Acid−Base Reactions of Methylnickel Hydroxo, Alkoxo, and Amide Complexes with Carbon Acids. Studies on the Reactivity of Noncyclic Nickel Enolates

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Basic organonickel hydroxo, alkoxo, or amido complexes of composition Ni(Me)(X)(dippe) (X = OH, *t*-BuO, *cyclo*-NC_4H_8; dippe = *i*-$Pr_2PCH_2CH_2P$*i*-Pr_2) react with enolizable ketones, esters, and nitriles, producing the corresponding enolate complexes. In the case of the hydroxo and alkoxo complexes, these reactions may lead to equilibrium mixtures, allowing a comparison of their respective basicities, while the amido compound reacts clean and quantitatively in all cases, allowing the isolation of the corresponding enolates. While the ketone derivatives display oxygen-bound enolate ligands, the ester and nitrile enolates bind the metal center through the carbon atom. The acetophenone enolate complex has strong nucleophilic properties and rapidly reacts with aldehydes (PhCHO) or CO_2, affording the corresponding aldolate and carboxylate addition products.

The chemistry of late transition metal enolates has attracted much attention in the last decades due to its implication in many metal-mediated organic transformations.[1] In part, the development of these synthetic methodologies has been facilitated by the previous understanding of the chemistry of this kind of compounds. Studies on late transition metal enolates have focused mainly on C−C bond-forming reactions, such as aldol-type condensations,[2,3] cross-coupling reactions with aryl halides,[4] and, more recently, conjugated additions to α,β-unsaturated ketones.[5] In general, it is widely admitted that precoordination of the electrophile to the metal center plays an important role in the reactivity of enolates,[1a,2,6] enhancing their reactivity and stereoselectivity (Scheme 1), but a precoordinative step is not a strict requisite for these reactions. Our group has carried out several studies on O-bound metallacyclic enolate complexes of nickel of composition Ni(OC(=CRR′)-*o*-C_6H_4)(dippe), where the enolate functionality is rigidly held apart from the metal center.[7] This situation prevents the interaction of the electrophilic reagent with the metal center, as well as the migration of the latter from one oxygen atom to another in the corresponding addition products. The latter effect leads to some interesting differences in the nature of the final products generated in the addition reactions of metallacyclic and nonmetallacyclic enolates. Rather curiously, most nickel enolate complexes reported to date have cyclic structures displaying O-bonded coordination,[7,8] with the exception of the noncyclic cyclopentadienyl

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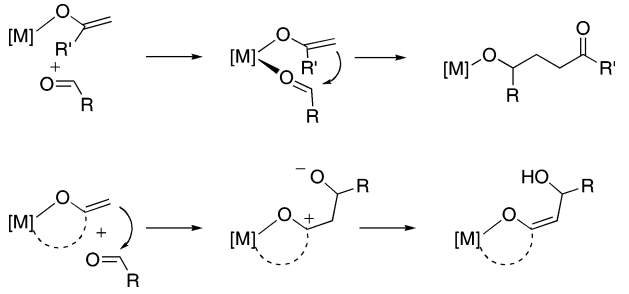
Scheme 1

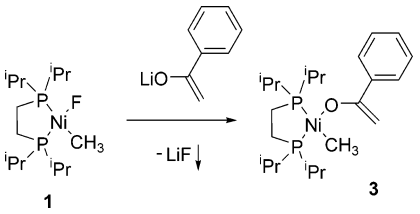


derivatives Ni(Cp)(PR_3)(CH_2COR),[2c] which display a C-bonded coordination mode. This is in contrast with the relatively large number of nonmetallacyclic enolate derivatives reported for Pd,[4d,9] Rh,[2b−d,10] Ru,[5c,11] and other late transition elements.[12] Open structures allow facile changes of the enolate fragment coordination mode, which are not limited to the well-known σ C- and O-bound modes, but include also η^3 (pseudoallylic)[2a,d,10,13] or bridging (in binuclear species),[9b,14] which facilitate access to many different reactivity paths.

Recently, we have shown that the reaction of the fluoro complex Ni(Me)(F)(dippe) (**1**) with lithium hydroxide, alkoxides, or amides cleanly leads to the corresponding monomeric complexes Ni(Me)(X)(dippe) (**2**, X = OH, OR, NR_2), providing a convenient route to these otherwise difficult to prepare species.[15] As a continuation of our previous work, herein we describe the use of these highly basic[16] compounds as precursors for the generation of noncyclic enolate complexes from enolizable ketones, esters, and nitriles and the reactivity of the ketone enolates toward benzaldehyde, CO, and CO_2. In contrast with aldol-type addition reactions, there is little information about the reactivity of transition metal enolates toward carbon dioxide,[17] despite the importance of this kind of process for carbon dioxide assimilation in biological systems.[18]

Results and Discussion

Synthesis and Characterization of the Acetophenone Enolate Complex 3. The starting point for the present work is the preparation of an example of a noncyclic ketone enolate complex, following our original procedure, i.e., fluoride displacement from **1** with a lithium ketone enolate. Acetophenone lithium enolate was generated according to the classic method by treating acetophenone with LDA in thf, and the resultant solution was reacted with **1**. NMR monitoring of this reaction by $^{31}P\{^1H\}$ NMR revealed the formation of a single product, **3**, characterized by two singlet resonances at δ 64.7 and 76.6 ppm, that could be isolated in 45% yield as a orange crystalline solid, stable in the solid state and in solution for extended periods of time at room temperature. The NMR spectra of **3** are fully consistent with the O-bound enolate structure shown in eq 1. Thus, the terminal methylene group gives rise to two singlets at δ 4.56 and 4.85 ppm in its ^1H NMR spectrum. The corresponding ^{13}C resonance appears at δ 80.1 ppm and the $^1J_{CH}$ coupling constant, 153 Hz, is consistent with its sp^2 character. The absence of resonances in the proximity of 200 ppm rules out the presence of a carbonyl group, but instead the oxygen-bound quaternary carbon atom resonates at δ 166.3 ppm. In addition, the IR spectrum displays a strong absorption at 1590 cm^{-1}, which can be assigned to the C═CH_2 bond stretch. These features are comparable to those of the cyclic O-enolate Ni(OC(═CH_2)-*o*-C_6H_4)(dippe),[7a] as well as those of O-bound acetophenone enolates of Ti,[6a] Zr,[19] and Rh.[2b] The formulation of enolate complex **3** has been confirmed by a single-crystal diffraction study, illustrated by the ORTEP diagram shown in Figure 1.



The molecule displays slightly distorted square-planar geometry with the enolate ligand lying perpendicular to the coordination plane, in contrast to the related hydroxide, alkoxide, and amide complexes.[15] The Ni−O bond distance, 1.9043(17) Å, is somewhat longer than that in Ni(Me)(OH)(dippe) (1.877(4) Å),[15b] probably due to steric effects. Whereas the olefinic C16−C17 bond length (1.343(4) Å) is close to the standard C═C bond length (ca. 1.40 Å), the C−O bond distance (1.318(3) Å) lies in between the typical values for C−O (1.43 Å) and C═O (1.20 Å) bonds, suggesting a significant delocalization of the π system. As expected, the two Ni−P distances display appreciably different lengths, due to the weaker *trans* influence of the enolate fragment as compared with the methyl group. In complex **3** the $d_{Ni-P1}-d_{Ni-P2}$ difference (0.096 Å) is similar to that of fluoride complex **1** (0.090 Å)[15a] and larger than in the related hydroxide (0.057 Å)[15a] or methoxide (0.065 Å) complexes,[15b] suggesting that the *trans* influence of the enolate ligand is small, more similar to that of fluoride than to other covalently bound O-donor anionic ligands.

Equilibria Involving Hydroxide, Alkoxide, and Amido Complexes and Weak Carbon Acids. Once we established the identity of complex **3** and its stability in solution, we wished

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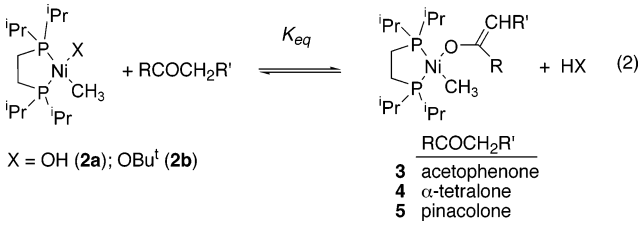
to investigate the ability of complexes of type Ni(Me)(X)(dippe) (X = OH, **2a**, *t*-BuO, **2b**, and *cyclo*-NC_4H_8, **2c**) to deprotonate different weakly acidic organic compounds (ketones, esters, and nitriles), as a measure of their relative basicities.

