Sn,H}$ = 52.0 Hz, CH_2P), 6.76 (3H, m, *p*- and *m*-C*H*(NPh)), 6.99 (6H, m, *p*- and *m*-C*H*(PPh_2)), 7.18 (2H, m, o-C*H*(NPh)), 7.66 (4H, m, *o*-C*H*(PPh_2)). ^{13}C NMR (C_6D_6) δ −7.4 (d + sat, $^3J_{P,C}$ = 1.5 Hz, $^1J_{Sn,C}$ = 362.0 Hz, Sn(CH_3)$_3$), 12.0 (d + sat, $^1J_{P,C}$ = 75.0 Hz, $^1J_{Sn,C}$ = 296.0 Hz, CH_2P), 117.1 (s, *p*-*C*H(NPh)), 123.2 (d, $^3J_{P,C}$ = 20.0 Hz, *m*-*C*H(NPh)), 128.6 (d, $^3J_{P,C}$ = 11.0 Hz, *o*-*C*H(NPh)), 129.7 (d, $^3J_{P,C}$ = 12.0 Hz, *m*-*C*H(PPh_2)), 131.6 (d, $^2J_{P,C}$ = 9.0 Hz, *o*-*C*H(PPh_2)), 133.8 (d, $^3J_{P,C}$ = 3.0 Hz, *p*-*C*H(PPh_2)), 134.9 (d, $^1J_{P,C}$ = 87.0 Hz, C^{IV}(PPh_2)), 152.8 ($^2J_{P,C}$ = 3.0 Hz, C^{IV}-(NPh)).

Synthesis of 8. 8 (103 mg, 85%) was obtained by a procedure similar to that employed for **7**, using a solution of 1-cyano-2,5-diphenylphosphole (0.23 mmol, 0.06 g) in THF (2 mL) and a solution of **2** (0.23 mmol, 0.100 g) in THF (3 mL). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −23.7 (d, $^2J_{P,P}$ = 48.5 Hz, P^{III}), 0.8 (d, $^2J_{P,P}$ = 48.5 Hz, P^V). ^1H NMR (C_6D_6): δ 2.75 (2H, dd, $^2J_{P,H}$ = 10.0 Hz, $^2J_{P,H}$ = 4.0 Hz, PCH_2P), 6.82 (6H, td, $J_{H,H}$ = 7.5 Hz, $J_{P,H}$ = 3.0 Hz, *m*- and *p*-C*H*(PPh_2)), 6.91 (6H, m, *m* and *p*-C*H*($Ph_{phosphole}$)), 7.02 (6H, m, *m*- and *p*-C*H*(NPh)), 7.07 (2H, d, $^3J_{P,H}$ = 8.0 Hz, $CH_{\beta\,phosphole}$), 7.45 (4H, dd, $^3J_{P,H}$ = 11.5 Hz, $^3J_{H,H}$ = 7.0 Hz, *o*-C*H*(PPh_2)), 7.52 (4H, dd, $^3J_{H,H}$ = 7.0 Hz and $^4J_{P,H}$ = 1.0 Hz, *o*-C*H*($Ph_{phosphole}$)), 7.61 (2H, m, *o*-C*H*(NPh)). ^{13}C NMR (C_6D_6): δ 24.8 (dd, $^1J_{P,C}$ = 44.0 Hz, $^1J_{P,C}$ = 37.5 Hz, PCH_2), 117.6 (s, *C*H(Ph)), 123.6 (s, C^{IV}-($Ph_{phosphole}$)), 123.9 (s, *C*H(Ph)), 126.7 (d, $^3J_{P,C}$ = 5.0 Hz, *o*-*C*H($Ph_{phosphole}$)), 127.8 (d, $^3J_{P,C}$ = 8.0 Hz, *o*-*C*H(NPh)), 128.8 (d, $J_{P,C}$ = 9.0 Hz, *C*H(Ph)), 131.3 (s, *C*H-(Ph)), 131.5 (s, *C*H(Ph)), 131.8 (d, $J_{P,C}$ = 3.0 Hz, *C*H(Ph)), 132.3 (d, $^2J_{P,C}$ = 9.0 Hz, *o*-*C*H(PPh_2)), 132.5 (d, $^2J_{P,C}$ = 9.0 Hz, $C_{\beta\,phosphole}$), 135.6 (dd, $^1J_{P,C}$ = 97.0 Hz and $^3J_{P,C}$ = 8.0 Hz, C^{IV}-(PPh_2), 136.5 (d, $^2J_{P,C}$ = 17.0 Hz, C^{IV}-(NPh)), 152.4 (d, $^1J_{P,C}$ = 68.0 Hz, $C_{\alpha\,phosphole}$).

