

Fluoride Displacement by Lithium Reagents. An Improved Method for the Synthesis of Nickel Hydroxo, Alkoxo, and Amido Complexes

Juan Cámpora,^{*,†} Inmaculada Matas,[†] Pilar Palma,[†] Claudia Graiff,[‡] and Antonio Tiripicchio[‡]

Instituto de Investigaciones Químicas, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla. Avda. Américo Vespucio 49, 41092 Sevilla, Spain, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma, Italy

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Summary: The complex $Ni(Me)(F)(dippe)$ undergoes clean fluoride displacement reactions with $Li(OH)$, $Li(O^tBu)$, and $Li(NC_4H_8)$, affording the corresponding *cis* hydroxo, alkoxo, and amido methyl derivatives. These compounds display limited thermal stability and decompose by β -hydrogen elimination or disproportionation processes under mild conditions.

Although considerable progress has been made in the field of late-transition-metal complexes containing non-dative metal–oxygen and –nitrogen single bonds,¹ the development of general synthetic routes to mononuclear derivatives remains a challenge. These compounds have attracted much attention, due to their high reactivity² and their implication as intermediates in various types of catalytic reactions.^{1b,3} Recent work in our group has focused on the development of synthetic methods to obtain Ni and Pd complexes of this kind and the study of their reactivity. Thus, we have reported the synthesis of new monomeric hydroxide, alkoxide, and amide derivatives of Ni and Pd featuring terminally bound OH, OR, and NH₂ ligands, which were stabilized against dimerization by the use of the tridentate pincer ligand 2,6-bis(diisopropylphosphino)methylphenyl (PCP), which enforces a *trans* geometry.⁴ In contrast with these complexes, catalysts for C–N and C–O coupling often display chelating diphosphines, which favor a *cis* arrangement of the alkyl or aryl and alkoxo or amido ligands.⁵ Although a number of Pd and Pt alkyl alkoxo and aryl amido complexes bearing chelating diphosphines have been described,^{5e,6} the analogous nickel

derivatives are rare.⁷ Herein we wish to report the development of a synthetic route to monomeric square-planar alkyl hydroxo, alkoxo, and amide Ni(II) complexes bearing the chelating diphosphine ligand 1,2-bis(diisopropylphosphino)ethane (*dippe*).

We have previously shown that the treatment of nickel complexes of composition $Ni(o-C_6H_4COCHR_2)(Cl)(dippe)$ with *t*-BuOK leads to the formation of metallacyclic species displaying aryl and oxygen-bound enolate functionalities.⁸ To generate similar noncyclic complexes containing *dippe*, alkyl, and OR ligands, we have investigated the reaction of methyl derivatives $Ni(Me)(X)(dippe)$ ($X = Cl$ (**1a**), F (**1b**)) with alkaline hydroxides or alkoxides. Complex **1a** was readily prepared by treatment of $NiMe_2(dippe)$ ⁹ with $HNMe_3Cl$. The fluoride **1b** was synthesized by following a similar procedure, employing triethylammonium trifluoride (TREAT HF) as the source of HF. Recently, TREAT HF ($Et_3N \cdot 3HF$) has found wide application as an efficient reagent for the synthesis of organometallic fluorides.¹⁰ We found that TREAT HF reacts with $Ni(CH_3)_2(dippe)$ in *thf* in a 1:3 molar ratio, affording the corresponding fluoride complex in high yield (78%) as orange crystals (Scheme

[†] Consejo Superior de Investigaciones Científicas-Universidad de Sevilla.

[‡] Università di Parma.

(1) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.

(2) (a) Mayer, J. M. *Comments Inorg. Chem.* **1998**, *8*, 125. (b) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115. (c) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799. (d) Macgregor, S. A.; Neave, G. W. *Organometallics* **2003**, *22*, 4547.

(3) See, for example: (a) Jira, R. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 2002. (b) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (c) Taggi, A. E.; Hafez, A. M.; Lectka, T. *Acc. Chem. Res.* **2003**, *36*, 10. (d) Watanabe, M.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2003**, *125*, 7508. (e) Trost, B. M.; Toste, D.; Greenman, K. *J. Am. Chem. Soc.* **2003**, *125*, 4518.

