Monomeric Alkoxo and Amido Methylnickel(II) Complexes. Synthesis and Heterocumulene Insertion Chemistry

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Fluoride displacement from the complex Ni(Me)(F)(dippe) by LiOR or LiNRR′ provides an efficient method for the synthesis of the corresponding mononuclear Ni(II) alkoxo or amido complexes. These complexes undergo addition reactions to heterocumulenes (CO_2, PhNCO, PhNCS), leading to the formal insertion of these molecules into the Ni−O or Ni−N bonds. The dialkylamido complexes decompose through β-hydrogen elimination processes, which selectively afford η^2-imine Ni(0) compounds.

Introduction

Late transition metal complexes displaying covalent, nondative M−X bonds, where X is a hard heteroatom donor (F, OR, NR_2), have received much attention in recent years[1] because of their implication as reactive intermediates in important catalytic transformations.[1b,2] Their strongly basic and nucleophilic reactivity has been interpreted as a result of the strong polarization of the M−X bond and the absence of important π metal−ligand (p−d) interactions.[3]

As a continuation of our current work on Ni and Pd complexes displaying covalent M−O and M−N bonds,[4] we have recently communicated[5] that the synthesis of the corresponding hydroxo, alkoxo, and amido derivatives from a Ni(Me)(X)(dippe) (dippe = $^{i}Pr_2PCH_2CH_2P^{i}Pr_2$) and lithium hydroxide, *tert*-butoxide, or pyrrolidinide is greatly improved when X = F. However, while the hydroxide complex could be structurally characterized, the thermal instability of the *tert*-butoxide and pyrrolidinide derivatives prevented their isolation. In this contribution we extend the scope of our synthetic methodology, reporting the synthesis, isolation, and structural characterization of new alkoxo and amido complexes of nickel of the type Ni(Me)(OR)(dippe) and Ni(Me)(NRR′)(dippe) (R, R′ = alkyl). The latter are highly unusual compounds since most of the available examples of group 10 amido complexes are currently limited to arylamides,[3c,6] silylamides,[7] and the parent amidonickel complex (PCP^{iPr})Ni-NH_2[4a] (PCP^{iPr} = C_6H_3-2,6-$(CH_2P^{i}Pr_2)_2$). In addition, we explore the reactivity of those complexes toward heterocumulenes (CO_2, PhNCO, and PhNCS), a reaction that has been used as a probe to gauge the nucleophilicity of metal alkoxo and amido complexes.[1d,6a,8]

Results and Discussion

Synthesis and Characterization of Ni Alkoxo and Amido Complexes. Transition metal alkoxides and amides are usually prepared by simple halide metathesis reactions with the corresponding alkaline derivatives,[9] but this method often proves

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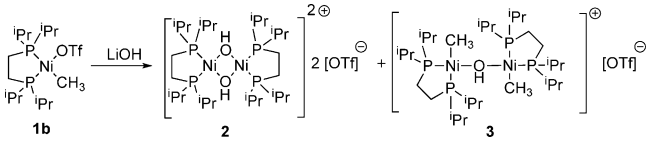
Scheme 1

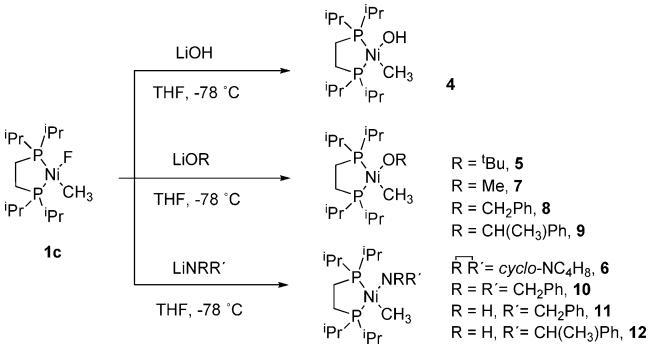


difficult in the case of the late transition elements.[1a] One of the most frequent alternatives to this procedure is to replace halide by a weakly coordinated ligand that can be easily displaced, such as triflate.[3c] With the aim of developing a general method for the synthesis of monomeric nickel complexes displaying a chelating diphosphine and mutually *cis* alkyl and alkoxo and amido compounds, we have investigated the reaction of the methyl complexes Ni(Me)(X)(dippe) (X = Cl (**1a**), OTf (**1b**), and F (**1c**)) with alkaline hydroxides, alkoxides, and amides. The chloro and fluoro complexes are prepared in good yields from $NiMe_2$(dippe)[10] upon reaction with NMe_3·HCl and NEt_3·3HF, respectively, as we reported in preliminary form.[5] Similarly, the triflate **1b** was generated in THF solution by reaction with HOTf and used directly. The $^{31}P\{^1H\}$ spectrum of the reaction mixture showed that **1b** is cleanly formed (two resonances at δ 65.6 and 77.8 ppm), but attempts to isolate the product were complicated by partial hydrolysis to the dinuclear hydroxide $[Ni(\mu\text{-OH})(dippe)_2]^{2+}(OTf^-)_2$, **2**.[11] Pörschke has prepared related triflate [Ni(Me)(OTf)(dtbpe)] (dtbpe = 1,2-(di-*tert*-butyl)phosphino)ethane) following a similar procedure.[12]

Preliminary exploration of **1a** and **1b** as starting materials in ligand metathesis reactions was not satisfactory and did not allow the isolation of the desired hydroxo or alkoxo products. Thus, the chloro precursor **1a** does not react with sodium or lithium hydroxide in THF and upon exposure to MO^{t}Bu (M = Li, K) undergoes incomplete chloride displacement. The reaction of **1b** with lithium hydroxide is more complex and leads to a mixture of **2** and a new product, tentatively formulated as the dinuclear hydroxide **3** on the basis of its ^1H NMR spectrum, which displays characteristic OH (δ −2.28) and CH_3 (δ 0.39) resonances with 1:6 intensity ratio (Scheme 1). Several dinuclear Pd and Pt complexes bridged by a single hydroxide ligand are known.[13] These results suggest that, while chloride displacement by hydroxide or alkoxide ligands is a difficult process on the coordination sphere of nickel, the lability of the triflate group favors the formation of kinetically stable dinuclear species, complicating the outcome of the exchange reaction.

In contrast with **1a** and **1b**, the fluoride precursor **1c** proved to be a valuable starting material for the synthesis of the desired products. Monitoring the reactions of this compound with LiOH, LiO^{t}Bu, and $LiNC_4H_8$ in THF by $^{31}P\{^1H\}$ NMR showed them to proceed cleanly with quantitative transformation of **1c** into the corresponding hydroxo (**4**), alkoxo (**5**), and amido (**6**) derivatives (Scheme 2).[5] Late transition metal fluoride complexes are reactive compounds[14] that display higher basicity or nucleophilicity than the related halides,[15] but it has been shown

Scheme 2



that typically soft, late transition metals such as Pt display only slightly less affinity for the hard fluoride anion than for the heavier halides.[16] In Co and Rh complexes, this affinity decreases in the order F > Cl > Br > I.[17] Therefore, it seems likely that the driving force for this reaction is not the (presumed) weakness of the late transition metal−fluoride bond, but the formation of the very stable salt LiF. The contribution of this factor to the overall energy balance of the reaction can be estimated as ca. 200−300 kJ mol^{-1}, if the lattice energy of LiF, 1030 kJ mol^{-1}, is compared to that of LiCl (834 kJ mol^{-1}), NaCl (769 kJ mol^{-1}), or KCl (701 kJ mol^{-1}).[18]

As represented in Scheme 2, we have successfully extended this strategy to the synthesis of a number of new alkoxo (**7**−**9**) and amido complexes (**10**−**12**). Direct monitoring of the reaction of **1c** with the corresponding lithium alkoxides and amides shows that these transformations also take place in a very selective manner, affording a single product in each case, together with a precipitate of insoluble LiF.

In contrast to the thermally unstable *tert*-butoxide **5**, the alkoxides **7**−**9** could be obtained as crystalline orange solids, in 45, 62, and 58% isolated yield, respectively. They have been fully characterized by elemental analysis and NMR. Apart from the expected signals of the OR group, these spectra are very similar to those of the hydroxide **4**. For example, their $^{31}P\{^1H\}$ spectra display characteristic AX spin systems with $\delta_A \approx 64$ and $\delta_X \approx 75$ ppm and $J_{AX} = 7-11$ Hz. In addition, the methoxide **7** has been subjected to an X-ray diffraction study, as the number of structurally characterized monomeric alkoxides of Ni is small.[3c,4a,19]

An ORTEP representation of one of the two independent molecules found in the asymmetric unit (which display no significant differences) is shown in Figure 1, together with some selected bond distances and angles. The molecule displays a slightly distorted square-planar structure, with the Ni−O−CH_3 fragment lying nearly coplanar with the mean coordination plane (dihedral angle, 17.1(3)°). As it is often found in late transition metal alkoxides,[1a,20] the C−O bond length (1.345(4) Å) is somewhat shorter than the standard C−O bond (1.43 Å). Although this C−O bond shortening has been connected with the tendency of alkoxides to decompose via β-hydride elimina-

(10) This compound is readily obtained from $NiCl_2$(dippe) and LiMe (see Experimental Section). Its synthesis from $NiMe_2$(pyridine)$_2$ and dippe has been reported before: Cámpora, J.; López, J. A.; Maya, C.; Palma, P.; Carmona, E.; Valerga, P. *J. Organomet. Chem.* **2002**, *643*, 331.

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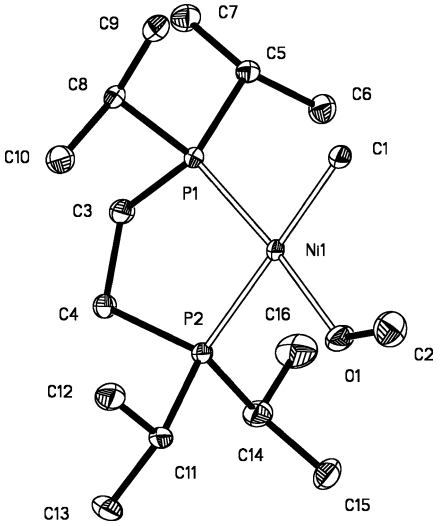

Figure 1. ORTEP view of **7**. Selected bond lengths (Å) and angles (deg) (one of two independent molecules in the asymmetric unit): Ni(1)−O(1), 1.878(2); Ni(1)−C(1), 1.954(2); Ni(1)−P(1), 2.1264(7); Ni(1)−P(2), 2.1911(7); O(1)−C(2), 1.345(4); O(1)−Ni(1)−C(1), 94.27(10); C(1)−Ni(1)−P(1), 91.20(16); O(1)−Ni(1)−P(2), 88.60(14); P(2)−Ni(1)−P(1), 89.22(6); Ni(1)−O(1)−C(2), 125.8(2).