Synthesis of 9. S_8 (0.03 mmol, 7.5 mg) was added in the glovebox to a solution of anion **2** (0.23 mmol, 0.100 g) in THF (3 mL) to give a yellow-orange solution from which a precipitate formed. After the mixture was stirred for 3 h at room temperature, the precipitate was isolated by filtration, washed with THF, and dried in vacuo to yield **9** as a white solid (447 mg, 55%). $^{31}P\{^1H\}$ NMR (Pyr-d_5): δ 21.3 (s). ^1H NMR (Pyr-d_5): δ 1.80 (4H, m, CH_2(THF)), 3.84 (4H, m, OCH_2(THF)), 4.18 (2H, d, $^2J_{P,H}$ = 7.0 Hz, PCH_2), 6.89 (1H, t, $^3J_{H,H}$ = 7.0 Hz, *p*-C*H*(NPh)), 7.28 (2H, t, $^3J_{H,H}$ = 7.0 Hz, *m*-C*H*(NPh)), 7.40 (2H, t, $^3J_{H,H}$ = 7.0 Hz, *o*-C*H*(NPh)), 7.54 (4H, td, $^3J_{H,H}$ = 7.5 Hz and $^4J_{P,H}$ = 1.0 Hz, *m*-C*H*($_{PPh_2}$)), 7.64 (2H, t, $^3J_{H,H}$ = 7.5 Hz, *p*-C*H*(PPh_2)), 8.22 (4H, dd, $^3J_{HH}$ = 7.5 Hz and $^3J_{P,H}$ = 9.5 Hz, *o*-C*H*(PPh_2)). ^{13}C NMR (Pyr-d_5): δ 28.2 (s, CH_2(THF)), 31.5 (d, $^1J_{P,C}$ = 88.0 Hz, PCH_2), 70.2 (s, OCH_2(THF)), 119.8 (s, *p*-*C*H(NPh)), 125.4 (d, $^3J_{P,C}$ = 17.6 Hz, *o*-*C*H(NPh)), 131.1 (d, $^3J_{P,C}$ = 10.5 Hz, *m*-*C*H(PPh_2)), 131.6 (d, $^3J_{P,C}$ = 1.0 Hz, *m*-*C*H(NPh)), 133.6 (d, $^1J_{P,C}$ = 78.5 Hz, C^{IV}-(PPh_2)), 134.1 (d, $^4J_{P,C}$ = 2.5 Hz, *p*-*C*H(PPh_2)), 135.4 (d, $^2J_{P,C}$ = 8.0 Hz, *o*-*C*H(PPh_2)), 155.8 (d, $^2J_{P,C}$ = 5.5 Hz, C^{IV}-(NPh)).

Synthesis of 10. To obtain **10**, $HBF_4(Et_2O)_2$ (0.46 mmol, 63 μL) was added to a solution of **9** (0.23 mmol, 0.100 g) in THF to lead to a colorless solution. The solvent was removed, CH_2Cl_2 (5 mL) was added, and the salts were removed by filtration under N_2. Then, evaporation of the solvent afforded the aminophosphonium compound **10** (67 mg, 71%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.9 (s). ^1H NMR ($CDCl_3$): δ 2.00 (1H, td, $^3J_{H,H}$ = 9.0 Hz and $^3J_{P,H}$ = 2.0 Hz, S*H*), 3.85 (2H, d, $^2J_{P,H}$ = 7.5 Hz, PCH_2), 6.80 (2H, d, $^3J_{H,H}$ = 7.5 Hz, *o*-C*H*(NPh)), 6.87 (1H, t, $^3J_{H,H}$ = 7.5 Hz, *p*-C*H*(NPh)), 7.00 (2H, t, $^3J_{H,H}$ = 7.5 Hz, *m*-C*H*(NPh)), 7.34 (1H, d, $^2J_{P,H}$ = 9.5 Hz, NH) 7.56 (4H, td, $^3J_{H,H}$ = 7.5 Hz and $^4J_{P,H}$ = 3.5 Hz, *m*-C*H*(PPh_2)), 7.69 (2H, t, $^3J_{H,H}$ = 7.5 Hz, *p*-C*H*(PPh_2)), 7.86 (4H, dd, $^3J_{H,H}$ = 7.5 Hz and $^3J_{P,H}$ = 9.5 Hz, *o*-C*H*(PPh_2)). ^{13}C NMR ($CDCl_3$): δ 18.7 (d, $^1J_{P,C}$ = 69.0 Hz, PCH_2), 116.8 (d, $^1J_{P,C}$ = 99.5 Hz, C^{IV}-(PPh_2)), 119.0 (d, $^3J_{P,C}$ = 17.6 Hz, *o*-*C*H(NPh)), 123.1 (s, *p*-*C*H(NPh)), 128.6 (s, *m*-*C*H(NPh)), 129.2 (d, $^3J_{P,C}$ = 13.5 Hz, *m*-*C*H(PPh_2)), 132.5 (d, $^2J_{P,C}$ = 10.5 Hz, *o*-*C*H(PPh_2)), 134.7 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-*C*H(PPh_2)), 136.3 (d, $^2J_{P,C}$ = 3.0 Hz, C^{IV}-(NPh)). Anal. Calcd for $C_{19}H_{19}BF_4NPS$: C, 55.50; H, 4.66; N, 3.41. Found: C, 55.21; H, 4.94; N, 3.09.