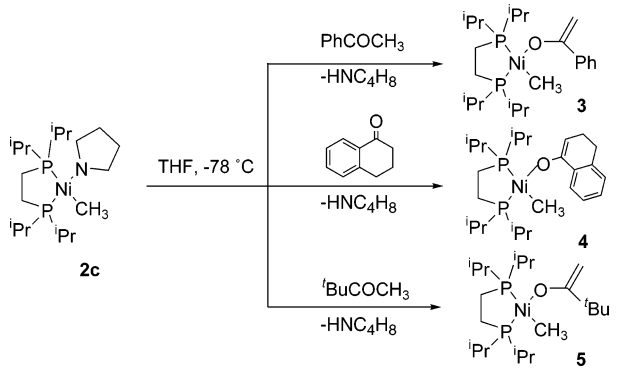
Addition of acetophenone or tetralone to thf solutions of **2a** leads to incomplete conversion to the enolate complexes **3** and **4**, respectively (eq 2). The relative concentration of the equilibrium components can be readily determined by $^{31}P\{^1H\}$ NMR, using an external reference of C_6D_6 for the lock signal. Given the structural similarity of these ketones, it is not surprising that the equilibrium constants, averaged over several measurements, amount to experimentally indistinguishable values $(2(1) \times 10^{-2}$ and $5(2) \times 10^{-2}$ for **3** and **4**, respectively, see Experimental Section). The less acidic ketone pinacolone



does not react appreciably with **2a**, even for a ketone/hydroxide reagent ratio as high as 35:1, providing an upper limit of 7×10^{-5} for K_{eq}. In contrast, the *tert*-butoxide derivative **2b** reacts quantitatively with acetophenone or tetralone to afford **3** and **4**. ^{31}P NMR monitoring shows that the reaction is slower in the latter case, requiring 5 h to complete the transformation. These reactions can be used for preparative purposes, allowing the isolation of the two enolate complexes in 45% and 40% yield, respectively. Compound **2b** reacts more slowly with pinacolone to afford the enolate **5**, taking 24 h to approach a situation of apparent equilibrium, with $K_{eq} \approx 6$, although some decomposition takes place during this time. Heating the reaction mixture to 50 °C accelerates the reaction, but does not avoid the decomposition processes. Considering the pK_a values of acetophenone[20a] (24.7) and pinacolone[20b] (27.7) in dmso, the K_{eq} value for the **2b** + acetophenone reaction can be estimated to be about 6×10^3, i.e., 5 orders of magnitude larger than the value measured for the hydroxide **2a**. The relative values of the two K_{eq} for acetophenone are consistent with the above limit given for the reaction of **2a** with pinacolone (K_{eq}(**2a**)/K_{eq}(**2b**) $< 7 \times 10^{-5}/6 \approx 10^{-5}$). These comparisons provide a clear indication of the much stronger basicity of the alkoxide as compared to the hydroxide complex.[21]

In spite of the low thermal stability of **2c**, it proves to be a preparatively useful reagent and reacts rapidly and quantitatively with acetophenone, tetralone, or pinacolone to afford the corresponding enolates in 60% (**3**), 50% (**4**), and 60% (**5**) isolated yield (Scheme 2). These experiments highlight the expected trend for the basicities of the three complexes **2**, which decreases in the order **2c** > **2b** > **2a**.

Scheme 2



The spectroscopic features of complexes **4** and **5** are comparable to those of **3**, indicating the presence of O-bound enolate groups. For instance, their IR spectra exhibit absorptions at 1600 cm^{-1} (**4**) or 1581 cm^{-1} (**5**), attributable to the ν(C=C) vibration, but no carbonyl bands are observed in the proximity of 1700 cm^{-1}, while the ^1H NMR spectrum shows the olefin resonances at δ 5.34 ppm in the case of **4** and δ 4.05 and 4.21 for **5**.

The difference between the chemical shifts of the α and β ^{13}C resonances of the enolate functionality has been correlated to the degree of polarization of the C=C bond of enolates displaying related structures, providing some indication of their relative reactivity.[22] It is interesting to note that this parameter is appreciably larger for compound **5** (102 ppm) than for **3** (86.2 ppm) and **4** (62.9 ppm), as it would be expected for the higher basicity of the alkyl-substituted enolate.

The facile deprotonation of ketones by the amide complex **2c** prompted us to examine the reaction of this compound with weaker acids, such as esters (methyl and phenyl acetate) and nitriles (acetonitrle). The outcome of these reactions is shown in Scheme 3.

Treatment of a thf solution of complex **2c** with a stoichiometric amount of methyl acetate or acetonitrile affords complexes **6** and **7**, displaying C-bound enolate ligands. These compounds have been isolated in 40−60% yield as orange solids, thermally stable in the solid state and in solution. At variance with the bis(cyanomethyl) complexes $Ni(CH_2CN)_2L_2$ (L = PPh_3, dppe or bipy), which decompose above −40 °C,[23] **7** is stable in C_6D_6 up to 60 °C.

As mentioned, the NMR spectra of **6** and **7** indicate the presence of C-bound enolate ligands. Thus, the ^1H and ^{13}C resonances corresponding to the Ni−CH_2 groups appear in the high-field region of the spectra and exhibit the expected couplings with the ^{31}P nuclei, e.g., at δ 17.4 ppm in the ^{13}C NMR spectrum with *trans* and *cis* $^2J_{CP}$ couplings of 53 and 11 Hz for **6**. The $^{31}P\{^1H\}$ NMR spectrum is also a useful diagnostic tool for the binding mode of the enolate, since the C-enolate derivatives provide an electronically more symmetric environment for the dippe ligand than O-enolates containing one Ni−CH_3 and one Ni−O bonds. Accordingly, a smaller separation of the two phosphorus signals is observed for **6** and **7** ($\Delta\delta = 8$ ppm) than for the O-enolates **3**−**5** ($\Delta\delta \approx 12$ ppm). The IR spectra of **6** and **7** display characteristic ν(C=O) and ν(C≡N) bands at 1681 and 2181 cm^{-1}, respectively. These frequencies are somewhat decreased with respect to the analogous absorp-

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(21) It is interesting to note that the basicities of the hydroxide **2a** and the *tert*-butoxide **2b** differ more than one would expect on the basis of the pK_a of water and *t*-BuOH, which are 15.5 and 17.0 in aqueous medium, i.e., a difference of less than 2 orders of magnitude. In dmso, the pK_a of water is even larger than that of *t*-BuOH (31.2 and 29.4, repectively), suggesting that hydroxides should be even stronger bases than alkoxides in aprotic solvents. The comparatively low basicity of the hydroxide complex could be due to the high thermodynamic stability of the partially ionic Ni−OH bond, which includes a strong electrostatic interaction between the metal center and the small hydroxo ligand.

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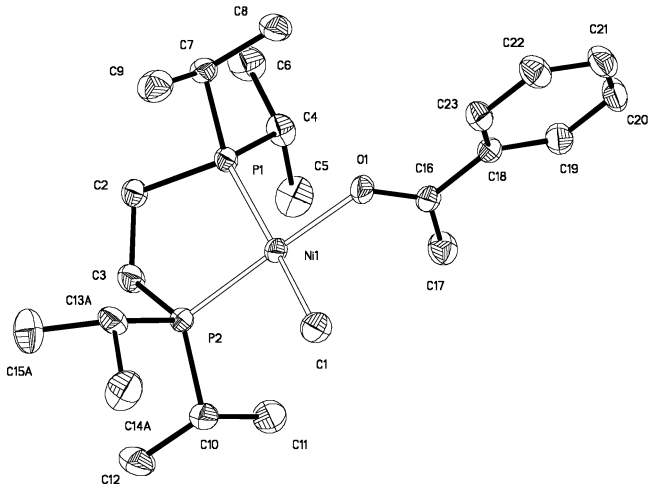


Figure 1. ORTEP view of **3**. Selected bond lengths (Å) and angles (deg): Ni−O1, 1.9043(17); Ni−C1, 1.955(3); Ni−P1, 2.2145(9); Ni−P2, 2.1177(8); O1−C16, 1.318(3); C16−C17, 1.343(4); O1−Ni−C1, 88.45(11); C1−Ni−P2, 90.63(9); O1−Ni−P1, 91.85(6); P2−Ni−P1, 89.15(3).

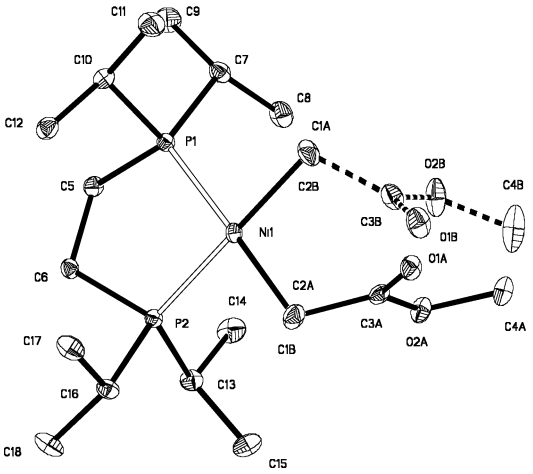
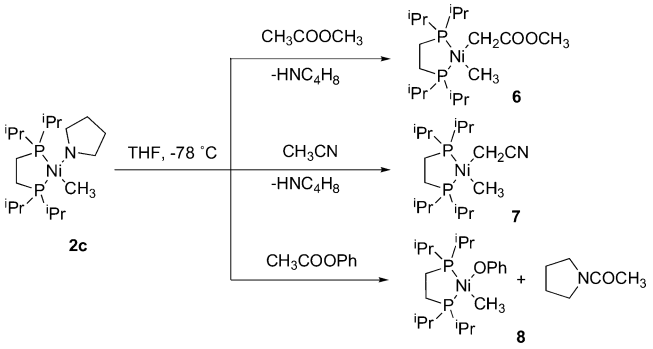


Figure 2. ORTEP view of **6**. Selected bond lengths (Å) and angles (deg): Ni−C1A, 1.9894(18); Ni−C2A, 2.0056(19); Ni−P1, 2.1669-(5); Ni−P2, 2.1724(5); O1A−C3A, 1.212(4); C2A−C3A, 1.524-(3); O2A−C3A, 1.368(4); C1A−Ni−C2A, 90.14(9); C1A−Ni−P1, 90.36(7); C2A−Ni−P2, 91.19(6); P1−Ni−P2, 88.400(18).

tions of free methyl acetate (1744 cm^{-1}) and acetonitrile (2254 cm^{-1}). Frequency shifts of ν(C═O) of a comparable magnitude are often observed for C-enolate complexes[2a,c,24] and have been attributed to the decrease of the C═O bond order as a result of the mesomeric interaction of the M−C and C═O bonds (β effect).