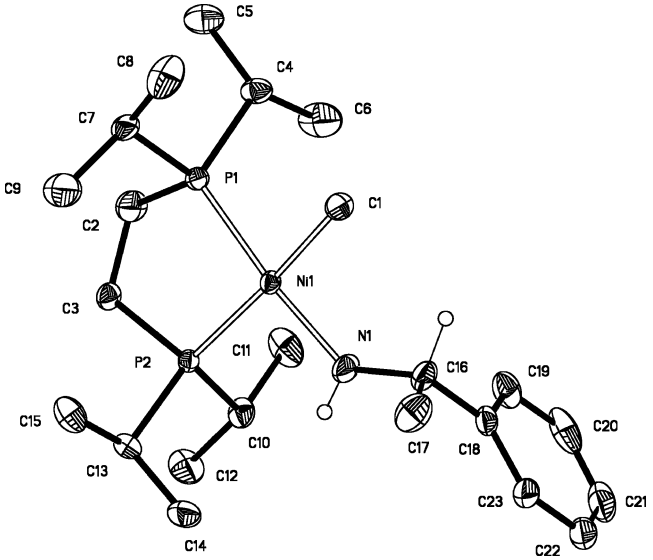

Figure 2. ORTEP view of **12**. Selected bond lengths (Å) and angles (deg): Ni(1)−N(1), 1.860(3); Ni(1)−C(1), 1.977(3); Ni(1)−P(1), 2.1248(8); Ni(1)−P(2), 2.2056(8); N(1)−C(16), 1.459(4); N(1)−Ni−C(1), 92.15(13); C(1)−Ni(1)−P(1), 87.87(10); N(1)−Ni(1)−P(2), 91.23(9); P(2)−Ni(1)−P(1), 88.78(3); C(16)−N(1)−Ni(1), 133.1(2); C(16)−N(1)−H(1N), 120.2; Ni(1)−N(1)−H(1N), 106.7.

tion,[21] it has also been explained as a result of a Coulombic attractive interaction between the carbon and oxygen atoms of the strongly polarized O−C functionality.[22] In any case, this bond contraction is less pronounced in complex **7** than in the related compounds Ni(PCP^{iPr})(OMe)[4a] and Ni(η^5-C_5Me_5)(PEt_3)(OMe).[3c] Other bond distances in this molecule can be considered normal for this kind of complexes. Thus, the Ni−O bond distance, 1.878(2) Å, is almost identical to that of hydroxide complex **4**, 1.877(4) Å. The methoxide and hydroxide ligands exert a similar *trans* influence, as indicated by the similar values of the (NiP1)−(NiP2) bond length differences (0.057 Å in **4** and 0.065 Å in **7**).

The lithium fluoride displacement reaction also proves useful in the synthesis of a range of secondary and primary amido complexes, including the previously reported pyrrolidinide **6**. The hydrolytic sensitivity and high solubility in hydrocarbon solvents thwarted the isolation of crystalline samples of **6**, **10**, and **11**. In addition, these compounds gradually decompose at room temperature, making it difficult to gather spectroscopic data. In spite of this, full NMR data (^{1}H, ^{13}C, and ^{31}P) have been obtained for complexes **10**−**12**, which confirm the proposed structures. Interestingly, the spectra of the primary and secondary amide complexes display some differences. For example, the ^{31}P{^{1}H} spectrum of **10** is fairly similar to that of **6**, both of them displaying two signals at ca. δ 50 and 69 ppm, with negligible $^2J_{PP}$ constants. In contrast, the corresponding ^{31}P{^{1}H} signals for the primary amides **11** and **12** occur at δ 69 and 78 ppm, with a noticeable coupling of ca. 5 Hz. The ^{1}H and ^{13}C{^{1}H} spectra of the four compounds display the expected signals for the amido and methyl fragments. Only one ^{1}H signal is observed for the non-diastereotopic benzyl methylene protons of **10** and **11**, but in the former this signal appears as a singlet at δ 4.10 ppm, while in the latter compound, it is shifted to lower field (δ 4.62 ppm) and split into a doublet of doublets by couplings with one of the ^{31}P (J_{HP} = 4 Hz) nuclei and the NH proton (J_{HH} = 7.5 Hz). The same couplings are also observed in the methyne resonance of **12**. The NH signal cannot be directly observed in the ^{1}H spectra of **11** and **12** because it is obscured by the intense resonances of the diphosphine ligand, but the coupling to the methylene or methyne protons allowed it to be located at ca. δ 1.1 ppm in the COSY spectra. There is also a difference in the ^{13}C{^{1}H} N-CH_2 signals of the dibenzylamide complex (δ 60.0, s) and the monobenzylamide, which appears ca. 8 ppm upfield (δ 51.7 ppm). The ^{13}C resonances of the N-bound carbon atoms of the two primary amides show couplings of 5 Hz with one phosphorus nucleus, which is not observed in the case of **10**. As shown below, secondary amides are very prone to undergo β-hydrogen elimination, while the decomposition of the primary derivatives involves a more complex process, apparently involving both β-elimination and disproportionation routes.[5] The small but noticeable differences observed in the NMR spectra of the two kinds of complexes suggest that the primary and secondary amido groups could adopt different conformations in solution, which could be connected to their different thermal behavior.

The lower solubility of compound **12** allowed the growth of dark red crystals from a concentrated pentane solution at −20 °C, which proved suitable for X-ray diffraction. The crystal structure of this compound is given in Figure 2. As can be immediately noticed, the amido ligand adopts a remarkable configuration. In contrast with most square-planar complexes, where bulky ligands tend to orient perpendicular to the coordination plane in order to minimize steric repulsions, the alkyl chain of the primary amido group lies almost exactly in the plane, bringing the N−C bond to the *syn-periplanar* position relative to the Ni−C bond, with a Me−Ni−N1−C16 dihedral angle of 1.1(4)°. Furthermore, the amine H atom has been located in a position that strongly suggests a planar configuration of the N atom. These features are strongly reminiscent of those found in Ni(NH_2)(PCP^{iPr}), which also displays a coplanar and apparently flat NH_2 group.[4a] Noteworthy, the metal−nitrogen bond (1.860(3) Å) is somewhat short compared to covalent Ni−N bonds in arylamides[6] (1.932 Å), amidates[6] (Ni−N(R)C-

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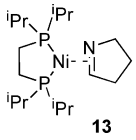


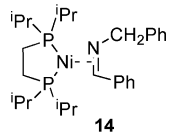


Figure 3. η^2-Imine complexes of Ni(0) **13** and **14**.

(O)R′ (ca. 1.98 Å), and pyrrolides[23] and other heterocyclic derivatives[24] (1.88−1.95 Å), or even in the parent amide Ni−NH_2 (1.872 Å).[4a]

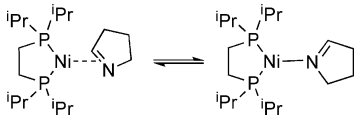
Planar nitrogen amido groups have been previously observed in group 10 arylamides,[6,25] but these display distinctly short N−C bonds, a feature that has been attributed to π delocalization of the nitrogen lone pair in the aromatic ring. In the case of aliphatic amides, planarity could arise from a hyperconjugative interaction of the nitrogen lone pair with empty σ^* orbitals of adjacent C−H or C−C bonds. However, the N−C distance in **12** (1.459(4) Å), similar to the standard value in aliphatic amines (ca. 1.45 Å), offers little support for such an effect. On the other hand, although the relatively short Ni−N could suggest the existence of some ligand to metal pπ−dπ donation, this is unlikely, as the only empty d orbital in the square-planar d^8 center ($d_{x^2-y^2}$) lacks the adequate symmetry for an *in-plane* π interaction with the amido group. In fact the Ni−N distance, albeit relatively short, is appreciably longer than in the formally 14 e, tricoordinated amide Ni(NH-$C_6H_3{}^iPr_2$-2,6)(dtbpe)$^+$ (1.768 Å), where such a π interaction becomes more likely.[6b] Therefore, we cannot offer a satisfactory explanation for the unusual conformation of the alkylamido group. However, the similar, nearly coplanar configuration of the methoxide group in **7** suggests that similar effects may be at play in both compounds. In fact, both complexes display very similar Ni−P bonds, indicating that these sense similar influences from the alkoxo and amido groups.

As previously mentioned, the amido complexes are thermally unstable in solution. Thermolysis of complexes **6** and **10** takes place over several hours at room temperature or within 30 or 45 min at 40 or 60 °C, respectively. The conversion is very clean at temperatures slightly above room temperature, affording the η^2-imine derivatives **13** and **14** (Figure 3), respectively, presumably through a β-hydrogen elimination reaction followed by reductive elimination of methane, which has been identified by GC.

The decomposition of the two primary amide derivatives, **11** and **12**, is less clean, affording a mixture of $NiMe_2$(dippe), Ni(dippe)$_2$, and the corresponding η^2-imine complexes, identified on the basis of their characteristic ^{31}P spectra, very similar to those of **13** and **14**, consisting of AB spin systems with relatively large values of the $^2J_{PP}$ constant (>65 Hz).

Complexes **13** and **14** have been obtained as a crystalline dark orange solid (**13**) and an orange oil (**14**), very soluble in hydrocarbon solvents. Their ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the proposed η^2-binding mode of the imine ligand and have been fully assigned with the aid of two-dimensional COSY, NOESY, and HMQC experiments. For example, the imine methyne carbon ^{13}C signal occurs at δ 71.7 for **13** and 74.0 ppm for **14**, in both cases split as a doublet by the coupling to one of the phosphorus nuclei. The side-on

Scheme 3



coordination of the imine introduces asymmetry in these molecules, causing chemical inequivalence of all four ^{i}Pr groups of the diphosphine as well as the methylene protons, which become diastereotopic. However, while the ^1H spectrum of **14** is sharp at room temperature, that of the pyrroline complex appears broad, gaining normal resolution below −20 °C (at 300 MHz). Heating above room temperature (35−45 °C) causes the signals of each pair of diastereotopic methylene protons to coalesce, while the complex pattern of the diphosphine ligand resonances simplifies. At the same time, the $^{31}P\{^1H\}$ spectrum becomes broader, but the fast exchange limit could not be reached because the complex decomposes above 55 °C. The energy barrier associated with this fluxional process can be estimated to amount to 15.5 kcal mol^{-1} on the basis of the coalescence temperatures of the methylenic signals. The apparent symmetrization of the molecule can be explained by a rapid, reversible dissociation of the η^2-imine ligand from nickel. However, since 1-pyrroline is known to be an unstable molecule,[26] it is likely that such dissociation is only partial, consisting in the exchange between the η^2 and η^1 coordination, as shown in Scheme 3. The readiness of the imine ligand motion in **13** contrasts with the nonfluxional behavior of the similar complex **14**. Although there is no obvious reason for this difference, the mobility of the pyrroline ligand is likely to be facilitated by the lack of steric hindrance at the nitrogen atom.