(4) (a) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (b) Cámpora, J.; Conejo, M. M.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 5653.

(5) (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2047. (b) Koo, K.; Hillhouse, G. L. *Organometallics* **1995**, *14*, 4421. (c) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (d) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (e) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (f) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775. (g) Macgregor, S. A.; Neave, G. W.; Smith, C. *Faraday Discuss.* **2003**, *124*, 111.

(6) (a) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (b) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (c) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (d) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939. (e) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (f) Belluco, U.; Bertani, R.; Coppetti, S.; Michelin, R. A.; Mozzon, M. *Inorg. Chim. Acta* **2003**, *343*, 329.

(7) (a) Miyashita, A.; Ishida, J.; Noria, H. *Tetrahedron Lett.* **1986**, *27*, 2127. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623. (c) Cámpora, J.; López, J. A.; Maya, C.; Palma, P.; Carmona, E.; Valera, P. *J. Organomet. Chem.* **2002**, *643*, 331.

(8) (a) Cámpora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Gutiérrez-Puebla, E.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1482. (b) Cámpora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Graiff, C.; Tiripicchio, A. *Chem. Commun.* **2003**, 1742.

(9) $NiMe_2(dippe)$ has been previously synthesized by reaction of $NiMe_2Py_2$ with *dippe*.^{7c}

(10) (a) Fraser, S. L.; Antipin, M. Y.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769. (b) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774. (c) Ilg, K.; Werner, H. *Organometallics* **1999**, *18*, 5426.

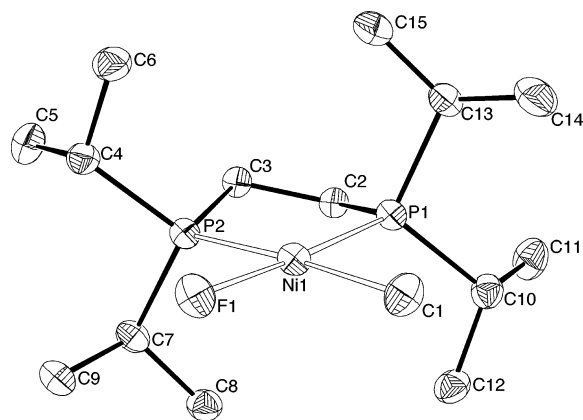


Figure 1. ORTEP view of **1b**. Selected bond distances (Å) and angles (deg): Ni–F, 1.860(2); Ni–C1, 1.950(4); Ni–P1, 2.1085(13); Ni–P2, 2.1988(13); F–Ni–C1, 90.02(16); P1–Ni–C1, 90.93(14); P1–Ni–P2, 89.14(5); P2–Ni–F1, 90.12(9).

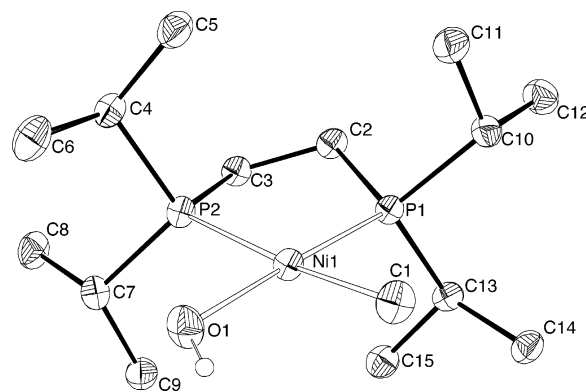
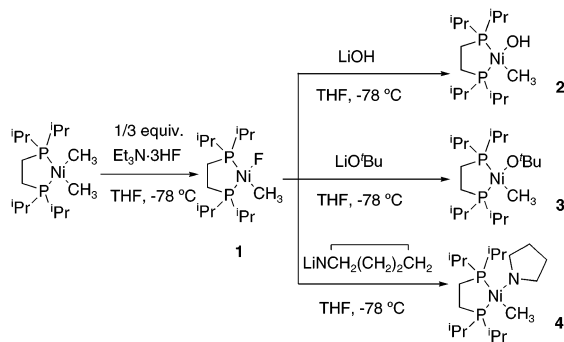