The crystal structure of compound **6** is shown in Figure 2. The methyl and the enolate fragments were found disordered, exchanging their mutual positions, with one of the two possible orientations (shown in Figure 2) being slightly more abundant than the other (64:34 ratio). The bond distances and angles are unexceptional and show no important deviations from their normal values. The two Ni−C carbon bonds have negligible differences, and the Ni−P bond lengths are the same within the experimental error. The enolate fragment is oriented perpendicularly to the coordination plane, and the C(2)−C(3) and C(3)═O distances (1.524(3) and 1.212(4) Å) can be considered normal. In contrast, other transition metal C-enolate

Scheme 3



derivatives often display relatively short C−C(O) and long C═O bonds, presumably as a consequence of the β effect.[2a,c,9c]

The preference of the ester and nitrile enolate ligands in **6** and **7** for binding the metal through the carbon atom contrasts with the behavior of nickel ketone enolates, which tend to adopt the opposite coordination mode. The spectral and structural data for **6** and **7** suggest that these compounds are best described as β-functionalized alkyl derivatives, displaying essentially covalent Ni−C bonds, while ketone enolates feature a polar Ni−O bond with a large ionic contribution.[25] Very likely, the O-bonded coordination mode is stabilized by the capability of the enolate ligand to disperse the partial negative charge originated in the highly polarized Ni−O bond. It is well known that this capability is less pronounced for esters or nitriles than for ketones (this being the reason usually invoked to explain the lower acidity of the former[26]), and this may help to explain the different preferences for the O- and C-coordination modes of the corresponding nickel enolate complexes. In any case, it is worth mentioning here that the preference of nickel ketone enolates for the O- over the C-bonded coordination mode is probably very small, as in some cases the two may be nearly energetically equivalent,[7a,b] or even the latter may be more stable.[2c]

As shown in Scheme 3, phenyl acetate reacts with **2c**, affording a different kind of product, the phenoxide complex **8**, which has been isolated in 55% yield as a red crystalline material. Monitoring the reaction by ^{31}P NMR allowed the detection of a transient species, **8′**, whose characteristic signals fade away in the course of the reaction. These consist of two singlets at δ 71.8 and 80.3, whose position and small separation (8.5 ppm) are strongly reminiscent of those of the ester enolate **6** ($\Delta\delta$ = 8.3 ppm), pointing out an analogous C-enolate structure for **8′**. This result can be explained as shown in Scheme 4. Phenyl acetate is deprotonated by **2c** in the same fashion as methyl acetate (path A). However, for the more reactive phenyl acetate, the acid−base reaction competes with the nucleophilic attack of **2c** on the aryloxycarbonyl group, which leads to the phenoxide **8** (path B). The latter compound is very stable, and its formation behaves as an effectively irreversible process, driving the formation of **8** at the expense of **8′**.

Carbonylation of Nickel O-Enolates. We have previously shown that the carbonylation of nickelacyclic enolates cleanly leads to the corresponding enol lactones and Ni(CO)$_2$(dippe).[7b,e] Apart from being a synthetically useful reaction, it proved to be an auxiliary tool for the characterization of enolate complexes that are difficult to isolate, allowing fixing their structures in organic products readily purified by standard chromatographic

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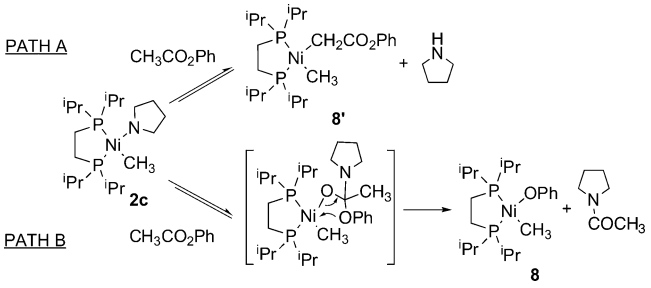
(25) (a) Holland, P. L.; Andersen, R. A.; Bergman, R.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800. (b) Holland, P. L.; Andersen, R. G.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115.

(26) Rablen, P.; Bentrup, K. H. *J. Am. Chem. Soc.*, **2003**, *125*, 2148, and references therein.

Scheme 4



techniques. The carbonylation of noncyclic enolates follows the same path and can be similarly used for the identification of enolate derivatives. Thus, compound **3** rapidly reacts with CO to afford acetophenone enol acetate, $PhC(=CH_2)OCOCH_3$, and $Ni(CO)_2(dippe)$. In order to check whether the reaction proceeds through CO insertion into the Ni−C or the Ni−O bond, a solution of **3** in toluene-d_8 was treated with ca. 0.75 equiv of CO at −60 °C. However, the reaction directly afforded 0.25 equiv of $Ni(CO)_2(dippe)$ and the enol acetate, leaving the remaining starting material unaltered. No intermediates could be detected, showing that these are too unstable under the experimental conditions, immediately evolving into the reductive elimination products.

The carbonylation of **3** can be efficiently performed using samples of the enolate complex generated *in situ* from **2c** and acetophenone. This stimulated us to apply this procedure to the investigation of the reaction of the amide reagent with the unsymmetric ketone 4-phenylbutan-2-one, where two regioisomeric enolates can possibly be formed (Scheme 5). When the reaction is carried out at −78 °C, ^{31}P NMR monitoring confirms the formation of a mixture of two enolate complexes, **9a**,**b** in a 6:1 ratio. Immediate carbonylation of the reaction mixture at −78 °C leads to the corresponding $Ni(CO)_2(dippe)$ and the enolate acetates **10a**,**b**, which were obtained as an insoluble mixture by spinning band chromatography. The ^1H and ^{13}C NMR spectra of this mixture show that the major isomer corresponds to the terminal enol ester **10a**, and hence the main enolate complex must be **9a**.

On standing at room temperature, the mixture of enolate complexes gradually equilibrates, eventually attaining the opposite isomer ratio (i.e., **9a:9b** 1:6). Thus, it can be concluded that the less hindered enolate is formed under kinetic control conditions, while thermodynamic control favors the most substituted isomer. This isomerization process is likely to be catalyzed by the pyrrolidine generated in the reaction or by traces of free ketone. The selectivity control observed in these reactions is analogous to that observed in the formation of alkaline enolates from the corresponding amides.[27]

Reaction of Enolate Complex 3 with Benzaldehyde and Carbon Dioxide. As already mentioned, the aldol reactivity of transition metal enolates has attracted much attention because of its possible application to asymmetric synthesis. Several catalytic processes of this kind, which are proposed to proceed via late transition metal enolate complexes, have been reported,[3] and in some cases, both enolate and aldolate complexes have been isolated.[2b] In our previous work, we found that nickelacyclic enolates react with enolizable and nonenolizable aldehydes, but these reactions lead to addition products containing substituted enolate functionalities, rather than classical aldolate complexes.[7a,b] On the other hand, cyclopentadienylnickel complexes displaying C-bound enolate ligands display a rather complex reactivity toward aldehydes, which involves the successive addition of two aldehyde molecules and leads to mixtures of two isomeric β-hydroxy esters.[2c] In order to check whether noncyclic O-enolates of nickel follow a classic addition pathway to aldehydes, we have investigated the reaction of complex **3** with benzaldehyde. Treatment of a solution of **3** in C_6D_6 with an equimolar amount of PhCHO led to the partial conversion of the former into a new product, **11**, characterized by a pair of doublets in the $^{31}P\{^1H\}$ spectrum at δ 63.5 and 75.1 ppm ($^3J_{PP}$ = 7 Hz), whose separation of 12 ppm is consistent with the presence of an O-bonded aldolate ligand. This compound gradually decays in solution, affording Ni(Me)(OH)(dippe), **2a**, as the major phosphorus-containing product, together with some $Ni(Me)_2(dippe)$, $Ni(dippe)_2$, and minor amounts of unidentified species. ^1H NMR and GC-MS analysis of the solution indicates the presence of *trans*-chalcone in the mixture. Under these reaction conditions, the formation and decomposition of **11** takes place at roughly similar rates, preventing the buildup of a concentration sufficient to allow a univocal identification. However, as shown in Scheme 6, treatment of **3** with a 2-fold excess of PhCHO caused its quantitative conversion into **11**. Under these conditions, useful ^1H and $^{13}C\{^1H\}$ NMR could be recorded, which confirm the identity of the product as an aldolate complex. The key feature of this compound is the presence of a chiral NiOC(Ph)HR unit. The asymmetry of this group causes the neighboring CH_2 protons to become diastereotopic, giving rise to two multiplets at δ 3.32 and 3.47 in the proton spectrum. The characteristic signals of the alkoxo α-methyne are a somewhat broadened ^1H signal at 5.70 ppm and a doublet at δ 73.0 ($^2J_{CP}$ = 5 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. These features are nearly identical to those originated by the alkoxo moiety in the complex Ni(CH_3)(OC(Ph)(Me)H)(dippe), recently reported by us.[15b] The vicinal ^1H coupling scheme and assignation of ^{13}C signals has been further confirmed by the 2D COSY and $^1H-^{13}C$ NMR heterocorrelation spectra.