The unusual dynamic behavior of complex **13** prompted us to confirm its structure by an X-ray diffraction study. Its crystal structure is shown in Figure 4. The formally three-coordinated complex displays the nickel atom in an approximately trigonal-planar environment, with the imine ligand occupying one of the coordination positions in the expected side-on coordination mode. The C−N bond distance (1.352(3) Å) is appreciably shorter than in a recently reported η^2-imine Ni(I) complex (1.435 Å).[26] This is somewhat surprising, as the strongly electron-back-donating Ni(0) center is expected to decrease the C═N bond order more efficiently than Ni(I). The C═N bond lengths in the other two Ni(0)-η^2-imine complexes are only slightly longer than that of **13**.[28]

Heterocumulene Insertion Reactions into Ni−N and Ni−O Bonds. Transition metal alkoxide or amide complexes are known to react with CO_2 to afford addition products where this molecule is formally inserted into the M−O or M−N bond.[29] Studies on the carboxylation of Mo, W, Mn, and Rh alkoxides show this reaction not to require prior coordination of CO_2 to the metal center, but it is a concerted process probably involving a four-center transition state where the oxygen atom of the alkoxide partially donates one of its lone electron pairs to the weakly electrophilic C atom of CO_2, simultaneously with the formation of the M−OC(O) bond.[8] Therefore, the feasibility of this reaction provides an indication of the nucleophilicity of

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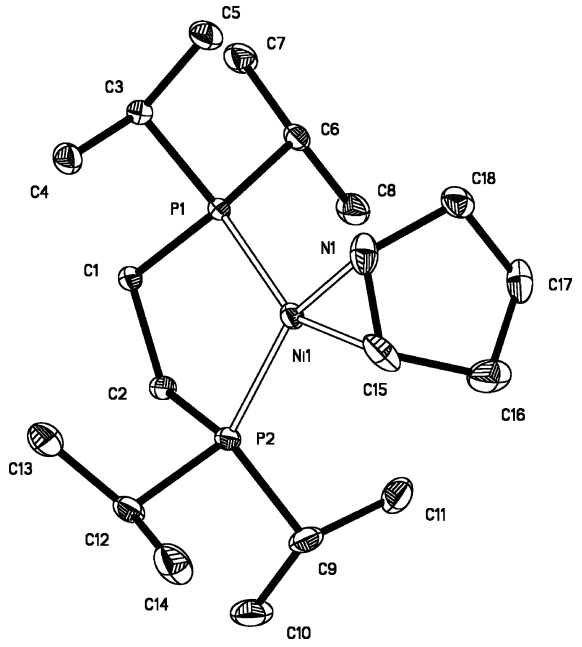
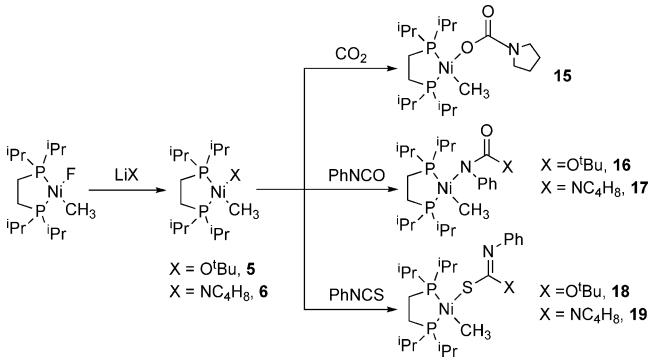


Figure 4. ORTEP view of **13**. Selected bond lengths (Å) and angles (deg) (one of two independent molecules in the asymmetric unit): Ni(1)−N(1), 1.9038(19); Ni(1)−C(15), 1.942(2); Ni(1)−P(1), 2.1561(5); Ni(1)−P(2), 2.1412(6); N(1)−C(15), 1.352(3); N(1)−Ni(1)−C(15), 41.13(10); N(1)−Ni(1)−P(1), 112.41(7); C(15)−Ni(1)−P(2), 114.85(8); P(2)−Ni(1)−P(1), 91.92(2).

Scheme 4



the alkoxide or amide ligands.[1a,b,8b,c] Related heterocumulene molecules such as carbon disulfide, isocyanates, or isothiocyanates react similarly to CO_2, giving rise to a variety of addition products.[1d,6a] We considered it worthwhile to examine the reactivity of *tert*-butoxide **5** and amide **6** with these heterocumulenes, in order have an indication of their relative nucleophilicities.

As shown in Scheme 4, complex **6** reacts cleanly with CO_2 to give a single product, **15**. The reaction is complete after dry CO_2 is bubbled for a few minutes into a solution of the amide, as indicated by the perceptible color lightening. Although the *tert*-butoxide **5** does also react under the same conditions, a complex mixture of products is produced, whose characterization was not attempted.

The spectral data of compound **15** support its formulation as a carbamate derivative. The presence of this functionality is evinced by a strong IR absorption at 1681 cm^{-1}, while its ^{31}P-{^{1}H} displays two resonances at δ 64.8 and 77.7 ppm, which resemble those of the alkoxide complexes **7**−**9**, as expected for a product displaying both Ni−Me and Ni−O bonds. The permanence of the methyl and pyrrolidine fragments is confirmed by the ^{1}H and the ^{13}C{^{1}H} spectra. The latter also displays a signal corresponding to the carboxylic carbon, whose position at δ 161.2 ppm can be considered typical of the carbamato ligand.[30]

Both the alkoxo and amido complexes react cleanly and selectively with phenyl isocyanate, yielding closely related addition products, **16** and **17**. Judging from the color change, similar to that observed in its carboxylation, the reaction of **6** with this heterocumulene is essentially instantaneous even at −80 °C. The reaction of **5** with PhNCO involves a more subtle color change, which is difficult to appreciate, but ^{31}P NMR monitoring shows it requires at least 15 min of stirring at room temperature to be complete. The elucidation of the structures of these two compounds poses the problem of assigning the precise coordination mode of the inserted functionality, which in principle may happen either through the N(Ph) or the O atoms. Both **16** and **17** display very similar spectroscopic properties, suggesting they share the same coordination mode. This can be noticed for example in the similarity of the ^{31}P-{^{1}H} spectra (two singlets at ca. δ 62 and 77 ppm) and the close chemical shifts of the ^{13}C resonance of the carbon atom of the inserted functionality (ca. δ 160 ppm). Unfortunately, the latter parameter appears to be quite insensitive to the structure of the XC(=Y)Z fragment, as it is also almost undistinguishable from those of carbamate **15**. The IR absorption bands of **16** and **17**, 1634 and 1659 cm^{-1}, respectively, are also similar to those of **15**. However, a positive structural assignment has been possible on the basis of the 2D NOESY spectra of the two compounds, both of them displaying NOE cross-peaks linking the signal corresponding to the *ortho* protons of the N-Ph group and one of the methyl groups of the diphosphine, revealing the spatial proximity of these two groups. Thus, on the basis of this clue, we favor the structures shown in Scheme 4 over the corresponding O-bound tautomers.

Incidentally, it must be mentioned that although spectroscopically pure samples of compound **17** have been obtained by simply dissolving in C_6D_6 the residue left after evaporation of the reaction of **6** with PhNCO, attempts to crystallize this compound led to the isolation of analytically pure samples of **17′**, a 1:1 adduct with the urea derivative *N*-phenylpyrrolydine-1-carboxamide, presumably arising from the reaction of **17** with small amounts of adventitious water. The NOESY ^{1}H NMR spectrum of this adducts displays EXSY cross-peaks linking the free and coordinated ureas, indicating that these undergo a slow exchange in solution.

Phenylisothiocyanate reacts selectively with **5** and **6**, but at a remarkably different rate. While the reaction with **5** takes several hours to complete, it is still very fast in the case of **6**, even at −80 °C. In the ^{31}P{^{1}H} spectra of the corresponding complexes **18** and **19**, one of the two signals appears at ca. 80 ppm, appreciably displaced to lower field than it is commonly observed in the remaining insertion products. This peculiarity may be attributed to the presence of Ni−S instead of Ni−O or Ni−N bonds, a proposal that has been confirmed by the determination of the crystal structure **19**. The methyl group and the S−C−NC$_4$H$_8$ part of the ligand were found distributed in two adjacent positions of the square-planar coordination, with occupancy factors of 0.6 and 0.4, respectively. In Figure 5 only one of the two disordered images is reported. A list of the most important bond distances and angles for the two disordered images is collected in the caption. The S-bound coordination mode is not unexpected, given the higher affinity of late

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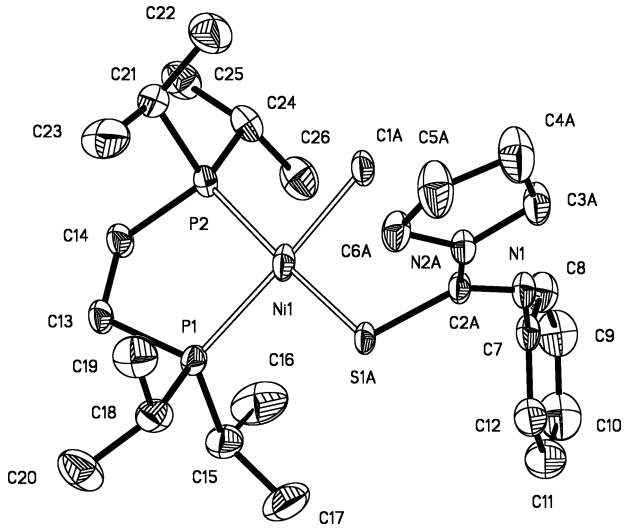

Figure 5. ORTEP view of **19** (only one of the two possible orientations of the organic moiety is represented for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−S(1A), 2.1224(9); Ni(1)−C(1A), 1.9998(11); Ni(1)−P(1), 2.1757(12); Ni(1)−P(2), 2.1471(11); N(1)−C(2A), 1.280(7); N(2A−C(2A), 1.347(8); S(1A)−Ni(1)−C(1A), 92.5(2); S(1A)−Ni(1)−P(1), 93.44(6); C(1A)−Ni(1)−P(2), 84.8(2); P(2)−Ni(1)−P(1), 89.26(4).

transition metals for sulfur than for the harder oxygen or nitrogen atoms. The S-bonded coordination mode can also be expected to be more stable because it preserves the stronger π-C═N rather than the weaker π-C═S bond.