Synthesis of 11. THF (1 mL) was added to a mixture of *trans*-[$PdCl_2(PPh_3)_2$] (35.5 mg, 0.05 mmol) and **9** (20.0 mg, 0.05 mmol). After 4 h of stirring the yellow slurry turned into an orange solution, from which THF was removed. Addition of dichloromethane (4 mL) induced the precipitation of the lithium salts, which were filtered off. After evaporation of dichloromethane, the obtained solid residue was washed with hexanes (3 mL) to give **11** as an orange solid (31.7 mg, 87%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.5 (d, $^3J_{P,P}$ = 6.5 Hz, P^{III}), 46.2 (d, $^3J_{P,P}$ = 6.5 Hz, P^V) (s). ^1H NMR ($CDCl_3$): δ 3.05 (2H, d, $^3J_{P,H}$ = 6.0 Hz, PCH_2), 6.67 (1H, tt, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 2.5 Hz, *p*-C*H*(NPh)), 6.85 (2H, m, *m*-C*H*(NPh)), 7.23−7.30 (8H, m, *o*-C*H*(NPh), *m*-(PPh_3)), 7.36 (3H, dt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{P,H}$ = 2.0 Hz, *p*-C*H*(PPh_3)), 7.43 (4H, td, $^3J_{H,H}$ = 7.5 Hz, $^4J_{P,H}$ = 3.0 Hz, *m*-C*H*(PPh_2)), 7.51−7.57 (8H, m, *p*-C*H*(PPh_2), *o*-C*H*(PPh_3)), 7.73 (4H, m, *p*-C*H*(PPh_2)). ^{13}C NMR ($CDCl_3$): δ 29.5 (dd, $^1J_{P,C}$ = 85.0 Hz, $^3J_{P,C}$ = 4.5 Hz, PCH_2), 123.3 (s, *p*-CH(NPh)), 128.5 (d, $^1J_{P,C}$ = 86.0 Hz, C^{IV}-(PPh_2)), 129.0 (s, *m*-*C*H(NPh)), 129.4 (d, $^3J_{P,C}$ = 11.0 Hz, *m*-*C*H(PPh_3)), 130.1 (dd,

$^3J_{P,C}$ = 10.5 Hz, $^4J_{P,C}$ = 1.0 Hz, *o-CH*(NPh)), 130.3 (d, $^3J_{P,C}$ = 11.5 Hz, *m-CH*(PPh$_2$)), 131.9 (d, $^1J_{P,C}$ = 53.5 Hz, C^{IV}-(PPh$_3$)), 132.2 (d, $^2J_{P,C}$ = 2.5 Hz, *p*-CH(PPh$_3$)), 134.4 (d, $^4J_{P,C}$ = 2.5 Hz, *p*-CH(PPh$_2$)), 134.9 (d, $^2J_{P,C}$ = 9.0 Hz, *o*-CH(PPh$_2$)), 136.5 (d, $^2J_{P,C}$ = 11.0 Hz, *o*-CH(PPh$_3$)) 149.6 (dd, $^2J_{P,C}$ = 3.0 Hz, $^3J_{P,C}$ = 1.5 Hz, *C*^{IV}-(NPh)). Anal. Calcd for $C_{37}H_{32}$ClNPdP2S: C, 61.17; H, 4.44; N, 1.93. Found: C, 61.03; H, 4.364; N, 2.02.