Figure 2. ORTEP view of **2**. Selected bond lengths (Å) and angles (deg): Ni–O, 1.877(4); Ni–C1, 1.958(5); Ni–P1, 2.1200(17); Ni–P2, 2.1769(15); C1–Ni–O, 91.5(2); C1–Ni–P1, 91.20(16); P1–Ni–P2, 89.22(6); O–Ni–P2, 88.60(14).

Scheme 1



1).¹¹ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of pure samples of **1b** in C_6D_6 displays two doublets at δ 78.4 ppm ($^2J_{\text{PF}} = 117$ Hz) and 64.6 ppm ($^2J_{\text{PF}} = 51$ Hz), while the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum consists of a doublet of doublets at δ –224.0 ppm. However, as observed previously by Grushin for Pd fluoro complexes, the P–F couplings are lost in the presence of trace amounts of water.

The molecular structure of complex **1b** was determined by single-crystal X-ray crystallography.¹² An ORTEP perspective of the molecule is shown in Figure 1. The molecule displays slightly distorted square planar geometry, with the four interligand *cis*-Ni(L)(L') angles approaching values of 90°. The Ni–F distance, 1.860(2) Å, can be considered normal for this type of bond and is very close to those found in *trans*-Ni(Ar)(F)(PR₃)₂ complexes.¹³ The Ni–P bond trans to the fluorine atom is ca. 0.1 Å shorter than the other, as a consequence of the stronger trans influence of the methyl group.

Treatment of **1a** with MOH (M = Li, Na) or MO^tBu (M = Na, K) caused incomplete displacement of Cl or

no reaction at all. In contrast, **1b** reacts rapidly with a stoichiometric amount of lithium hydroxide, *tert*-butoxide, or pyrrolidinide at –78 °C (Scheme 1). In the last case, the mixing of the reagents is followed by an immediate color change from orange to dark red. ^{31}P NMR monitoring of these reactions indicate quantitative conversion of **1b** into the products **2–4**, all of them characterized by a pair of ^{31}P resonances due to the inequivalent phosphorus atoms. Although late-transition-metal fluorides can be very reactive, it has been shown that in Rh and Co complexes the metal affinity for halide ligands decreases in the order F > Cl > Br > I.¹⁴ Therefore, it is likely that the formation of the very stable and insoluble salt LiF provides a driving force for these reactions. The contribution of this factor to the overall energy balance of the reaction can be estimated as ca. 200–300 kJ/mol, if the lattice energy of LiF, 1030 kJ/mol, is compared to that of LiCl (834 kJ/mol), NaCl (769 kJ/mol), or KCl (701 kJ/mol).¹⁵

The Ni hydroxide **2** was isolated as red-orange crystals in good yield (70%).¹⁶ In the proton NMR spectrum, the hydroxyl and methyl protons give rise to two doublets of doublets at δ –0.49 ppm ($^3J_{\text{HPtrans}} = 10.0$ Hz, $^3J_{\text{HPcis}} = 3.0$ Hz, OH) and δ 0.18 ppm ($^3J_{\text{HPtrans}} = 5.9$ Hz, $^3J_{\text{HPcis}} = 4.4$ Hz), corresponding to one and three protons, respectively, while in the $^{31}\text{P}\{^1\text{H}\}$ spectrum the inequivalent P nuclei resonate at δ 68.6 and 77.3 ppm, with $^2J_{\text{PP}} = 9$ Hz. These features are consistent with its formulation as monomeric hydroxide. In addition, the structure of **2** has been confirmed by a single-crystal diffraction study,¹⁷ illustrated by the ORTEP diagram shown in Figure 2. Like **1b**, this molecule displays a relatively undistorted square planar configuration, with

(14) Araghizadeh, F.; Branam, D. M.; Hoffman, N. W.; Jones, J. H.; McElroy, A.; Miller, C.; Ramage, D. L.; Battaglia Salazar, A.; Young, S. H. *Inorg. Chem.* **1988**, *27*, 3752, and references therein.