As anticipated, the NOESY spectra of the phenylisothiocyanate insertion products show no cross-peaks between the N-Ph signals and those of the Ni(dippe) fragment, adding credence to the opposite coordination mode assigned to **16** and **17**, which do show such spatial relationship. It is also interesting to compare the lower frequency of the IR band associated with the functionality arising from phenylisothiocyanate insertion (**18**, 1539; **19**, 1548 cm^{-1}) with the corresponding ones of **15** and **16**, all of them above 1600 cm^{-1}. This observation also points to the existence of a C═O in the latter compounds and a C═NPh in the former, since the C═X bond stretch is probably one of the main contributors to these bands.

As a final comment, the qualitative differences observed in the reaction rates of **5** and **6** toward PhNCO and PhNCS clearly stress the higher nucleophilicity of the amide as compared to the alkoxide complex. The structure of the insertion products confirms that the preference for C═X insertion decreases in the order C═S > C═NPh > C═O, which doubtless has a thermodynamic origin. The same trend has been previously observed in the insertion of heterocumulenes into M−X complexes of Pd,[31] Rh,[32] and Ir.[1d] In spite of the favorable thermodynamics of C═S insertion, PhNCO reacts faster than PhCNS with **5**. This result contrasts with the trend observed in the reaction of heterocumulenes with Ni−C bonds,[33] where a migratory insertion mechanism has been proposed to operate, but fits well with a direct nucleophilic attack of the alkoxide on the central carbon of the heterocumulene, as PhNCO is expected to behave as a stronger electrophile than PhNCS.[34]

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Conclusions

Mononuclear alkoxo and amido methylnickel(II) derivatives can be prepared by displacement of fluoride from the precursor complex Ni(Me)(F)(dippe) (**1c**) with the corresponding lithium alkoxides or amides. The alkoxides Ni(OR)(F)(dippe) (R = Me, CH_2Ph, CH(Me)Ph) show higher stability than the previously reported *tert*-butoxide, but amido complexes are thermally unstable and slowly decompose in solution at room temperature. Secondary amides Ni(Me)(NR_2)(dippe) (NR_2 = pyrrolidino, $N(CH_2Ph)_2$) undergo a β-hydrogen elimination reaction, which ultimately leads to the corresponding η^2-imine complexes. However, the decomposition of primary amides Ni(Me)(NHR)(dippe) is less selective, affording a mixture of products. The alkoxide and amide complexes **5** and **6** readily react with CO_2, PhNCO, and PhNCS, giving rise to products arising from the formal insertion of the heterocumulenes into the Ni−O or the Ni−N bond. These reactions proceed faster with **6** than with **5**, illustrating the higher nucleophilicity of amide complexes. While the structure of the addition products indicates that the thermodynamic preference for C═X addition decreases in the order C═S > C═N > C═O, PhNCO reacts faster with **5** than PhNCS, suggesting that a direct nucleophilic addition mechanism operates in these reactions.

Experimental Section

General Considerations. All preparations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. Carbon dioxide was dried over P_2O_5 in a Fisher-Porter reactor charged at 3 bar for at least 1 week. Infrared spectra were recorded on a Bruker Vector 22 spectrometer, and NMR spectra on Bruker DRX 300 and 400 MHz spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. ^{31}P resonances are referenced to external 85% H_3PO_4, and ^{19}F to external $CFCl_3$. GC analyses were performed by using a Hewlett-Packard Model HP 6890 chromatograph and GC-MS on a Thermoquest Automasss Multi gas chromatograph−mass spectrometer. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Compounds **5**, **10**, **11**, **14**, and **15** could not be isolated in crystalline form due to their exceedingly high solubility in organic solvents. This feature, combined with their thermal and hydrolytic sensitivity, prevented the gathering of accurate elemental analysis data for these compounds. Although the amido complex **12** could be crystallized, repeated attempts to accomplish elemental analysis failed, presumably due to its thermal lability.

Synthesis of Ni(dippe)(CH_3)$_2$.[10] A 7.1 mL portion of a 1.4 M solution (10 mmol) of LiMe was added to a suspension of 1.96 g of Ni(dippe)Cl_2 (5 mmol) in THF cooled at −78 °C. After stirring 15 min at room temperature solvent was removed under vacuum and the yellow solid was extracted with diethyl ether. Crystallization at −20 °C gave the product as yellow crystals in 85% yield.

Synthesis of Ni(dippe)(CH_3)(Cl) (1a). A 600 mg sample of Ni(dippe)$(CH_3)_2$ (1.7 mmol) was dissolved in 5 mL of THF and added to a suspension of 167 mg of $(CH_3)_3N{\cdot}HCl$ (1.7 mmol) in 10 mL of THF. After stirring 4 h at room temperature solvent was removed under vacuum and the orange solid was extracted with 10 mL of THF. Concentration to dryness gave the product as an orange solid in 71% yield. ^1H NMR (CD_2Cl_2, 400 MHz): δ −0.10 (pt, 3H, $J^*_{HP} \approx 5.7$ Hz, Ni-C*H*$_3$), 1.18 (dd, 6H, $^3J_{HP} = 12.7$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me), 1.24 (dd, 6H, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me)), 1.31 (dd, 6H, $^3J_{HP} = 15.5$ Hz, $^3J_{HH} = 6.7$ Hz, PCH*Me*Me), 1.36 (dd, 6H, $^3J_{HP} = 15.2$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 1.70 (m, 2H, C*H*$_2$), 2.23 (m, 4H, C*H*). $^{13}C\{^1H\}$ NMR

(CD_2Cl_2, 75 MHz): δ −0.29 (dd, $^2J_{CP}$ = 73, 37 Hz, Ni-*C*H_3), 17.7 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 11 Hz, *C*H_2), 18.7 (s, PCH*Me*Me), 19.8 (d, $^2J_{CP}$ = 4, PCH*Me*Me), 20.3 (s, PCH*Me*Me), 24.4 (pt, $J^*_{CP} \approx$ 24 Hz, *C*H_2), 24.7 (d, $^1J_{CP}$ = 17 Hz, P*C*HMe$_2$), 26.3 (d, $^1J_{CP}$ = 29 Hz, P*C*HMe$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ 69.4 (d, $^2J_{PP}$ = 10 Hz), 81.1 (d, $^2J_{PP}$ = 10 Hz).

Synthesis of Ni(dippe)(CH$_3$)(OTf) (1b). A 7.7 mL amount of a 0.13 M solution of trifluoromethanesulfonic (triflic) acid (1 mmol) was added to 350 mg of Ni(dippe)(Me)$_2$ (1 mmol) in 10 mL of THF cooled at −78 °C. The reaction mixture was allowed to reach room temperature. Monitoring by $^{31}P\{^1H\}$ NMR revealed quantitative conversion of the dialkyl complex to the new product **1b**. $^{31}P\{^1H\}$ NMR (THF, 121 MHz): δ 65.6, 77.8. Working up the reaction mixture leads to the isolation of the dinuclear hydroxide [Ni(dippe)(μ-OH)]$_2$·2(OTf) (**2**).[11] Selected spectroscopic data for **2**: ^1H NMR (CD_2Cl_2, 300 MHz) δ −1.51 (d, 1H, $^3J_{HP}$ = 1.9 Hz, O*H*), 1.25 (dd, 12H, $^3J_{HP}$ = 13.9 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.56 (d, 4H, $^2J_{HP}$ = 11.3 Hz, C*H*$_2$), 1.67 (dd, 12H, $^3J_{HP}$ = 17.9 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 2.38 (m, 4H, PC*H*Me$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ 88.0.

Synthesis of Ni(dippe)(CH$_3$)(F) (1c). To a cooled (−78 °C) solution of Ni(dippe)(Me)$_2$ (702 mg, 2 mmol) in 10 mL of THF was added 2.7 mL of a 0.25 M solution of Et$_3$N·3HF. The reaction mixture was allowed to reach room temperature. The solvent was removed under vacuum and the residue was extracted with 10 mL of THF to afford an orange solution, which was concentrated to yield the product as orange crystals. Yield = 78%. Anal. Calcd for $C_{15}H_{35}FNiP_2$: C, 50.74; H, 9.94. Found: C, 50.52; H, 9.99. ^1H NMR (C_6D_6, 400 MHz): δ 0.47 (m, 3H, Ni-C*H*$_3$), 0.72 (m, 2H, C*H*$_2$), 0.82 (dd, 6H, $^3J_{HP}$ = 13.3 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 0.93 (m, 2H, C*H*$_2$), 1.02 (dd, 6H, $^3J_{HP}$ = 12.8 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.10 (dd, 6H, $^3J_{HP}$ = 15.5 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.41 (dd, 6H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.63 (m, 2H, PC*H*Me$_2$), 1.92 (m, 2H, PC*H*Me$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 2.8 (dd, $^2J_{CP}$ = 83 and 37 Hz, Ni-*C*H$_3$), 16.6 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 11 Hz, *C*H$_2$), 18.5 (s, PCH*Me*Me), 18.9 (s, PCH*Me*Me), 19.6 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.9 (d, $^2J_{CP}$ = 2 Hz, PCH*Me*Me), 24.0 (d, $^1J_{CP}$ = 13 Hz, P*C*HMe$_2$), 24.5 (pt, $J^*_{CP} \approx$ 24 Hz, *C*H$_2$), 25.5 (d, $^1J_{CP}$ = 28 Hz, P*C*HMe$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 64.6 (d, $^2J_{PF}$ = 50 Hz), 78.4 (d, $^2J_{PF}$ = 117 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 376 MHz): −224.0 (dd, $^2J_{FP}$ = 117 and 50 Hz).

Reaction of Ni(dippe)(CH$_3$)(OTf) (1b) with Lithium Hydroxide. A 1.26 mL sample of a 0.35 M solution of triflic acid (0.44 mmol) was added to 5 mL of a THF solution containing 155 mg of Ni(dippe)(Me)$_2$ (0.44 mmol) at −78 °C. After reaching room temperature, the reaction mixture was cooled again and 0.44 mmol of LiOH was added. Solvent was removed under vacuum and the residue was extracted with 0.8 mL of CD_2Cl_2. ^1H and $^{31}P\{^1H\}$ NMR show resonances of the hydroxide **2**, together with those of the complex **3**. Evaporation of the sample and extraction of the residue with C_6D_6 allowed removal of most of **2** and the recording of NMR spectra of **3**. ^1H NMR (C_6D_6, 300 MHz): δ −2.28 (s, 1H, OH), 0.39 (pt, 6H, $J^*_{HP} \approx$ 4.5 Hz, Ni-C*H*$_3$), 0.94 (dd, 12H, $^3J_{HP}$ = 13.7 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.13 (m, 24H, PCH*Me*Me), 1.34 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.73 (m, 4H, PC*H*Me$_2$), 1.99 (m, 4H, PC*H*Me$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 62.7, 75.6.