On standing at room temperature, the C_6D_6 solution of **11**, containing only excess PhCHO, decays in the same fashion observed for partially converted mixtures, affording the hydroxide **2a** and *trans*-2-chalcone as the main product, the latter in 54% yield as determined by GC, with an estimated half-life of ca. 5 h. The fact that the formation of the α,β-unsaturated ketone takes place under rigorously anhydrous conditions, and that no free aldol or acetophenone could be detected by ^1H NMR or GC, suggests that this process takes place through the intramolecular abstraction of an acidic methylene proton by the alkoxo oxygen, with concomitant elimination of the hydroxide complex **2a**, as indicated in Scheme 6. However, more complex intermolecular processes involving the rapid dehydration of free aldol are also conceivable and cannot be ruled out at this stage. Whatever the exact mechanism of this transformation is, the generation of the hydroxide **2a**, together with the ability of this complex to react with acetophenone to regenerate the enolate, implies that this compound should be able to catalyze the aldol condensation of acetophenone and benzaldehyde. In fact, compound **2a**, as well as the amide **2c**, efficiently catalyzes the condensation of acetophenone and other ketones with aromatic aldehydes.[28]

In order to gain more insight into the nucleophilic reactivity of the enolate complexes, the reaction of complex **3** with carbon dioxide was also investigated. Bubbling dry CO_2 (1 equiv) through a solution of the enolate complex **3** causes the latter to

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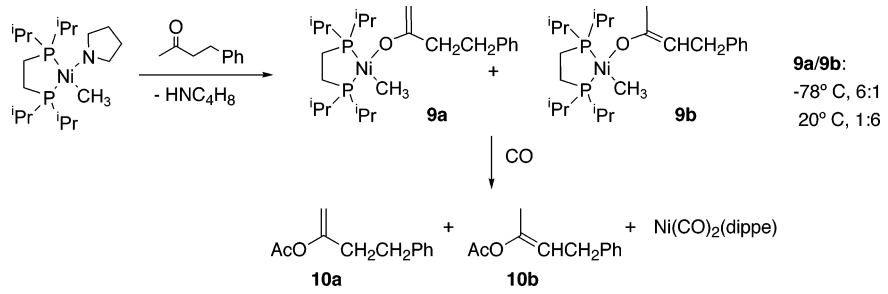
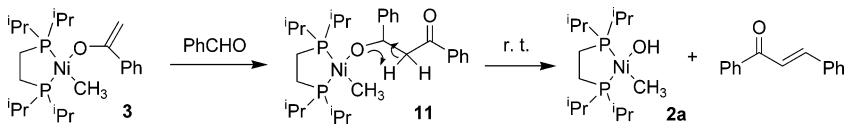
Scheme 5



Scheme 6



be quantitatively converted into a new compound, **12**, as deduced by $^{31}P\{^1H\}$ NMR monitoring of this reaction. Again, the spectrum features two ^{31}P resonances (δ 67.0 and 78.0) separated by 11 ppm, which is consistent with the simultaneous presence of one Ni−C and one Ni−O bond. Full NMR data have been obtained for **12** that are in agreement with the formulation represented in Scheme 7. Thus, the CH_2 unit of the β-ketocarboxylate ligand gives rise to a single ^1H resonance at δ 4.03 ppm and at δ 51.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The presence of two carbonyl groups is evinced by two ^{13}C resonances at low field (δ 169.9 and 194.5 ppm).

The reactivity of enolate **3** toward carbon dioxide differs from that of alkoxide and amide complexes, which experience the formal insertion of the heterocumulene in the Ni−X bond (X = O, N).[15b] In contrast, the formation of complex **12** can be envisaged as a nucleophilic attack of the β carbon of the enolate ligand to the carbon atom of CO_2, which leads to C−C bond formation. Therefore, the reactions of **3** with benzaldehyde and CO_2 can be considered as closely related reactions, exemplifying the characteristic reactivity of enolate complexes where the center of the nucleophilic reactivity sits in a position remote from the metal atom.

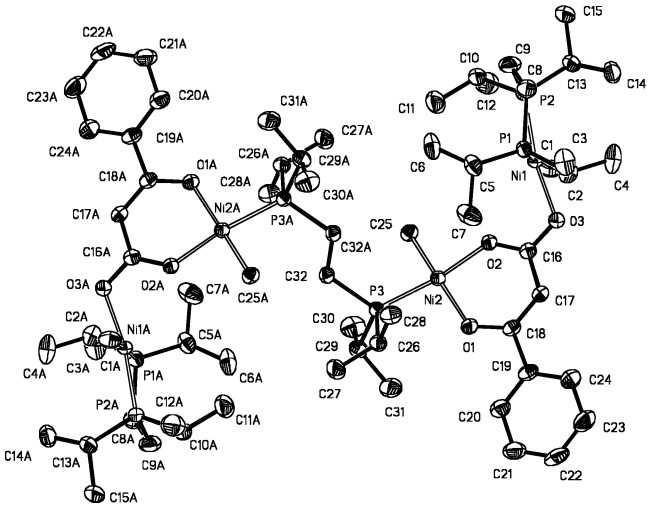


Figure 3. ORTEP view of **13**. Selected bond lengths (Å) and angles (deg): Ni1−O3, 1.9457(16); Ni2−O2, 1.9009(16); Ni2−O1, 1.9173(16); O1−C18, 1.300(3); O2−C16, 1.282(3); C16−C17, 1.442(3); C17−C18, 1.367(3); O3−Ni1−C1, 88.83(9); C1−Ni1−P2, 88.77(8); O3−Ni1−P1, 91.64(5); P2−Ni1−P1, 89.93(3); O2−Ni2−O1, 93.57(7); O2−Ni2−C25, 85.28(8); O1−Ni2−P3, 91.12(5); C25−Ni2−P3, 91.19(7).

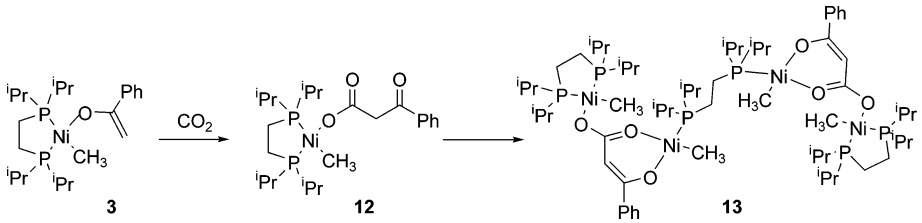
Attempts to isolate complex **12** were thwarted by its low stability in solution. After 24 h, the ^1H NMR spectrum of the C_6D_6 solution of **12** shows the presence of ca. 0.5 equiv of acetophenone, which gradually increases over several days. At the same time an insoluble material begins to precipitate. After a few days, crystals of the insoluble product **13** were collected and submitted for X-ray structure determination. As shown in Figure 3, this compound is a dimer comprising two identical binuclear fragments, linked by a bridging diphosphine ligand. Each binuclear moiety features a doubly deprotonated benzoylacetic acid unit, which coordinates to one Ni atom as a carboxylate and to the second Ni center as a 1,3-dionate ligand. Remarkably, each metal fragment retains its original methyl group.

The release of acetophenone during the formation of **13** implies a partial loss of carbon dioxide. The reversibility of the enolate carboxylation reaction has been fully demonstrated for palladium phosphinoenolate derivatives.[17] A possible mechanism for this process is shown in Scheme 8. The decarboxylation of **12** would restore compound **3**, the basic enolate complex deprotonating the acidic methylene group of a second molecule of **12**. This reaction releases acetophenone and gives rise to a transient binuclear species, **14**, which rapidly condensates into the tetranuclear product **13**, with elimination of 1 equiv of the diphosphine.