(15) *Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, 2003; pp 12–22.

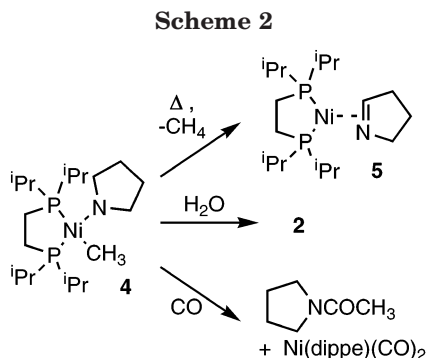
(16) Selected NMR data for **2**: ^1H NMR (C_6D_6 , 20 °C) δ –0.49 (dd, 1H, $^3J_{\text{HP}} = 10.0$ Hz, $^3J_{\text{HP}} = 3.0$ Hz, OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ –0.6 (dd, $^2J_{\text{CP}} = 82$ and 32 Hz, CH₃); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ 68.6 (d, $^2J_{\text{PP}} = 9$ Hz), 77.3 (d).

(17) Crystal data for **2** at 173(2) K: C₁₅H₃₆ONiP₂, *M_r* = 353.09, triclinic, space group P1̄, *a* = 7.523(3) Å, *b* = 18.015(5) Å, *c* = 7.514(3) Å, α = 90.03(3)°, β = 108.20(5)°, γ = 101.82(4)°, *V* = 944.6(6) Å³, *Z* = 2, ρ_{calcd} = 1.241, $\mu(\text{Cu K}\alpha)$ = 3.006 mm^{–1}, θ range 5.03–60.00°, 2810 unique reflections, final R1 = 0.0595 and wR2 = 0.1582 for 2192 reflections (*I* > 2 σ (*I*)), R1 = 0.0777 and wR2 = 0.1725 for all data, GOF = 1.037.

(11) Selected NMR data for **1b**: ^1H NMR (C_6D_6 , 20 °C) δ 0.47 (m, 3H, CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ 2.8 (dd, $^2J_{\text{CP}} = 83$ and 37 Hz, CH₃); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ 64.6 (d, $^2J_{\text{PF}} = 50$ Hz), 78.4 (d, $^2J_{\text{PF}} = 117$ Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ –224.0 (dd).

(12) Crystal data for **1b** at 173(2) K: C₁₅H₃₅FNiP₂, *M_r* = 355.08, monoclinic, space group P2₁/c, *Z* = 4, *a* = 7.727(3) Å, *b* = 13.228(5) Å, *c* = 18.666(5) Å, β = 96.02(5)°, *V* = 1897.4(11) Å³, ρ_{calcd} = 1.243, $\mu(\text{Cu K}\alpha)$ = 3.034 mm^{–1}, θ range 4.10–60.00°, 2757 unique reflections, final R1 = 0.0581 and wR2 = 0.1701 for 2537 reflections (*I* > 2 σ (*I*)), R1 = 0.0640 and wR2 = 0.1890 for all data, GOF = 1.078.

(13) (a) Cronin, L.; Higitt, C. L.; Karch, R.; Perutz, R. N. *Organometallics* **1997**, *16*, 4920. (b) Sladeck, M. L.; Braun, T.; Neumann, B.; Stammeler, H.-G. *Dalton Trans.* **2002**, 297.



two Ni–P bonds of different length, as a consequence of the stronger trans influences of the Me group. However, the difference between the two Ni–P distances is smaller in complex **2** (0.057 Å) than in **1b** (0.090 Å), indicating that the trans influence of the OH ligand is stronger than that of F. The Ni–OH bond length, 1.877(4) Å, is comparable to that found in Ni(PCP)(OH),^{4a} 1.865(2) Å, but in contrast with the latter, no intermolecular C–H···O contacts were found in the crystal structure of the former.