Synthesis of Ni(dippe)(CH$_3$)(OH) (4). Compound **1c** (355 mg, 1 mmol) dissolved in 10 mL of THF was added to a solution of LiOH in THF at −78 °C. The latter was previously prepared by adding 0.6 mL of a 1.6 M solution (1 mmol) of ^{n}BuLi in hexane to a cooled solution of 18 μL of water (1 mmol) in 10 mL of THF. After stirring to room temperature solvent was removed under reduced pressure, and the residue was extracted with 15 mL of diethyl ether. The product crystallized from this solution after cooling at −20 °C. Yield = 70%. Anal. Calcd for $C_{15}H_{36}ONiP_2$: C, 51.02; H, 10.28. Found: C, 50.85; H, 10.22. ^1H NMR (C_6D_6, 400 MHz): δ −0.49 (dd, 1H, $^3J_{HP}$ = 10.0, 3.0 Hz, O*H*), 0.18 (dd, 3H, $^3J_{HP}$ = 5.9, 4.4 Hz, Ni-C*H*$_3$), 0.79 (m, 2H, C*H*$_2$), 0.83 (dd, 6H, $^3J_{HP}$ = 9.9 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 0.97 (m, 2H, C*H*$_2$), 1.03 (dd, 6H, $^3J_{HP}$ = 12.5 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.10 (dd, 6H, $^3J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.51 (dd, 6H, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.68 (m, 2H, PC*H*Me$_2$), 2.13 (m, 2H, PC*H*Me$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ −0.6 (dd, $^2J_{CP}$ = 82 and 32 Hz, Ni-*C*H$_3$), 15.7 (pt, $J^*_{CP} \approx$ 19 Hz, *C*H$_2$), 16.9 (pt, $J^*_{CP} \approx$ 16 Hz, *C*H$_2$), 18.0 (s, PCH*Me*Me), 18.3 (s, PCH*Me*Me), 19.3 (s, PCH*Me*Me), 19.4 (s, PCH*Me*Me), 23.7 (m, P*C*HMe$_2$), 24.7 (d, $^1J_{CP}$ = 25 Hz, P*C*HMe$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 68.6 (d, $^2J_{PP}$ = 9 Hz), 77.3 (d).

Synthesis of Ni(dippe)(CH$_3$)(OC(CH$_3$)$_3$) (5). A 0.26 mL amount of a 1.7 M solution of LiBu^n (0.45 mmol) was added to 47 μL of *tert*-butanol (0.49 mmol) dissolved in 5 mL of THF at −78 °C. The reaction mixture was stirred and allowed to reach room temperature, then added to a cooled (−78 °C) solution of 160 mg of Ni(dippe)(Me)(F) (0.45 mmol) in 5 mL of THF. The solvent was removed under reduced pressure, and the residue was extracted with 0.8 mL of C_6D_6 and centrifuged to afford a dark red solution of the pure product. Previous attempts to crystallize this compound from cold hexane or pentane failed due to its high solubility in these solvents and low thermal stability. ^1H NMR (C_6D_6, 300 MHz): δ 0.22 (pt, 3H, $J^*_{HP} \approx$ 5.7 Hz, Ni-C*H*$_3$), 0.68 (m, 2H, C*H*$_2$), 0.86 (dd, 6H, $^3J_{HP}$ = 12.7 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.01 (dd, 6H, $^3J_{HP}$ = 11.9 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.14 (dd, 6H, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.49 (dd, 6H, $^3J_{HP}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me, 1.69 (s, 9H, C*Me*$_3$), 2.05 (m, 2H, PC*H*Me$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ −8.3 (dd, $^2J_{CP}$ = 80, 36 Hz, Ni-*C*H$_3$), 15.6 (dd, $^1J_{CP}$ = 15 Hz, $^2J_{CP}$ = 12 Hz, *C*H$_2$), 18.1 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.5 (d, $^2J_{CP}$ = 6 Hz, PCH*Me*Me), 19.6 (d, $^2J_{CP}$ = 3 Hz, PCH*Me*Me), 23.5 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 24.7 (d, $^1J_{CP}$ = 26 Hz, P*C*HMe$_2$), 35.9 (s, C*Me*$_3$), 70.1 (d, $^3J_{CP}$ = 4 Hz, *C*Me$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): δ 60.5 (d, $^2J_{PP}$ = 11 Hz), 70.4 (d).

Synthesis of [Ni(dippe)(CH$_3$)(NCH$_2$(CH$_2$)$_2$CH$_2$)] (6). A 0.22 mL amount of a 1.6 M solution of LiBu^n (0.35 mmol) in hexane was added at −78 °C to 32 μL of pyrrolidine (0.35 mmol) dissolved in 3 mL of THF. The reaction mixture was stirred and allowed to reach room temperature, then added to a cooled (−78 °C) solution of 123 mg of Ni(dippe)(Me)(F) (0.35 mmol) in 3 mL of THF. $^{31}P\{^1H\}$ NMR (THF, 121 MHz): δ 55.7 (d, $^2J_{PP}$ = 8 Hz), 72.3 (d). The low thermal stability of this compound prevented its isolation.

Synthesis of Ni(dippe)(CH$_3$)(OR) (R = CH$_3$, 7; CH$_2$Ph, 8; CH(CH$_3$)Ph, 9). These compounds were prepared by reaction of Ni(dippe)(CH$_3$)(F) **1c** with the lithium alkoxides as exemplified by the synthesis of compound **7**: 0.31 mL of a 1.6 M solution of LiBu^n (0.5 mmol) was added to 20 μL of methanol (0.5 mmol) dissolved in 5 mL of THF at −78 °C. The reaction mixture was stirred and allowed to reach room temperature, then added to a cooled (−78 °C) solution of 176 mg of Ni(dippe)(Me)(F) (0.5 mmol) in 3 mL of THF. After reaching room temperature, solvent was removed under reduced pressure and the solid was extracted with 5 mL of Et$_2$O. The product was obtained after crystallization at −20 °C in a 45% yield. Anal. Calcd for $C_{16}H_{38}ONiP_2$: C, 52.35; H, 10.43. Found: C, 52.40; H, 10.45. ^1H NMR (C_6D_6, 300 MHz): δ 0.23 (bs, 3H, Ni-C*H*$_3$), 0.84 (m, 6H, PCH*Me*Me), 1.07 (m, 12H, PCH*Me*Me), 1.45 (m, 6H, PCH*Me*Me), 1.70 (m, 2H, PC*H*Me$_2$), 2.05 (m, 2H, PC*H*Me$_2$), 4.08 (s, 3H, OC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ −1.8 (dd, $^2J_{CP}$ = 73 and 33 Hz, Ni-*C*H$_3$), 16.2 (dd, $^1J_{CP}$ = 16 Hz, $^2J_{CP}$ = 12 Hz, *C*H$_2$), 18.1 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.2 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.5 (d, $^2J_{CP}$ = 3 Hz, PCH*Me*Me), 23.4 (d, $^1J_{CP}$ = 14 Hz, P*C*HMeMe), 24.1 (dd, $^1J_{CP}$ = 25 Hz, $^2J_{CP}$ = 22 Hz, P*C*HMe$_2$), 24.8 (d, $^1J_{CP}$ = 25 Hz,

PC*H*Me$_2$), 52.9 (d, $^3J_{CP}$ = 4 Hz, OC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 63.6 (d, $^2J_{PP}$ = 8 Hz), 75.5 (d).

Compound 8: 62% yield after cristallization from Et_2O. Anal. Calcd for $C_{22}H_{42}ONiP_2$: C, 59.62; H, 9.55. Found: C, 59.16; H, 9.53. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.18 (pt, 3H, $J^*_{HP} \approx$ 5.0 Hz, Ni-C*H*$_3$), 0.77 (m, 2H, C*H*$_2$), 0.84 (dd, 6H, $^3J_{HP}$ = 12.8 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 0.98 (dd, 6H, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.10 (dd, 6H, $^3J_{HP}$ = 15.3 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.42 (dd, 6H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.68 (m, 2H, PC*H*Me$_2$), 2.04 (m, 2H, PC*H*Me$_2$), 5.20 (d, 2H, $^4J_{HP}$ = 3.2 Hz, OC*H*$_2$Ph), 7.18 (m, 1H, C$_{ar}$*H*$_p$), 7.39 (t, 2H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}$*H*$_m$), 7.86 (d, 2H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −2.2 (dd, $^2J_{CP}$ = 72 and 34 Hz, Ni-*C*H$_3$), 16.1 (dd, $^1J_{CP}$ = 17 Hz, $^2J_{CP}$ = 12 Hz, *C*H$_2$), 18.1 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.3 (d, $^2J_{CP}$ = 6 Hz, PCH*Me*Me), 19.5 (d, $^2J_{CP}$ = 3 Hz, PCH*Me*Me), 23.5 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 23.9 (dd, $^1J_{CP}$ = 25 Hz, $^2J_{CP}$ = 22 Hz, P*C*HMe$_2$), 24.9 (d, $^1J_{CP}$ = 26 Hz, P*C*HMe$_2$), 66.7 (d, $^3J_{CP}$ = 5 Hz, OCH$_2$Ph), 124.7 (s, *C*$_{ar}$H$_p$), 126.7 (s, *C*$_{ar}$H$_o$), 151.1 (s, *C*$_{ar}$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 64.1 (d, $^2J_{PP}$ = 8 Hz), 75.5 (d).

Compound 9: 58% yield after crystallization from pentane at −80 °C. Anal. Calcd for $C_{23}H_{44}ONiP_2$: C, 60.42; H, 9.70. Found: C, 59.82; H, 9.88. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.06 (pt, 3H, $J^*_{HP} \approx$ 5.1 Hz, Ni-C*H*$_3$), 0.79 (m, 6H, PCH*Me*Me), 1.02 (m, 6H, PCH*Me*Me), 1.40 (dd, 6H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.52 (dd, 6H, $^3J_{HP}$ = 14.5 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.63 (m, 2H, PC*H*Me$_2$), 1.76 (d, 3H, $^3J_{HH}$ = 6.2 Hz, OCH(C*H*$_3$)Ph), 2.08 (m, 2H, PC*H*Me$_2$), 5.27 (bs, 1H, OC*H*(CH$_3$)Ph), 7.19 (m, 1H, C$_{ar}$*H*$_p$), 7.40 (t, 2H, $^3J_{HH}$ = 7.4 Hz, C$_{ar}$*H*$_m$), 7.87 (d, 2H, $^3J_{HH}$ = 7.1 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −3.3 (dd, $^2J_{CP}$ = 72 and 34 Hz, Ni-*C*H$_3$), 18.0 (s, PCH*Me*Me), 18.5 (s, PCH*Me*Me), 19.1 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 23.2 (d, $^1J_{CP}$ = 13 Hz, P*C*HMeMe), 23.9 (d, $^1J_{CP}$ = 15 Hz, P*C*HMe$_2$), 24.9 (dd, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 8 Hz, P*C*HMe$_2$), 30.6 (s, OCH(*C*H$_3$)Ph), 69.3 (d, $^3J_{CP}$ = 5 Hz, O*C*H(CH$_3$)Ph), 124.7 (s, *C*$_{ar}$H$_p$), 126.5 (s, *C*$_{ar}$H$_o$), 155.4 (s, *C*$_{ar}$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 63.2 (d, $^2J_{PP}$ = 7 Hz), 75.2 (d).