Synthesis of 12. THF (2 mL) was added to a mixture of dichloro(*p*-cymene)ruthenium(II) dimer (23.2 mg, 0.038 mmol) and **9** (30.0 mg, 0.076 mmol) at room temperature, immediately giving a red solution. After 2 h of stirring, THF was removed. The residue was dissolved in dichloromethane (3 mL), inducing the precipitation of the lithium salts, which were filtered off. After evaporation of dichloromethane, the obtained solid residue was washed with hexanes (3 mL) to give **12** as a red solid (34 mg, 76%). ^{31}P{^{1}H} NMR (d_8-THF): δ 36.9 (s). ^{1}H NMR (CDCl$_3$): δ 1.15 (6H, d, $^3J_{H,H}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.99 (3H, s, C*H*$_3$), 2.67 (1H, d, $^3J_{H,H}$ = 13.0 Hz, PC*H*$_2$), 2.80 (1H, sept, $^3J_{H,H}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 4.12 (1H, vt, $^3J_{H,H}$ = $^2J_{P,H}$ = 13.0 Hz, PC*H*$_2$), 4.64 (1H, d, $^3J_{H,H}$ = 5.5 Hz, CH(*p*-cymene)), 4.76 (2H, d, $^3J_{H,H}$ = 5.5 Hz, CH(*p*-cymene)), 4.90 (1H, d, $^3J_{H,H}$ = 5.5 Hz, CH(*p*-cymene)), 6.64 (1H, vtd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 0.5 Hz, *p*-CH(NPh)), 6.85 (2H, t, $^3J_{H,H}$ = 7.5 Hz, *o*-CH(PPh$_2$)), 7.18 (2H, m, *m*-CH(PPh$_2$)), 7.25 (1H, t, $^3J_{H,H}$ = 7.0 Hz, *p*-CH(PPh$_2$)), 7.38 (2H, d, $^3J_{H,H}$ = 7.5 Hz, *m*-C*H*(NPh)), 7.52 (4H, td, $^3J_{H,H}$ = 7.0 Hz, $^3J_{P,H}$ = 11.5 Hz, *o*-C*H*(PPh$_2$)), 7.57 (1H, d, $^3J_{H,H}$ = 7.0 Hz, *p*-C*H*(PPh$_2$)), 7.82 (2H, dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{P,H}$ = 10.1 Hz, *m*-C*H*(PPh$_2$)). ^{13}C NMR (CDCl$_3$): δ 14.0 (s, CH$_3$), 18.3, 18.5 (s, CH(*C*H$_3$)$_2$), 27.07 (s, *C*H(CH$_3$)$_2$), 28.8 (d, $^1J_{P,C}$ = 84.0 Hz, PCH$_2$), 73.2, 79.2, 79.3, 80.8 (s, *C*H(*p*-cymene)), 90.9, 99.0 (s, *C*^{IV}-(*p*-cymene)), 118.3 (d, $J_{P,C}$ = 2.0 Hz, *p*-CH(NPh)), 124.0 (d, $J_{P,C}$ = 1.0 Hz, *C*H(NPh)), 124.4 (d, $J_{P,C}$ = 9.0 Hz, *C*H(PPh$_2$)), 124.6 (d, $J_{P,C}$ = 11.50 Hz, *C*H(PPh$_2$)), 125.3 (d, $J_{P,C}$ = 7.0 Hz, *C*H(NPh)), 126.1 (d, $^1J_{P,C}$ = 89.0 Hz, *C*^{IV}-(PPh$_2$)), 127.9 (s, *C*H-(PPh$_2$)), 128.4 (s, *C*H(PPh$_2$)), 129.8 (d, $J_{P,C}$ = 9.0 Hz, *C*H(PPh$_2$)), 130.1 (d, $J_{P,C}$ = 9.0 Hz, *C*H(PPh$_2$)), 151.2 (s, *C*^{IV}-(NPh)). Anal. Calcd for $C_{29}H_{31}$ClNPRuS: C, 58.72; H, 5.27; N, 2.36. Found: C, 58.61; H, 5.20; N, 2.21.

Table 1. Crystal Data and Structure Refinement Details for 11

mol formula	$C_{37}H_{32}ClNP_2PdS$
mol wt	726.49
cryst habit	orange block
cryst dimens (mm)	0.14 × 0.12 × 0.10
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.612(1)
b (Å)	16.430(1)
c (Å)	21.208(1)
α (deg)	90.00
β (deg)	102.922(1)
γ (deg)	90.00
V (Å^3)	3264.5(4)
Z	4
d (g cm^{-3})	1.478
F(000)	1480
μ (cm^{-1})	0.840
θ_{max} (deg)	27.47
hkl ranges	−9 to +12; −21 to +19; −27 to +27
no. of measd/indep rflns	23 979/7391
no. of rflns used	4991
R_{int}	0.0449
abs cor	multiscan; 0.8915 min, 0.9207 max
no. of params refined	388
rflns/param	12
R1/wR2 ($I > 2\sigma(I)$)	0.0405/0.0970
GOF	0.956
difference peak/hole (e Å^{-3})	0.938(0.090)/−0.626(0.090)
CCDC number	784153

X-ray Crystallography. Data were collected at 150 K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.710 69 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structure was solved using SIR 97[20] and Shelxl-97.[21] ORTEP drawings were made using ORTEP III for Windows.[22]

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Supporting Information Available: CIF files giving crystallographic data for **3**, **6**, and **11**, figures giving ORTEP plots of **3** and **6**, and tables giving crystal data and structural refinement details for **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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