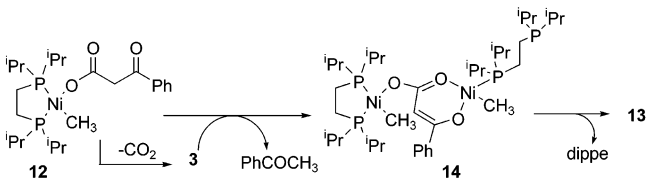
As a final comment, it is worth comparing the reactivity of enolate **3** and that of its closely related cyclic analogue Ni(OC(=CH_2)-*o*-C_6H_4)(dippe). The rigid structure of the latter compound makes it unlikely that the enolate attack on the aldehyde might involve the previous coordination of the aldehyde to the metal center (see Scheme 1). On the contrary, precoordination of the aldehyde to the nickel center becomes possible for the noncyclic enolate **3**. Such precoordination increases the electrophilicity of the aldehyde and brings it to a favorable position for an intramolecular nucleophilic attack of the enolate ligand. Therefore, the reaction of compound **3** with benzaldehyde was expected to be appreciably faster than that of the cyclic enolate. However, both enolate complexes react at similar rates under similar experimental conditions (C_6D_6, room temperature, ca. 0.16 M of each reagent).[29] Therefore, aldehyde precoordination does not appear to be important for the reactivity of these nickel enolates. The facile reaction of **3** with carbon dioxide provides further support for this conclusion,

(29) For the cyclic enolate, the reaction takes ca. 4 h to complete under these conditions.

Scheme 7



Scheme 8



since CO_2 coordination to the four-coordinated Ni(II) center appears unlikely to play any important role.

Conclusions

In summary, the synthesis and reactivity of some nickel alkyl-enolate complexes has been investigated. Ketone enolates can be generated from the fluoro precursor **1** and lithium enolates or by acid−base exchange reactions of the alkyl-hydroxo, -alkoxo, and -amido Ni(II) complexes **2a**−**c** with enolizable ketones. The positions of the equilibria associated with the latter acid−base exchanges confirm the expected basicity order: Ni−OH < Ni−OR < Ni−NR_2. Nickel amides behave as highly basic reagents, reacting rapidly and quantitatively not only with ketones but also with less acidic carbon acids such as esters and nitriles. While the ester and nitrile enolates adopt the C-bonded coordination mode, the more polar O-bonded tautomer is preferred in the case of the ketone enolates, presumably as a result of the ability of the latter ligands to disperse negative charge.

The methylnickel enolates are highly reactive compounds that undergo clean reactions with CO, CO_2, and aldehydes. The carbonylation reaction leads to the corresponding enol acetates, and this reaction has been used to explore the regioselectivity of the deprotonation of a nonsymmetric ketone with the amide complex **2c**. Like lithium amides, the nickel reagent affords preferentially the less hindered enolate complex under kinetic control conditions (−78 °C), but this slowly equilibrates at room temperature, with the most stable product displaying the most substituted double bond.

The reaction of the acetophenone enolate **3** with PhCHO or CO_2 proceeds similarly, giving rise to the thermally unstable addition products **11** and **12**. The nickel aldolate **11** decomposes in solution, eliminating hydroxide complex **2a** and giving *trans*-chalcone. Complex **12** experiences a slow decarboxylation process to afford the tetranuclear compound **13**, containing doubly deprotonated phenylacetate ligands. The fact that compound **3** does not react more rapidly with PhCHO than the cyclic enolate Ni(OC(=CH_2)-*o*-C_6H_4)(dippe) suggests that the previous coordination of the aldehyde to the metal center does not play an important role in either of 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. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer, and NMR spectra on Bruker DRX 300 and 400 MHz spectrometers. The ^{1}H and ^{13}C-{^{1}H} NMR resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. ^{31}P NMR resonances are referenced to external 85% H_3PO_4. GC analyses were performed in a Agilent model HP 6890 chromatograph and GC-MS on a Thermoquest Automass Multi gas chromatograph−mass spectrometer, both of them equipped with a Technokroma HP1 column. Carbon dioxide was dried by storage in a Fischer−Porter reactor containing P_2O_5. Nickel complexes **2a**, **2b**, and **2c** were prepared as reported previously.[15] For the present work, solutions of **2c** in thf were generated as follows.

Preparation of a thf Solution of 2c. A solution of 0.5 mmol of lithium pyrrolidinide, prepared by adding 0.3 mL of a 1.6 M hexane solution (0.5 mmol) of ^{n}BuLi to a cooled solution (−78 °C) of 42 μL of pyrrolidine (0.5 mmol) in 2 mL of thf and allowing it to warm to room temperature, was added to a solution of 176 mg of the fluoro complex **1** (0.5 mmol) in 3 mL of thf, cooled to −78 °C. The color changed from orange to dark red, indicating the formation of **2c**. The solution was allowed to warm to room temperature and then cooled again to −78 °C and used. Compound **2c** is thermally unstable, and this solution cannot be stored.

Synthesis of Ni(dippe)(CH_3)(OC(CH_2)Ph) (3). Method A. A solution of lithium enolate of acetophenone (1 mmol) was prepared by reacting equimolar amounts of lithium diisopropylamide and acetophenone at −78 °C in 5 mL of thf and then allowed to warm to room temperature. This solution was added dropwise to a stirred solution of compound **1** (335 mg, 1 mmol) in thf (5 mL) cooled to −78 °C. The cooling bath was removed and the mixture stirred at room temperature. The solvent was removed under vacuum and the residue extracted with 5 mL of thf. This solution was concentrated and treated with ca. 2 mL of diethyl ether. Then the solid residue was separated by centrifugation. After cooling the solution to −20 °C, orange crystals were obtained. Yield: 200 mg (45%).

Method B. A 0.96 mL amount of a 1.7 M solution of Li^{n}Bu (0.5 mmoL) in hexane was added to 3 mL of thf at −78 °C containing 48 μL of *tert*-butanol (0.5 mmoL). The mixture was stirred and allowed to warm to room temperature, then added to a solution of 176 mg of Ni(dippe)(Me)(F) (0.5 mmoL) in 3 mL of thf stirred at −78 °C. The mixture was warmed to room temperature and cooled again at −78 °C. Then, 58 μL (0.5 mmol) of acetophenone was added. The cooling bath was removed and the mixture allowed to reach the room temperature. The solvent was removed under reduced pressure and the residue extracted with 3 mL of thf. The product was obtained in a 45% yield after adding some diethyl ether and cooling at −30 °C.

Method C. To a thf solution of **2c** (0.5 mmol) cooled to −78 °C was added 58 μL (0.5 mmol) of acetophenone. The dark red color of the solution lightened. The cooling bath was removed, the solution was allowed to reach room temperature, the solvent was removed under vaccuum, the solid residue was extracted with 3 mL of thf, and solid LiF was removed by centrifugation. The product was isolated as orange crystals in 60% yield (270 mg) after addition of diethyl ether to this solution and cooling to −30 °C.

Anal. Calcd for $C_{23}H_{42}ONiP_2$: C, 60.68; H, 9.30. Found: C, 60.49; H, 9.05. IR (Nujol mull): ν(C═C) 1590 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.40 (pt, 3H, $J^*_{HP} \approx 5.2$ Hz, Ni−CH_3), 0.83 (m, 2H, CH_2), 0.87 (dd, 6H, $^3J_{HP} = 13.3$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 0.98 (dd, 6H, $^3J_{HP} = 12.7$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 1.03 (m, partially obscured by peaks at 0.98 and 1.12, CH_2), 1.12 (dd, 6H, $^3J_{HP} = 15.5$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me), 1.31 (dd, 6H, $^3J_{HP} = 14.9$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me), 1.70 (m, 2H, PC*H*Me$_2$), 1.85 (m, 2H, PC*H*Me$_2$), 4.56 (s, 1H, OCC*H*H), 4.85 (s, 1H, OCC*H*H), 7.12 (m, 1H, *p*-C*H*, Ph), 7.26 (t, 2H, $^3J_{HH} = 7.6$ Hz, *m*-C*H*, Ph), 8.19 (d, 2H, $^3J_{HH} = 7.2$ Hz, *o*-C*H*, Ph). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ −0.1 (dd, $^2J_{CP} = 71$ and 35 Hz, Ni−*C*H$_3$), 17.1 (dd, $^1J_{CP} = 19$ Hz, $^2J_{CP} = 11$ Hz, *C*H$_2$), 16.9 (pt, $J^*_{CP} \approx 16$ Hz, *C*H$_2$), 18.6 (s, PCH*Me*Me), 18.8 (s, PCH*Me*Me), 19.5 (d, $^2J_{CP} = 5$ Hz, PCH*Me*Me), 20.0 (d, $^2J_{CP} = 3$ Hz, PCH*Me*Me), 24.2 (m, *C*H$_2$), 24.4 (d, $^1J_{CP} = 14$ Hz, P*C*HMe$_2$), 25.6 (d, $^1J_{CP} = 27$ Hz, P*C*HMe$_2$), 80.1 (s, OC═*C*H$_2$), 126.3 (s, *C*H, Ph), 126.5 (s, *C*H, Ph), 127.6 (s, *C*H, Ph), 145.2 (d, $^4J_{CP} = 4$ Hz, $C_{q,}$ Ph), 166.3 (s, O*C*═CH$_2$). ^{13}C NMR (gated, C_6D_6, selected data): 80.1 (d, $^1J_{CH} = 153$ Hz, OC═C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 64.7, 76.6.