Synthesis of Ni(dippe)(CH$_3$)(N(CH$_2$Ph)$_2$) (10). A 0.15 mL amount of a 1.6 M solution of LiBu^n (0.25 mmol) was added to 50 μL of dibenzylamine (0.25 mmol) dissolved in 3 mL of THF at −78 °C. The purple mixture was allowed to reach room temperature and then added to a cooled (−78 °C) solution of 90 mg of Ni(dippe)(Me)(F) (0.25 mmol) in 3 mL of THF. After reaching room temperature, solvent was removed under vacuum and the dark red residue was extracted with 0.6 mL of C_6D_6. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.25 (bs, 3H, Ni-C*H*$_3$), 0.87 (dd, 12H, $^3J_{HP}$ = 12.0 Hz, $^3J_{HH}$ = 6.9 Hz, PCH*Me*Me), 1.11 (dd, 6H, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.21 (dd, 6H, $^3J_{HP}$ = 14.8 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.69 (m, 2H, PC*H*Me$_2$), 1.85 (m, 2H, PC*H*Me$_2$), 4.10 (s, 4H, C*H*$_2$Ph), 7.18 (m, 2H, C$_{ar}$*H*$_p$), 7.33 (t, 4H, $^3J_{HH}$ = 6.9 Hz, C$_{ar}$*H*$_m$), 7.88 (d, 4H, $^3J_{HH}$ = 6.9 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −2.2 (dd, $^2J_{CP}$ = 68 and 29 Hz, Ni-*C*H$_3$), 18.1 (s, PCH*Me*Me), 18.3 (s, PCH*Me*Me), 19.5 (s, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 22.0 (pt, $J^*_{CP} \approx$ 19 Hz, P*C*HMe$_2$), 23.5 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 24.2 (m, P*C*HMe$_2$), 60.0 (s, *C*H$_2$Ph), 125.2 (s, *C*$_{ar}$H), 126.7 (s, *C*$_{ar}$H), 129.7 (s, *C*$_{ar}$H), 146.6 (s, *C*$_{ar}$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C, 121 MHz): δ 49.7, 69.2.

Synthesis of Ni(dippe)(CH$_3$)(NHCH$_2$Ph) (11). This complex is prepared following the method described above for complex **10**, using benzylamine instead of dibenzylamine. Like in the case of **10**, the residue obtained after removing the solvent was extracted with 0.6 mL of C_6D_6. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.32 (dd, 3H, $^3J_{HP}$ = 6.9 and 4.5 Hz, Ni-C*H*$_3$), 0.79−1.14 (m, 12H, PCH*Me*Me), 1.27 (dd, 6H, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.30 (dd, 6H, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.79 (m, 4H, PC*H*Me$_2$), 4.62 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 3.5 Hz, NHC*H*$_2$-Ph), 7.14 (m, 1H, C$_{ar}$*H*$_p$), 7.32 (t, 2H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}$*H*$_m$), 7.84 (d, 2H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −2.4 (dd, $^2J_{CP}$ = 68 and 34 Hz, Ni-*C*H$_3$), 18.1 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.0 (d, $^2J_{CP}$ = 6 Hz, PCH*Me*Me), 19.6 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 23.0 (dd, $^1J_{CP}$ = 24 Hz, $^2J_{CP}$ = 19 Hz, *C*H$_2$), 23.9 (d, $^1J_{CP}$ = 13 Hz, P*C*HMe$_2$), 24.9 (d, $^1J_{CP}$ = 24 Hz, P*C*HMe$_2$), 51.7 (d, $^3J_{CP}$ = 5 Hz, NH*C*H$_2$Ph), 124.8 (s, *C*$_{ar}$H), 151.5 (s, *C*$_{ar}$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 69.7 (d, $^2J_{PP}$ = 5 Hz), 78.5 (d).

Synthesis of Ni(dippe)(CH$_3$)(NHCH(CH$_3$)Ph) (12). A 0.21 mL portion of a 1.7 M solution of LiBu^n (0.35 mmol) was added to 45 μL of 1-phenylethylamine (0.35 mmol) dissolved in 3 mL of THF at −78 °C. The mixture was allowed to reach room temperature and added to a cooled (−78 °C) solution of 124 mg of Ni(dippe)(Me)(F) (0.35 mmol) in 3 mL of THF. After reaching room temperature, solvent was removed under vacuum and the dark red residue was extracted with 3 mL of pentane. The product was obtained after crystallization at −20 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.27 (dd, 3H, $^3J_{HP}$ = 7.1 and 4.5 Hz, Ni-C*H*$_3$), 0.84 (m, 12H, PCH*Me*Me), 1.12 (m, 12H, PCH*Me*Me), 1.72 (m, 2H, PC*H*Me$_2$), 1.77 (d, 3H, $^3J_{HH}$ = 6.4 Hz, NHCH(C*H*$_3$)Ph), 1.90 (m, 2H, PC*H*Me$_2$), 4.80 (m, 1H, NHC*H*(CH$_3$)Ph), 7.15 (m, 1H, C$_{ar}$*H*$_p$), 7.37 (t, 2H, $^3J_{HH}$ = 7.6 Hz, C$_{ar}$*H*$_m$), 7.90 (d, 2H, $^3J_{HH}$ = 7.2 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −3.2 (dd, $^2J_{CP}$ = 68 and 34 Hz, Ni-*C*H$_3$), 17.9 (s, PCH*Me*Me), 18.0 (s, PCH*Me*Me), 18.3 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 18.9 (d, $^2J_{CP}$ = 6 Hz, PCH*Me*Me), 19.2 (d, $^2J_{CP}$ = 6 Hz, PCH*Me*Me), 19.6 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 19.7 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 22.9 (dd, $^1J_{CP}$ = 24 Hz, $^2J_{CP}$ = 18 Hz, *C*H$_2$), 23.7 (d, $^1J_{CP}$ = 13 Hz, P*C*HMe$_2$), 24.4 (d, $^1J_{CP}$ = 13 Hz, P*C*HMe$_2$), 25.1 (d, $^1J_{CP}$ = 24 Hz, P*C*HMe$_2$), 31.1 (d, $^4J_{CP}$ = 3 Hz, NHCH(*C*H$_3$)Ph), 54.1 (d, $^3J_{CP}$ = 5 Hz, NH*C*H(CH$_3$)Ph), 124.5 (s, *C*$_{ar}$H), 126.0 (s, *C*$_{ar}$H), 126.8 (s, *C*$_{ar}$H), 156.0 (s, *C*$_{ar}$). ^{31}P{^{1}H} NMR ($C_6D_6$121 MHz): δ 68.8 (d, $^2J_{PP}$ = 5 Hz), 78.0 (d).

Synthesis of [Ni(dippe)(η^2-N=C(H)CH$_2$CH$_2$CH$_2$)] (13). A solution of lithium pyrrolidinide (38 mg, 0.5 mmol) in 3 mL of THF was added to a cooled solution (−78 °C) of Ni(dippe)(Me)(F) (178 mg, 0.5 mmol) in 3 mL of THF. The cooling bath was removed and the solution heated at 40 °C for 30 min. The solvent was then removed under vacuum and the residue extracted with hexane. Crystallization at −20 °C gave the product as a dark orange solid. Yield = 35%. Anal. Calcd for $C_{18}H_{39}NNiP_2$: C, 55.41; H, 10.08; N, 3.59. Found: C, 55.14; H, 10.63; N, 3.37. ^{1}H NMR (toluene-d_8, −20 °C, 300 MHz): δ 0.87 (m, 9H, PCH*Me*Me), 1.00 (m, 12H, C*H*$_3$), 1.34 (dd, 3H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 6.9 Hz, PCH*Me*Me), 1.72 (m, 4H, C*H*), 2.03 (m, 1H, C*H*$_2$ imine), 2.31 (m, 1H, C*H*$_2$ imine), 2.53 (m, 1H, C*H*$_2$ imine), 3.67 (m, 1H, C*H*$_2$ imine), 4.08 (m, 1H, C*H*$_2$ imine), 4.41 (d, 1H, $^3J_{HP}$ = 12.7 Hz, N=C*H* imine). ^{13}C{^{1}H} NMR (toluene-d_8, −20 °C, 75 MHz): δ 17.9 (s, PCH*Me*Me), 18.3 (s, PCH*Me*Me), 18.8 (s, PCH*Me*Me), 19.2 (s, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 19.9 (s, PCH*Me*Me), 20.1 (s, PCH*Me*Me), 20.4 (s, PCH*Me*Me), 20.6 (pt, $J^*_{CP} \approx$ 19 Hz, *C*H$_2$), 21.4 (pt, J^*_{CP} = 20 Hz, *C*H$_2$), 24.0 (dd, $^1J_{CP}$ = 11 Hz, $^3J_{CP}$ = 3 Hz, P*C*HMe$_2$), 24.4 (pt, $J^*_{CP} \approx$ 4 Hz, P*C*HMe$_2$), 24.6 (d, $^1J_{CP}$ = 5 Hz, P*C*HMe$_2$), 24.8 (dd, $^3J_{CP}$ = 6 Hz, obscured by peak at 24.4, P*C*HMe$_2$), 30.4 (s, *C*H$_2$ imine), 35.2 (d, $^3J_{CP}$ = 3 Hz, *C*H$_2$ imine), 61.3 (d, $^3J_{CP}$ = 2 Hz, *C*H$_2$ imine), 71.68 (d, $^2J_{CP}$ = 19 Hz, N=*C*H imine). ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C, 121 MHz): δ 57.7 (d, $^2J_{PP}$ = 81 Hz), 68.8 (d, $^2J_{PP}$ = 81 Hz).