The high reactivity of products generated from lithium *tert*-butoxide (**3**) or pyrrolidinide (**4**) complicates their isolation. Compound **3** was obtained as a spectroscopically pure oil, very soluble in hydrocarbon solvents.¹⁸ Its ³¹P{¹H} NMR spectrum consists of two doublets at δ 60.5 and δ 70.4 ppm (²J_{PP} = 11.3 Hz). In the ¹H NMR spectrum, the *tert*-butyl and methyl groups give rise to two signals of relative intensity 9:3 at δ 1.69 and 0.22 ppm, respectively.

Compound **4** is thermally unstable and decomposes at room temperature (see below). Although this has prevented the isolation of this compound, its ³¹P{¹H} spectrum in THF displays two doublets at δ 55.7 and 72.3 ppm with ²J_{PP} = 8.1 Hz, which are reminiscent of those of **1b**, **2**, and **3**. Its chemical reactivity (Scheme 2) is consistent with the simultaneous presence of methyl and amido groups. Thus, as observed in the case of **3**, it reacts rapidly and quantitatively with water, giving the hydroxide **2**. It also reacts with CO, yielding Ni(dippe)(CO)₂ and *N*-acetylpyrrolidine (identified by GC-MS spectroscopy) as the only observed products.¹⁹

At room temperature, in C₆D₆ or THF solution, compound **4** gives rise to a new product, **5**, whose ³¹P{¹H} spectrum displays a characteristic AB spin system with δ_A 68.8 ppm, δ_B 57.7 ppm, and J_{AB} = 80.6 Hz. Under these conditions, the conversion of **4** into **5** in THF takes ca. 4 h and is accompanied by the formation of minor amounts of byproducts (NiMe₂(dippe)⁹ and Ni(dippe)₂,²⁰ identified by their ³¹P resonances), but at 40 °C the transformation is highly selective and complete within 30 min. Compound **5** was isolated as an orange crystalline solid that does not react with water.²¹ The

¹H and ¹³C NMR spectra show no signals attributable to a Ni-bound methyl group, but they reveal the presence of three methylene groups and one methyne group, indicating that the pyrrolidine ring has been transformed into a cyclic imine by means of a β-hydrogen elimination reaction, as shown in Scheme 2. The relatively low chemical shift of the methyne ¹³C resonance (δ 71.7 Hz) and its coupling to one of the phosphorus nuclei (J_{CP} = 19 Hz) support a η² coordination mode for the imine functionality.²² The NMR spectra of this compound are somewhat broad at room temperature but become sharp when they are recorded in toluene-*d*₈ at –20 °C, presumably due to a slow rotational movement of the imine ligand.

The low thermal stability of compound **4** is not surprising, since it is known that late-transition-metal alkoxides and amides can decompose through β-hydrogen²³ or reductive elimination.⁵ These processes play an important role in some catalytic transformations, and we have investigated the thermal decomposition of **2** and **3**, which lack β-hydrogen atoms. Although more robust than **4**, they decompose in solution under mild conditions. Monitoring a sample of **3** in C₆D₆ at room temperature by ³¹P NMR showed that it disappears after 3 days, producing NiMe₂(dippe) as the major P-containing product (37%), together with a small amount of Ni(dippe)₂ and a complex mixture of unidentified P-containing products, accounting for 31% of the starting material. Compound **2** is stable in C₆D₆ at room temperature but decomposes on heating the solution at 50 °C for 24 h. In this case, the P-containing products are Ni(dippe)₂ (35%), NiMe₂(dippe) (13%), and a similar mixture of unidentified products (25%). The complex product distributions observed in these decompositions are in contrast with the clean thermolysis of the analogous sulfur derivative Ni(Me)(SH)(dippe), which cleanly affords the dimeric sulfide [Ni(μ-S)(dippe)]₂.²⁴ The decomposition reactions of **2** and **3** are accompanied by darkening and precipitation of a small amount of solid. GC analysis of the supernatant solutions shows the formation of a small amount of ^tBuOH (11%) in the case of **3** but does not reveal the formation of reductive coupling products (MeOH and ^tBuOMe). These results suggest that the decomposition of **2** and **3** could involve a disproportionation²⁵ process to produce NiMe₂(dippe) and NiX₂(dippe) (X = OH, ^tBuO), followed by the transformation of the latter into insoluble and/or unidentified products.²⁶ However, the formation of significant amounts of Ni(dippe)₂ cannot be readily explained. Thermal decomposition of NiMe₂(dippe) can be ruled out