Synthesis of Ni(dippe)(CH$_3$)(OC(CH(C$_6$H$_4$-*o*-CH$_2$CH$_2$) (4). Method A. A solution of 0.5 mmol of lithium *tert*-butoxide in 3 mL of thf (see synthesis of **3**, method B) was added to a cold (−78 °C) solution of 176 mg of **1** (0.5 mmol) dissolved in 3 mL of thf. The mixture was allowed to reach room temperature and cooled again at −78 °C. Then, 66 μL (0.5 mmol) of α-tetralone was added. After stirring at room temperature for 5 h, the solvent was removed under reduced pressure and the solid was extracted with 3 mL of thf. The insoluble solid (LiF) was removed by centrifugation, some diethyl ether was added, and the solution was cooled to −30 °C, to yield the product in 40% yield (190 mg).

Method B. A solution of **2c** (0.5 mmol) in 3 mL of thf was cooled to −78 °C, and 66 μL (0.5 mmol) of α-tetralone was added. The dark red color characteristic of **2c** immediately changed to bright orange. The mixture was warmed to room temperature, the solvent removed under reduced pressure, and the solid extracted with 3 mL of thf. After centrifugation, diethyl ether was added and the solution was cooled to −30 °C to afford **4** in 50% yield. Anal. Calcd for $C_{23}H_{42}ONiP_2$: C, 62.39; H, 9.22. Found: C, 62.08; H, 8.92. IR (Nujol mull): ν(C═C) 1600 cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.42 (pt, 3H, $J^*_{HP} \approx 5.1$ Hz, Ni−CH_3), 0.83 (dd, 6H, $^3J_{HP} = 13.1$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 0.97 (dd, 6H, $^3J_{HP} = 12.4$ Hz, $^3J_{HH} = 7.1$ Hz, PCH*Me*Me), 1.10 (dd, 6H, $^3J_{HP} = 15.5$ Hz, $^3J_{HH} = 7.1$ Hz, PCH*Me*Me), 1.36 (dd, 6H, $^3J_{HP} = 14.9$ Hz, $^3J_{HH} = 7.1$ Hz, PCH*Me*Me), 1.65 (m, 2H, C*H*), 1.88 (m, 2H, C*H*), 2.73 (m, 2H, CH_2), 2.98 (t, 2H, $^3J_{HH} = 7.5$ Hz, CH_2), 5.36 (t, 1H, $^3J_{HH} = 4.2$ Hz, OC═C*H*), 7.16 (s, 2H, C$_{ar}$*H*), 7.40 (m, 1H, C$_{ar}$*H*), 8.37 (d, 1H, $^3J_{HH} = 7.3$ Hz, C$_{ar}$*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −0.2 (dd, $^2J_{CP} = 71$, 35 Hz, Ni−*C*H$_3$), 16.5 (dd, $^1J_{CP} = 18$ Hz, $^2J_{CP} = 11$ Hz, *C*H$_2$ (dippe)), 18.1 (s, PCH*Me*Me), 18.3 (s, PCH*Me*Me), 19.0 (d, $^2J_{CP} = 5$ Hz, PCH*Me*Me), 19.5 (d, $^2J_{CP} = 3$ Hz, PCH*Me*Me), 23.7 (s, P*C*HMe$_2$), 24.5 (s, *C*H$_2$), 25.1 (d, $^1J_{CP} = 27$ Hz, P*C*HMe$_2$), 30.7 (s, *C*H$_2$), 95.3 (s, OC═*C*H), 123.3 (s, *C$_{ar}$*H), 125.3 (s, *C$_{ar}$*H), 125.6 (s, *C$_{ar}$*H), 126.2 (s, *C$_{ar}$*H), 137.8 (s, *C$_{ar}$*), 140.3 (s, *C$_{ar}$*), 158.2 (s, O*C*CH). ^{13}C NMR (gated, C_6D_6, selected data): δ 95.3 (d, $^1J_{CH} = 152$ Hz, OC═C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz) δ 64.4, 76.3.

Synthesis of Ni(dippe)(CH$_3$)(OC(CH$_2$)C(CH$_3$)$_3$) (5). A solution of **2c** (0.5 mmol) in 3 mL of thf was cooled at −78 °C, and 62 μL (0.5 mmol) of pinacolone was added. The color of the solution changed from red to orange. After warming at room temperature, the solvent was removed under reduced pressure and the solid residue was extracted in 3 mL of hexane. Then the solid residue was separated by centrifugation. The product crystallized out from this solution at −78 °C as a dark orange solid in a 60% yield. No satisfactory analytical data could be gathered for this compound, probably due to its low stability. IR (Nujol mull): ν(C═C) 1581 cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.47 (pt, 3H, $J^*_{HP} = 5.3$ Hz, Ni−CH_3), 0.82 (dd, 6H, $^3J_{HP} = 13.1$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 0.98 (dd, 6H, $^3J_{HP} = 12.5$ 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, $^3J_{HP} = 15.1$ Hz, $^3J_{HH} = 7.1$ Hz, PCH*Me*Me), 1.54 (s, 9H, C*Me*$_3$), 1.67 (m, 2H, PC*H*Me$_2$), 1.89 (m, 2H, PC*H*Me$_2$), 4.05 (s, 1H, OC═CH*H*), 4.21 (s, 1H, OC═CH*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 0.5 (dd, $^2J_{CP} = 69$, 35 Hz, Ni−*C*H$_3$), 16.8 (dd, $^1J_{CP} = 18$ Hz, $^2J_{CP} = 12$ Hz, *C*H$_2$), 18.0 (s, PCH*Me*Me), 18.3 (s, PCH*Me*Me), 19.2 (d, $^2J_{CP} = 6$ Hz, PCH-*Me*Me), 19.5 (d, $^2J_{CP} = 3$ Hz, PCH*Me*Me), 23.8 (d, $^1J_{CP} = 14$ Hz, P*C*HMe$_2$), 25.1 (d, $^1J_{CP} = 27$ Hz, P*C*HMe$_2$), 30.0 (s, C*Me*$_3$), 37.7 (s, *C*Me$_3$), 75.4 (s, OC ═ *C*H$_2$), 177.5 (s, O*C*═CH$_2$). ^{13}C NMR (gated, C_6D_6, selected data): δ 75.4 (d, $^1J_{CH} = 152$ Hz, OC═C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 64.8, 76.6.

Table 1. Equilibrium Constants for the Neutralization of 2a with Ketones

2a + acetophenone			**2a** + α-tetralone		
ketone equiv	K_{eq}	K_{eq}(average)	ketone equiv	K_{eq}	K_{eq}(average)
3	3.1×10^{-2}	$2(1) \times 10^{-2}$	5	3.2×10^{-2}	$5(2) \times 10^{-2}$
6	2.0×10^{-2}		10	5.1×10^{-2}	
10	1.5×10^{-2}		15	7.3×10^{-2}	
20	0.7×10^{-2}				

Measurement of Enolate Formation Equilibrium Constants. In a typical experiment, the hydroxide complex **2a** (30 mg, 85 μmol) was dissolved in 0.5 mL of thf and placed in a NMR tube. Then, 1 equiv of acetophenone was added, and the solution monitored by ^{31}P NMR spectroscopy, which indicated that the equilibrium was immediately reached. Increasing amounts of acetophenone were added (up to 20 equiv). The ratios of the enolate and hydroxide complexes were determined by integration of the ^{31}P NMR spectra. Table 1 shows the values of the equilibrium constants (K_{eq}) obtained. Neutralization experiments using **2b** were carried out in a similar manner, using samples of *tert*-butoxide complex generated *in situ* from **1** and LiO-*t*-Bu. These reactions proceeded more slowly and were monitored until no further change was observed. For acetophenone and tetralone, the equilibrium was fully shifted to the enolate complexes and the constants could not be determined. During the slow neutralization of **2b** by pinacolone, some decomposition took place, but an equilibrium constant $K_{eq} \approx 6$ could be estimated.