Synthesis of Ni(dippe)(η^2-PhCH$_2$N=CHPh) (14). Complex **10** was prepared *in situ* according to the method described above. After removing the cooling bath, the reaction mixture was heated at 60 °C for 45 min. Evaporation of the solvent afforded a dark red residue, which was extracted with 0.6 mL of C_6D_6. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.34 (dd, 3H, $^3J_{HP}$ = 15.2 and 7.1 Hz, PCH*Me*Me), 0.62 (pt, 3H, $^3J_{HP} \approx {}^3J_{HH} \approx$ 8.2, PCH*Me*Me), 1.05−1.83 (m, 12H, PCH*Me*Me), 1.14 (dd, 3H, $^3J_{HP}$ = 14.2 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.27 (dd, 3H, $^3J_{HP}$ = 14.3 Hz, $^3J_{HH}$ = 6.9 Hz,

PCH*Me*Me), 1.52 (m, 1H, PC*H*Me$_2$), 1.60−1.86 (m, 3H, PC*H*Me$_2$), 4.00 (d, 1H, $^2J_{HH}$ = 14.5 Hz, PhC*H*HN=CHPh), 4.92 (dd, 1H, $^2J_{HH}$ = 14.5 Hz, $^4J_{HP}$ = 3.0 Hz, PhCH*H*N=CHPh), 4.98 (d, 1H, $^3J_{HP}$ = 6.5 Hz, PhCH$_2$N=C*H*Ph), 6.94 (t, 1H, $^3J_{HH}$ = 6.9 Hz, C$_{ar}H_p$), 7.08 (t, 1H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}H_p$), 7.14−7.27 (m, 4H, C$_{ar}H_m$), 7.65 (d, 2H, $^3J_{HH}$ = 7.5 Hz, C$_{ar}H_o$), 7.76 (d, 2H, $^3J_{HH}$ = 7.4 Hz, C$_{ar}H_o$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 15.5 (d, $^1J_{CP}$ = 21 Hz, *C*H$_2$), 16.8 (d, $^2J_{CP}$ = 3 Hz, PCH*Me*Me), 17.4 (s, PCH*Me*Me), 18.8 (pt, $J^*_{CP} \approx$ 8 Hz, P*C*HMe$_2$), 19.6 (s, PCH*Me*Me), 19.9 (s, PCH*Me*Me), 20.0 (s, PCH*Me*Me), 20.7 (pt, $J^*_{CP} \approx$ 19 Hz, *C*H$_2$), 23.6 (dd, $^1J_{CP}$ = 15 Hz, $^3J_{CP}$ = 6 Hz, P*C*HMe$_2$), 24.0 (dd, $^1J_{CP}$ = 11 Hz, $^3J_{CP}$ = 5 Hz, P*C*HMe$_2$), 24.3 (dd, $^1J_{CP}$ = 18 Hz, $^3J_{CP}$ = 3 Hz, P*C*HMe$_2$), 24.8 (pt, $J^*_{CP} \approx$ 3 Hz, P*C*HMe$_2$), 62.7 (s, PhCH$_2$N=CHPh), 74.0 (d, $^2J_{CP}$ = 15 Hz, PhCH$_2$N=*C*HPh), 121.6 (s, C$_{ar}$H$_p$), 124.1 (s, C$_{ar}$H$_o$), 125.5 (s, C$_{ar}$H$_p$), 126.7 (s, C$_{ar}$H$_o$), 127.9 (s, C$_{ar}$H$_m$), 145.3 (s, C$_{ar}$), 149.0 (s, C$_{ar}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121 MHz): δ 67.5 (d, $^2J_{PP}$ = 69 Hz), 68.7 (d).

Synthesis of Ni(dippe)(CH$_3$)(OC(O)NC$_4$H$_8$) (15). A solution of lithium pyrrolidinide (26 mg, 0.35 mmol) in 3 mL of THF was added to a cooled solution (−78 °C) of Ni(dippe)(Me)(F) (124 mg, 0.35 mmol) in 2 mL of THF. After removing the cooling bath, dry CO_2 was bubbled through the resulting solution for 5 min. The volatiles were removed *in vacuo*, and the residue was extracted with 2 mL of diethyl ether. Evaporation to dryness afforded the product as an orange oil. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.47 (s, 3H, Ni-C*H*$_3$), 0.86 (dd, 6H, $^3J_{HP}$ = 13.0 Hz, $^3J_{HH}$ = 6.9 Hz, PCH*Me*Me), 1.03 (dd, 6H, $^3J_{HP}$ = 11.8 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.15 (dd, 6H, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.43 (dd, 6H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.69 (m, 2H, PC*H*Me$_2$), 2.05 (m, 2H, PC*H*Me$_2$), 1.57 (s, 4H, NCH$_2$C*H*$_2$), 3.71 (s, 4H, NC*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 1.2 (dd, $^2J_{CP}$ = 71 and 34 Hz, Ni-C*H*$_3$), 16.4 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 11 Hz, *C*H$_2$), 18.0 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.2 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.7 (d, $^2J_{CP}$ = 2 Hz, PCH*Me*Me), 23.6 (t, J_{CP} = 23 Hz, *C*H$_2$), 24.3 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 25.4 (d, $^1J_{CP}$ = 28 Hz, P*C*HMe$_2$), 26.1 (s, NCH$_2$*C*H$_2$), 46.9 (bs, N*C*H$_2$CH$_2$), 161.2 (s, O*C*O). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 64.8, 77.7.

Synthesis of Ni(dippe)(CH$_3$)(N(Ph)CO$_2$^{t}Bu) (16). A solution of lithium *tert*-butoxide (0.35 mmol) in 3 mL of THF was added to a cooled solution (−78 °C) of Ni(dippe)(Me)(F) (125 mg, 0.35 mmol) in 3 mL of THF. The reaction mixture was allowed to reach room temperature and then cooled again at −78 °C. Then 38 μL (0.35 mmol) of PhNCO was added and the resulting solution stirred for 15 min at room temperature. The volatiles were removed under vacuum, and the solid was extracted with 3 mL of Et$_2$O. Orange crystals of product **16** were obtained in 53% yield by concentrating and cooling this solution at −20 °C. Anal. Calcd for C$_{26}$H$_{49}$NO$_2$NiP$_2$: C, 59.11; H, 9.35; N, 2.65. Found: C, 58.51; H, 8.68; N, 2.69. IR (Nujol mull): ν(N−C=O) 1634 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.10 (dd, 3H, $^3J_{HP}$ = 6.5 and 4.7 Hz, Ni-C*H*$_3$), 1.00 (bs, 12H, PCH*Me*Me), 1.26 (dd, 6H, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.40 (dd, 6H, $^3J_{HP}$ = 15.5 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 2.26 (m, 4H, PC*H*Me$_2$), 1.51 (s, 9H, C(C*H*$_3$)$_3$), 6.74 (t, 1H, $^3J_{HH}$ = 7.3 Hz, C$_{ar}H_p$), 7.11 (t, 2H, $^3J_{HH}$ = 7.8 Hz, C$_{ar}H_m$), 7.83 (d, 2H, $^3J_{HH}$ = 7.3 Hz, C$_{ar}H_o$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ −2.1 (dd, $^2J_{CP}$ = 71 and 37 Hz, Ni-*C*H$_3$), 17.0 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 12 Hz, *C*H$_2$), 18.7 (s, PCH*Me*Me), 20.1 (s, PCH*Me*Me), 23.8 (pt, $J^*_{CP} \approx$ 22 Hz, *C*H$_2$), 25.7 (d, $^1J_{CP}$ = 28 Hz, P*C*HMe$_2$), 29.5 (s, C(*C*H$_3$)$_3$), 76.1 (s, *C*(CH$_3$)$_3$), 119.2 (s, C$_{ar}$H$_p$), 125.7 (s, C$_{ar}$H$_o$), 127.5 (s, C$_{ar}$H$_m$), 152.1 (s, C$_{ar}$), 159.0 (s, N*C*O$_2$C(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C, 121 MHz): δ 62.2, 75.9.

Synthesis of Ni(dippe)(CH$_3$)(N(Ph)C(O)NC$_4$H$_8$) (17). A solution of 0.35 mmol of complex **6** was generated at −78 °C as described above. Addition of 38 μL (0.35 mmol) of PhNCO to the reaction mixture caused an immediate color change from dark red to dark orange. After the solution reached room temperature, solvent was removed under reduced pressure, and the resulting residue was extracted with 0.6 mL of C$_6$D$_6$, thus affording an orange solution of pure complex **17**. Extraction of the same reaction crude with 5 mL of diethyl ether and crystallization at −20 °C led to the isolation of the adduct **17**·PhNHC(O)NC$_4$H$_8$ (**17′**) in 50% yield. Compound **17**: ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.35 (s, 3H, Ni-C*H*$_3$), 0.89−1.21 (m, 24H, PCH*Me*Me), 1.66 (m, 2H, PC*H*Me$_2$), 1.78 (m, 2H, PC*H*Me$_2$), 1.40 (s, 4H, NCH$_2$C*H*$_2$), 3.48 (s, 4H, NC*H*$_2$CH$_2$), 6.76 (t, 1H, $^3J_{HH}$ = 7.7 Hz, C$_{ar}H_p$), 7.23 (t, 2H, $^3J_{HH}$ = 8.3 Hz, C$_{ar}H_m$), 7.54 (d, 2H, $^3J_{HH}$ = 7.8 Hz, C$_{ar}H_o$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ −1.7 (dd, $^2J_{CP}$ = 73 and 37 Hz, Ni-*C*H$_3$), 17.1 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 14 Hz, *C*H$_2$), 17.6 (s, PCH*Me*Me), 18.2 (d, $^2J_{CP}$ = 3 Hz, PCH*Me*Me), 18.9 (s, PCH*Me*Me), 19.8 (s, PCH*Me*Me), 23.0 (pt, $J^*_{CP} \approx$ 22 Hz, *C*H$_2$), 25.0 (s, P*C*HMe$_2$), 25.7 (s, NCH$_2$*C*H$_2$), 48.2 (s, N*C*H$_2$CH$_2$), 116.5 (s, C$_{ar}$H$_p$), 123.5 (s, C$_{ar}$H$_o$), 153.8 (s, C$_{ar}$), 162.2 (s, N*C*O). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 61.9, 78.0. Compound **17′**: Anal. Calcd for C$_{37}$H$_{62}$N$_4$O$_2$NiP$_2$: C, 62.11; H, 8.73; N, 7.83. Found: C, 62.19; H, 8.80; N, 7.81. IR (Nujol mull): ν(N−C=O) 1659, 1595 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.41 (d, 3H, $^3J_{HP}$ = 1.7 Hz, Ni-CH$_3$), 0.82 (m, 2H, PCH*Me*Me), 0.89 (dd, 6H, $^3J_{HP}$ = 12.5 Hz, $^3J_{HH}$ = 6.7 Hz, PCH*Me*Me), 1.02 (m, 6H, PCH*Me*Me), 1.27 (m, 12H, PCH*Me*Me), 1.66 (m, 2H, PC*H*Me$_2$), 1.76 (m, 2H, PC*H*Me$_2$), 1.28 (t, 4H, $^3J_{HH}$ = 3.0 Hz, NCH$_2$C*H*$_2$), 1.40 (t, 4H, $^3J_{HH}$ = 6.6 Hz, NCH$_2$C*H*$_2$), 3.05 (s, 4H, NC*H*$_2$CH$_2$), 3.52 (s, 4H, NC*H*$_2$CH$_2$), 6.56 (bs, 1H, NH), 6.81 (t, 1H, $^3J_{HH}$ = 7.2 Hz, C$_{ar}H_p$), 6.92 (t, 1H, $^3J_{HH}$ = 7.3 Hz, C$_{ar}H_p$), 7.23 (t, 2H, $^3J_{HH}$ = 7.9 Hz, C$_{ar}H_m$), 7.27 (t, 2H, $^3J_{HH}$ = 7.8 Hz, C$_{ar}H_m$), 7.59 (d, 2H, $^3J_{HH}$ = 7.6 Hz, C$_{ar}H_o$), 7.84 (d, 2H, $^3J_{HH}$ = 8.3 Hz, C$_{ar}H_o$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz): δ −1.2 (dd, $^2J_{CP}$ = 71 and 34 Hz, Ni-*C*H$_3$), 16.4 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 11 Hz, *C*H$_2$), 18.0 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.2 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.7 (d, $^2J_{CP}$ = 2 Hz, PCH*Me*Me), 23.6 (t, J_{CP} = 23 Hz, *C*H$_2$), 24.3 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 25.4 (d, $^1J_{CP}$ = 28 Hz, P*C*HMe$_2$), 25.7 (s, NCH$_2$*C*H$_2$), 26.1 (s, NCH$_2$*C*H$_2$), 45.8 (s, N*C*H$_2$CH$_2$), 48.8 (s, N*C*H$_2$CH$_2$), 117.2 (s, C$_{ar}$H$_p$), 119.7 (s, C$_{ar}$H$_p$), 122.3 (s, C$_{ar}$H$_o$), 124.0 (s, C$_{ar}$H$_o$), 141.4 (s, C$_{ar}$), 154.1 (s, N*C*O), 154.3 (s, C$_{ar}$), 162.8 (s, N*C*O). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 61.9, 78.1.