(21) Selected NMR data for **5**: ¹H NMR (toluene-*d*₈, –20 °C) δ 2.03, 2.53, 3.67, 4.08 (m, CHH, 1H, two diastereotopic methylene resonances obscured by the dippe signals), 4.41 (d, ³J_{HP} = 12.7 Hz, N=CH); ¹³C{¹H} NMR (toluene-*d*₈, –20 °C) δ 30.4 (s, CH₂), 35.2 (d, J_{CP} = 3 Hz, CH₂), 61.3 (s, CH₂), 71.7 (dd, ²J_{CP} = 160, 19 Hz, N=CH); ³¹P{¹H} NMR (tol-*d*₈, –20 °C) δ 68.8 (d, ²J_{PP} = 80.6 Hz), 57.7 (d).

(22) Gabor, B.; Krüger, C.; Marczinke, B.; Mynott, R; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666.

(23) (a) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (b) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C-17. (c) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (d) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(24) Vicić, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 4070.

(25) (a) Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493. (b) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087. (c) Suzuki, Y.; Yagyu, T.; Yamamura, Y.; Mori, A.; Osakada, K. *Organometallics* **2002**, *21*, 5254.

(26) Sacco, A.; Martorilli, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2761.

(18) Selected NMR data for **3**: ¹H NMR (C₆D₆, 20 °C) δ 0.22 (pt, 3H, J_{HPapp} ≈ 5.7 Hz, CH₃), 1.69 (s, 9H, C(CH₃)₃); ¹³C{¹H} NMR (C₆D₆, 20 °C) δ –8.3 (dd, ²J_{CP} = 80 and 36 Hz, CH₃), 35.9 (s, C(CH₃)₃), 70.1 (d, ³J_{CP} = 4 Hz, C(CH₃)₃); ³¹P{¹H} NMR (C₆D₆, 20 °C) δ 60.5 (d, ²J_{PP} = 11 Hz), 70.4 (d, ²J_{PP} = 11 Hz).

(19) A number of similar carbonylation reactions are known to occur readily. See for instance: (a) Carmona, E.; Marín, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *28*, 1895. (b) Cámpora, J.; Gutiérrez, E.; Monge, A.; Palma, P.; Poveda, M. L.; Ruiz, C.; Carmona, E. *Organometallics* **1994**, *558*, 1728. (c) Matsunaga, P. T.; Hess, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 3665.

(20) Vicić, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855.

as a source of Ni(dippe)₂, since an independent experiment showed that the former is stable in C₆D₆ at 50 °C for long periods of time, in contrast with the case for NiMe₂(dbpe) (dbpe = 1,2-bis(*tert*-butylphosphino)ethane), which decomposes readily to give Ni(0) compounds.²⁷

In conclusion, we have shown that displacement of a fluoride ligand from Ni(Me)(F)(dippe) (**1b**) with lithium hydroxide, alkoxide, or amide provides an excellent method for the synthesis of the corresponding mononuclear Ni(II) derivatives **2–4**, which are difficult to prepare by conventional procedures. Complexes **1b** and **2** have been isolated and structurally characterized. Compounds **2** and **3** are moderately stable in solution, experiencing a slow decomposition process, while **4** is less stable and undergoes a β -hydrogen elimination

(27) Bach, I.; Pörschke, K. R.; Goddard, R.; Kopsike, C.; Krüger, C.; Rufinska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959.

process that leads to the η^2 -imine complex **5** in quantitative yield. Further studies on the reactivity of these compounds and their application in catalysis are currently under way.

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Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and tables of crystallographic X-ray data; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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