Synthesis of Ni(dippe)(CH$_3$)(CH$_2$CO$_2$CH$_3$) (6). A solution of 0.5 mmol of **2c** in 3 mL of thf, prepared as described before, was cooled at −78 °C, and 39 μL (0.5 mmol) of methyl acetate was added. The dark red solution lightened immediately. The cooling bath was removed and the mixture stirred while warming to room temperature. Then, the solvent was removed under reduced pressure and the solid extracted with 3 mL of Et$_2$O. Then the solid residue was separated by centrifugation. The product was obtained in 60% yield as orange crystals after partial evaporation of the solvent and cooling at −20 °C. Anal. Calcd for $C_{18}H_{40}O_2NiP_2$: C, 52.84; H, 9.85. Found: C, 52.03; H, 10.24. IR (Nujol mull): ν(C═O) 1681 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.53 (dd, 3H, $^3J_{HP} = 8.1$, 4.3 Hz, Ni−CH_3), 0.79 (dd, 6H, $^3J_{HP} = 12.8$ Hz, $^3J_{HH} = 7.0$ Hz, PCH*Me*Me), 0.84 (dd, 6H, $^3J_{HP} = 11.9$ Hz, $^3J_{HH} = 7.3$ Hz, PCH*Me*Me), 0.94 (m, 2H, CH_2), 1.02 (dd, 6H, $^3J_{HP} = 15.1$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me), 1.17 (dd, 6H, $^3J_{HP} = 14.9$ Hz, $^3J_{HH} = 7.2$ Hz, PCH*Me*Me), 1.83 (m, 2H, PC*H*Me$_2$), 2.07 (m, 2H, PC*H*Me$_2$), 2.23 (dd, 2H, $^3J_{HP} = 10.6$, 6.3 Hz, CH_2CO$_2$CH$_3$), 3.72 (s, 3H, CH$_2$CO$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −1.0 (dd, $^2J_{CP} = 66$, 27 Hz, Ni−*C*H$_3$), 17.4 (dd, $^2J_{CP} = 53$, 12 Hz, *C*H$_2$-CO$_2$CH$_3$), 18.2 (s, PCH*Me*Me), 19.7 (s, PCH*Me*Me), 21.5 (dd, $^1J_{CP} = 22$ Hz, $^2J_{CP} = 18$ Hz, CH_2), 24.5 (pt, $J^*_{CP} \approx 20$ Hz, P*C*HMe$_2$), 49.1 (s, CH$_2$CO$_2$*C*H$_3$), 180.2 (s, CH$_2$*C*O$_2$CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 71.4, 79.5.

Synthesis of Ni(dippe)(CH_3)(CH_2CN) (7). A solution of 0.5 mmol of **2c** (0.5 mmol) in 3 mL of thf was cooled to −78 °C, and 26 μL (0.5 mmol) of acetonitrile was added. The color changed from dark red to orange. The solvent was removed under vacuum, the residue extracted with 5 mL of diethyl ether, and then the solid residue separated by centrifugation. Upon filtration and evaporation, the product was obtained as an orange solid. Yield: 30%. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.43 (dd, 3H, $^3J_{HP}$ = 8.1 and 4.1 Hz, Ni−C*H*$_3$), 0.80 (dd, 12 H, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 1.05 (dd, 12 H, $^3J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 7.7 Hz, PCH*Me*Me), 1.25 (dd, 2H, $^3J_{HP}$ = 11.0 and 4.9 Hz, NiC*H*$_2$CN), 1.80 (m, 4H, PC*H*MeMe). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ −6.5 (dd, $^2J_{CP}$ = 61, 14 Hz, Ni−*C*H$_2$CN), 1.6 (dd, $^2J_{CP}$ = 67, 26 Hz, Ni−*C*H$_3$), 18.6 (s, PCH*Me*Me), 19.8 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 20.1 (d, $^2J_{CP}$ = 4 Hz, PCH*Me*Me), 21.9 (pt, $J^*_{CP} \approx$ 20 Hz, *C*H$_2$), 24.8 (d, $^1J_{CP}$ = 6 Hz, P*C*HMe$_2$), 27.9 (d, $^1J_{CP}$ = 11 Hz, P*C*HMe$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 73.3, 81.3.

Synthesis of Ni(dippe)(CH_3)(OPh) (8). A solution of **2c** (0.5 mmol) in 3 mL of thf, prepared as described above, was cooled at −78 °C, and 63 μL (0.5 mmol) of phenyl acetate was added. After reaching room temperature, solvent was removed under reduced pressure, and the residue was extracted in 5 mL of diethyl ether. After centrifugation, the solution was cooled at −20 °C. The product crystallized as red crystals. Yield: 55%. Anal. Calcd for $C_{21}H_{40}ONiP_2$: C, 58.77; H, 9.39. Found: C, 58.26; H, 9.47. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.29 (pt, 3H, $J^*_{HP} \approx$ 5.0 Hz, Ni−C*H*$_3$), 0.70 (m, 2H, C*H*$_2$), 0.80 (dd, 6 H, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 7.0 Hz, PCH*Me*Me), 0.93 (dd, 6 H, $^3J_{HP}$ = 12.6 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.07 (dd, 6H, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.28 (dd, 6H, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.61 (m, 2H, PC*H*Me$_2$), 1.80 (m, 2H, PC*H*Me$_2$), 6.78 (t, 1H, $^3J_{HH}$ = 7.0 Hz, *p*-C*H*, Ph), 7.30 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *o*-C*H*, Ph), 7.42 (t, 2H, J_{HH} = 7.4 Hz, *m*-C*H*, Ph). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 0.0 (dd, $^2J_{CP}$ = 72, 35 Hz, Ni−*C*H$_3$), 16.1 (dd, $^1J_{CP}$ = 18 Hz, $^2J_{CP}$ = 11 Hz, *C*H$_2$), 18.0 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.0 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.5 (s, PCH*Me*Me), 23.7 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 25.1 (d, $^1J_{CP}$ = 27 Hz, P*C*HMe$_2$), 112.3 (s, *p*-*C*H, Ph), 121.9 (s, *o*-*C*H, Ph), 128.8 (s, *m*-*C*H, Ph), 169.4 (s, O−*C*, Ph). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 64.0, 76.5.

Carbonylation of Enolate 3. A solution of **2c** (0.5 mmol) in 3 mL of thf was cooled to −78 °C. Then, 58 μL (0.5 mmol) of acetophenone was added. After reaching room temperature, the mixture was brought back to −78 °C and CO was bubbled in for 5 min, turning the initial orange color of the solution to pale yellow. Solvent was removed under reduced pressure when room temperature was reached, and the oily residue was extracted with 5 mL of ether and filtered. Acetophenone acetate[30] was separated from Ni(dippe)(CO)$_2$ by spinning band chromatography, with a eluent mixture of hexane/ether (19:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.27 (s, 3H, C*H*$_3$), 5.01 (d, 1H, $^2J_{HH}$ = 2.2 Hz, OC=C*H*H), 5.47 (d, 1H, $^2J_{HH}$ = 2.2 Hz, OC=CH*H*), 7.32 (m, 3H, Car*H*), 7.45 (m, 2H, Car*H*).

This reaction was also carried out starting from an isolated sample of enolate complex **3**: to this compound (115 mg, 25 μmol), which was dissolved in 0.7 mL of toluene-d_8 in a NMR tube, was added 0.75 equiv (4.2 mL) of dry CO at −60 °C. A ^{31}P NMR spectrum of the reaction mixture indicated the presence of the starting material and Ni(CO)$_2$(dippe) in a 1:0.25 ratio.

Carbonylation of the Enolates of 4-Phenylbutan-2-one: $CH_3CO_2C(=CH_2)(CH_2)_2Ph$ (10a) and $CH_3CO_2C(=CHCH_2Ph)CH_3$ (10b). 4-Phenylbutan-2-one (72 μL, 0.5 mmol) was added to 3 mL of a cooled (−78 °C) thf solution containing 0.5 mmol of **2c**. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture displayed characteristic signals corresponding complexes **9a** and **9b** as the only P-containing products (**9a**/**9b** = 6:1). CO was bubbled for 5 min at −78 °C, changing the color from orange to pale yellow. The mixture was warmed at room temperature and the solvent was removed under vacuum. The residue was extracted in ether (5 mL). Compounds **10a**[31] and **10b** were separated from Ni(dippe)(CO)$_2$ by spinning band chromatography using a 10:1 hexane/ether mixture as eluent. It was not possible to resolve the mixture of **10a** and **10b**, which were found to be in a 4:1 ratio. In a similarly performed experiment, a solution containing **9a** and **9b** was allowed to stand for several hours at room temperature. The inversion of the isomer ration was established by ^{31}P{^{1}H} NMR.

Compound **10a**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.10 (s, 3H, C*H*$_3$), 2.53 (t, 2H, $^3J_{HH}$ = 7.8 Hz, C*H*$_2$), 2.80 (t, 2H, $^3J_{HH}$ = 7.8 Hz, C*H*$_2$), 4.74 (s, 1H, =CH*H*), 4.75 (s, 1H, =C*H*H), 7.26 (m, 5H, Car*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.0 (s, *C*H$_3$), 32.9 (s, *C*H$_2$), 35.0 (s, *C*H$_2$), 101.8 (s, =*C*H$_2$), 126.1 (s, *C*$_{ar}$H), 128.3 (s, *C*$_{ar}$H), 128.4 (s, *C*$_{ar}$H), 140.9 (s, *C*$_{ar}$), 155.7 (s, O*C*=CH), 169.2 (s, O$_2$*C*CH$_3$).

Compound **10b**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.93 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$), 3.27 (d, 2H, $^3J_{HH}$ = 7.3 Hz, C*H*$_2$), 5.19 (t, 1H, $^3J_{HH}$ = 6.9 Hz, =C*H*), 7.26 (m, 5H, C$_{ar}$*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.6 (s, *C*H$_3$), 20.8 (s, *C*H$_3$), 31.8 (s, *C*H$_2$), 115.7 (s, =*C*H), 126.1 (s, *C*$_{ar}$H), 128.3 (s, *C*$_{ar}$H), 128.4 (s, *C*$_{ar}$H), 140.1 (s, *C*$_{ar}$), 145.6 (s, O*C*=CH$_2$), 169.0 (s, O$_2$*C*CH$_3$).