Synthesis of Ni(dippe)(CH$_3$)(SC(NPh)O^{t}Bu) (18). A solution of lithium *tert*-butoxide (0.30 mmol) in 3 mL of THF was added to a cooled solution (−78 °C) of Ni(dippe)(Me)(F) (106 mg, 0.30 mmol) in 3 mL of THF. The reaction mixture was allowed to reach room temperature and then cooled again at −78 °C. Then 36 μL (0.30 mmol) of PhNCS was added and the resulting solution stirred for 4 h at room temperature. The volatiles were removed under vacuum, and the solid was extracted with 5 mL of Et$_2$O. Orange crystals of product **18** were obtained in a 45% yield after concentrating and cooling this solution. Anal. Calcd for C$_{26}$H$_{49}$NONiSP$_2$: C, 57.36; H, 9.07; N, 2.57. Found: C, 56.89; H, 8.77; N, 2.60. IR (Nujol mull): ν(S−C=N) 1584 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.51 (dd, 3H, $^3J_{HP}$ = 6.6 and 4.3 Hz, Ni-C*H*$_3$), 0.73 (m, 12H, PCH*Me*Me), 0.90 (m, 2H, C*H*$_2$), 1.00 (dd, 6H, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.3 Hz, PCH*Me*Me), 1.08 (dd, 6H, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.82 (s, 9H, C(C*H*$_3$)$_3$), 6.97 (t, 1H, $^3J_{HH}$ = 7.1 Hz, C$_{ar}H_p$), 7.35 (m, 4H, C$_{ar}H_o$ + C$_{ar}H_m$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ −3.6 (dd, $^2J_{CP}$ = 62 and 31 Hz, Ni-*C*H$_3$), 18.0 (s, PCH*Me*Me), 19.1 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 19.4 (s, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 22.9 (t, J_{CP} = 22 Hz, *C*H$_2$), 24.5 (d, $^1J_{CP}$ = 18 Hz, P*C*HMe$_2$), 25.2 (d, $^1J_{CP}$ = 25 Hz, P*C*HMe$_2$), 28.8 (s, C(*C*H$_3$)$_3$), 79.8 (s, *C*(CH$_3$)$_3$), 120.7 (s, C$_{ar}$H$_p$), 122.9 (s, C$_{ar}$H$_m$), 128.4 (s, C$_{ar}$H$_o$), 152.7 (s, C$_{ar}$), 166.1 (s, S*C*N). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121 MHz): δ 72.5 (d, $^2J_{PP}$ = 20 Hz), 80.0 (d).

Synthesis of Ni(dippe)(CH$_3$)(SC(NPh)NC$_4$H$_8$) (19). Addition of 37 μL (0.35 mmol) of PhNCS to a cooled (−78 °C) THF solution containing 0.35 mmol of complex **6** caused an immediate color change from dark red to dark orange. After the solution reached room temperature, solvent was removed under reduced pressure,

Table 1. Crystal and Refinement Data for Compounds 7, 12, 13, and 19

	7	12	13	19
empirical formula	$C_{16}H_{38}NiOP_2$	$C_{23}H_{45}NNiP_2$	$C_{18}H_{39}NNiP_2$	$C_{26}H_{48}N_2NiP_2S$
fw	367.11	456.25	390.15	541.37
temperature, K	100(2)	100(2)	100(2)	293(2)
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P\bar{1}$
a, Å	7.9694(6)	8.9113(6)	9.7279(7)	10.3613(16)
b, Å	14.1687(11)	14.9674(8)	14.9737(9)	10.3787(16)
c, Å	17.4841(14)	10.0496(6)	c15.2632(11)	14.333(2)
α, deg	92.906(2)	90	80.308(2)	100.194(2)
β, deg	95.309(2)	111.331(2)	77.419(2)	93.297(2)
γ, deg	90.651(2)	90	79.294(2)	99.191(2)
volume, Å^3	1963.0(3)	1248.58(13)	2113.1(3)	1491.7(4)
Z	4	2	4	2
calcd density, g/cm^3	1.242	1.214	1.226	1.205
absorp coeff, mm^{-1}	1.147	0.913	1.068	0.843
F(000)	800	496	848	584
no. of reflns collected	30 564	13 396	32 087	15 881
no. of indep reflns	11 798 [*R*(int) = 0.0454]	7144 [*R*(int) = 0.0364]	12 759 [*R*(int) = 0.0327]	6955 [*R*(int) = 0.0223]
no. of params refined	361	245	397	350
final $R_1(F)$ index[a] [$[F^2 > 2\sigma(F^2)]$]	0.0499	0.0467	0.0427	0.0585
$wR_2(F^2)$ index[b] (all data)	0.1510	0.1134	0.1287	0.2087
S[c] (all data)	1.041	0.998	1.117	0.902
absolute struct param		0.023(12)		

[a] $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$ for the observed reflections [$F^2 > 2\sigma(F^2)$]. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$. [c] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = number of reflections, p = number of parameters).

and the resulting residue was extracted with 3 mL of THF. Concentration and cooling at −20 °C gave orange crystals of the product in 55% yield. Anal. Calcd for $C_{25}H_{44}N_2NiSP_2$: C, 57.16; H, 8.44; N, 5.33. Found: C, 56.95; H, 8.41; N, 4.93. IR (Nujol mull): ν(S−C═N) 1539 cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.24 (d, 3H, $^3J_{HP}$ = 2.3 Hz, Ni−C*H*$_3$), 0.77 (m, 2H, PCH*Me*Me), 0.99 (dd, 6H, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 6.6 Hz, PCH*Me*Me), 0.93 (m, 2H, C*H*$_2$), 1.15 (dd, 6H, $^3J_{HP}$ = 14.5 Hz, $^3J_{HH}$ = 6.4 Hz, PCH*Me*Me), 1.65 (t, 4H, $^3J_{HH}$ = 6.3 Hz, NCH$_2$C*H*$_2$), 1.82 (m, 4H, PC*H*MeMe), 4.02 (t, 4H, $^3J_{HH}$ = 6.3 Hz, NC*H*$_2$CH$_2$), 6.98 (t, 1H, $^3J_{HH}$ = 7.2 Hz, C$_{ar}$*H*$_p$), 7.36 (t, 2H, $^3J_{HH}$ = 7.7 Hz, C$_{ar}$*H*$_m$), 7.49 (d, 2H, $^3J_{HH}$ = 7.9 Hz, C$_{ar}$*H*$_o$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −2.9 (dd, $^2J_{CP}$ = 61 and 31 Hz, Ni-*C*H$_3$), 18.1 (s, PCH*Me*Me), 19.1 (s, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 22.8 (t, J_{CP} = 22 Hz, *C*H$_2$), 24.5 (d, $^1J_{CP}$ = 17 Hz, P*C*HMe$_2$), 25.3 (d, $^1J_{CP}$ = 25 Hz, P*C*HMe$_2$), 25.8 (s, NCH$_2$*C*H$_2$), 49.3 (bs, N*C*H$_2$CH$_2$), 119.3 (s, *C*$_{ar}$H$_p$), 124.4 (s, *C*$_{ar}$H$_o$), 155.7 (s, *C*$_{ar}$), 160.2 (d, $^3J_{CP}$ = 15 Hz, S*C*N). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 73.4 (d, $^2J_{PP}$ = 11 Hz), 80.4 (d).

X-ray Crystal Structure Analyses of 7, 12, 13, and 19. A single crystal, of each representative compound, of suitable size was mounted on a glass fiber using perfluoropolyether oil (FOMBLIN 140/13, Aldrich) in the cold N_2 stream of a low-temperature device attachment (**7**, **12**, and **13**) or using a glue (**19**). A summary of crystallographic data is reported in Table 1. Intensity data for complexes **7**, **12**, and **13** were collected on a Bruker-AXS X8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Mo K$_{\alpha1}$ (λ = 0.71073 Å) and a Bruker Cryo-Flex low-temperature device. The data of compound **19** were collected at rt on a Bruker AXS SMART 1000 single-crystal diffractometer equipped with an area detector using graphite-monochromated λ(Mo K$_{\alpha1}$) = 0.71073 Å radiation. A semiempirical absorption correction was applied (SADABS).[35] The structures were solved by direct (SIR-2002)[36] and Patterson methods and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[37] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms.

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Supporting Information Available: X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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