Reaction of Enolate Complex 3 with Benzaldehyde. Characterization of Ni Aldolate 11. A 21 μL portion of benzaldehyde (0.2 mmol) was added to a solution of complex **3** (48 mg, 0.1 mmol) in 0.5 mL of C_6D_6. ^{31}P and ^{1}H NMR monitoring revealed quantitative formation of aldolate **11**. The reaction mixture was allowed to stand at room temperature for 2 days. ^{31}P NMR indicated total consumption of **11** to give Ni(Me)(OH)(dippe) as the major P-containing product. The yield of *trans*-chalcone in the mixture, determined by GC, was 54%. Compound **11**: ^{1}H NMR of (C_6D_6, 300 MHz): δ −0.23 (s, 3H, Ni−C*H*$_3$), 0.75 (d, 6H, PCH*Me*Me), 0.99 (m, 12H, PCH*Me*Me), 1.39 (dd, 6H, $^3J_{HP}$ = 14.2, 6.3 Hz, PCH*Me*Me), 1.53 (m, 2H, PC*H*Me$_2$), 1.98 (m, 2H, PC*H*Me$_2$), 3.32 (d, 1H, $^2J_{HH}$ = 9.9 Hz, Ni−OCH(Ph)C*H*H(COPh)), 3.47 (pt, 1H, J^*_{HH} = 10.5 Hz, Ni−OCH(Ph)CH*H*C(O)Ph), 5.70 (bs, 1H, Ni−OC*H*(Ph)), 7.00 (d, 1H, $^3J_{HH}$ = 7.1 Hz, C$_{ar}$*H*), 7.34 (t, 2H, J_{HH} = 7.0 Hz, C$_{ar}$*H*), 7.86 (d, 2H, $^3J_{HH}$ = 7.0 Hz, C$_{ar}$*H*), 8.14 (s, 2H, C$_{ar}$*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ −2.9 (dd, $^2J_{CP}$ = 70, 35 Hz, Ni−*C*H$_3$), 16.1 (pt, J^*_{CP} = 11 Hz, *C*H$_2$), 17.9 (d, $^2J_{CP}$ = 11 Hz, PCH*Me*Me), 18.2 (d, $^2J_{CP}$ = 16 Hz, PCH*Me*Me), 19.2 (s, PCH*Me*Me), 19.4 (s, PCH*Me*Me), 23.1 (d, $^1J_{CP}$ = 13 Hz, P*C*HMe$_2$), 24.9 (pt, $J^*_{CP} \approx$ 26 Hz, *C*H$_2$), 53.4 (s, Ni−OCH(Ph)*C*H$_2$(COPh)), 73.0 (d, $^3J_{CP}$ = 5 Hz, Ni−O*C*H(Ph)), 125.1 (s, *C*$_{ar}$H), 126.6 (s, *C*$_{ar}$H), 127.8 (s, *C*$_{ar}$H), 131.3 (s, *C*$_{ar}$H), 139.0 (s, *C*$_{ar}$), 153.4 (s, *C*$_{ar}$), 199.5 (s, Ni−OCH(Ph)CH$_2$(*C*OPh)). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 63.5 (d, $^2J_{PP}$ = 7 Hz), 76.1 (d).

Reaction of Enolate Complex 3 with Carbon Dioxide. Synthesis of Complexes 12 and 13. A 6.3 mL (0.28 mmol) sample of dry CO_2 was carefully bubbled into a solution of 129 mg (0.28 mmol) of the enolate complex **3** in 0.8 mL of C_6D_6. ^{31}P{^{1}H}, ^{1}H, and ^{13}C{^{1}H} NMR monitoring of the mixture revealed quantitative formation of complex **12**. Insoluble crystals of the tetranuclear complex **13** were obtained when the solution was allowed to stand at room temperature for several days.

12: ^{1}H NMR (C_6D_6, 300 MHz): δ 0.21 (t, 3H, $^3J_{HP}$ = 4.8 Hz, Ni−C*H*$_3$), 0.85 (m, 12H, PCH*Me*Me), 1.06 (dd, 6H, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.2 Hz, PCH*Me*Me), 1.20 (dd, 6H, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*Me), 1.67 (m, 4H, PC*H*Me$_2$), 4.03 (s, 2H, OC(O)C*H*$_2$C(O)Ph), 7.11 (m, 3H, C$_{ar}$*H*), 8.27 (m, 2H, C$_{ar}$*H*). ^{13}C-{^{1}H} NMR of **3** (C_6D_6, 75 MHz): δ −0.7 (dd, $^2J_{CP}$ = 67 and 36 Hz, Ni−*C*H$_3$), 16.2 (dd, $^1J_{CP}$ = 25 Hz, $^2J_{CP}$ = 11 Hz, *C*H$_2$), 18.1 (s, PCH*Me*Me), 18.2 (s, PCH*Me*Me), 19.0 (d, $^2J_{CP}$ = 5 Hz, PCH*Me*Me), 19.6 (s, PCH*Me*Me), 23.9 (d, $^1J_{CP}$ = 14 Hz, P*C*HMe$_2$), 25.4 (d, $^1J_{CP}$ = 29 Hz, P*C*HMe$_2$), 51.2 (s, OC(O)*C*H$_2$C(O)Ph), 125.7

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Table 2. Summary of Crystallographic Data and Structure Refinement Results for 3, 6, and 13.

	3	**6**	**13**
formula	$C_{23}H_{42}NiOP_2$	$C_{18}H_{40}NiO_2P_2$	$C_{72}H_{136}Ni_4O_8P_6$
fw	455.22	409.15	1550.47
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	14.496(5)	10.1804(7)	14.2577(11)
b, Å	10.941(3)	16.4024(11)	15.5013(12)
c, Å	16.481(5)	13.0782(9)	18.3160(15)
α, deg	90.0	90.0	90.0
β, deg	105.09(3)	98.6330(10)	96.4120(10)
γ, deg	90.0	90.0	90.0
V, Å^3	2524(1)	2159.1(3)	4022.7(5)
Z	4	4	2
F(000)	984	888	1668
D_{calc}, Mg m^{-3}	1.198	1.259	1.280
μ, mm^{-1}	0.906	1.054	1.089
θ_{min}; θ_{max}, deg	2.36; 28.12	2.94; 28.70	2.32; 28.67
temp, *K*	293	100	100
no. refins collected	14 396	7715	25 484
no. reflns used; *R*(int)	5543; 0.029	5438; 0.020	9358; 0.016
no. reflns obsd [$I > 2\sigma(I)$]	3711	3332	8252
no. of params	253	245	452
$R_1(F)$ [$I > 2\sigma(I)$][a]	0.0371	0.0276	0.0406
$wR_2(F^2)$[b] (all data)	0.1026	0.0702	0.1165
S[c] (all data)	0.943	1.026	1.032
largest diff peak and hole, e Å^{-3}	0.377; −0.297	0.415, −0.309	1.310, −0.641

[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).

(s, C_{ar}H), 129.2 (s, C_{ar}H), 131.7 (s, C_{ar}H), 138.1 (s, C_{ar}), 169.9 (s, OC(O)CH$_2$*C*(O)Ph), 194.5 (s, O*C*(O)CH$_2$C(O)Ph). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 67.0, 78.0. **13**·2thf: IR (Nujol mull): ν(C═O) + ν(C═C) 1586, 1533 cm^{-1}. Anal. Calcd for $C_{72}H_{136}Ni_4O_8P_6$: C, 55.78; H, 8.84. Found: C, 55.66; H, 8.73.

X-ray Crystal Structure Analyses of 3, 6, and 13. A single crystal of each representative compound (yellow prism **3**, orange plate **6**, and orange block **13**) of suitable size was mounted on a glass fiber using glue (**3**) or using perfluoropolyether oil (FOMBLIN 140/13, Aldrich) in the cold N_2 stream of the a low-temperature device attachment (**6** and **13**). A summary of crystallographic data and structure refinement is reported in Table 2. Intensity data for **3** were collected on a Bruker AXS SMART 1000 single-crystal diffractometer equipped with a CCD area detector using a graphite monochrotomator λ(Mo Kα_1) = 0.71073 Å, whereas the data collections for complexes **6** and **13** were performed on a Bruker-AXS X8Kappa diffractometer equipped with an APEXII CCD area detector, using a graphite monochromator λ(Mo Kα_1) = 0.71073 Å and a Bruker Cryo-Flex low-temperature device. The data collection strategy used in all instances was phi and omega scans with narrow frames. Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times, and no decay was observed. The data were reduced (SAINT)[32] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (SADABS).[33] The structures were solved by direct methods (SIR-2002)[34] and Patterson methods and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.14),[35] minimizing $w[F_o^2 - F_c^2]^2$. One isopropyl group of the diphosphine ligand of compound **3** was observed disordered in two positions with occupancy factors first refined and later fixed to 0.60 and 0.40. The −CH$_3$ and −CH$_2$-COOCH$_3$ groups on the nickel metal of compound **6** were also observed disordered, both in two positions with occupancy factors first refined and later fixed to 0.64 and 0.36. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined as riding contributions with isotropic displacement parameters 1.5 (methyl groups) times those of their respective attached carbon 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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