Self-Addition of Metallacyclic Nickel Enolate Complexes Stabilized by Monodentate Phosphine Ligands†

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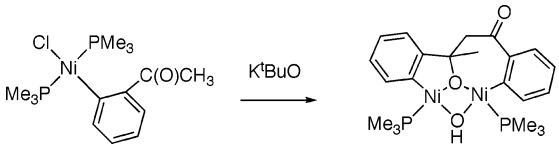
In contrast with their stable counterparts bearing the chelating diphosphines, the nickelacyclic *O*-enolate complexes stabilized by monodentate ligands $Ni(OC(=CHR)\text{-}o\text{-}C_6H_4)L_2$ (R = H, Me, L = PMe_3; R = H, L = PMe_2Ph) undergo an unusual self-addition process leading to dinuclear alkoxo-hydroxo derivatives. The α-substituted enolate complexes (R = Me) are less prone to undergo this transformation, and the corresponding nickelacycles with L = PMe_3 or PMe_2Ph can be isolated in pure form.

Introduction

Because of their relevance to many metal-mediated organic transformations,[1] late-transition metal enolate complexes have received continued attention in recent years. The enolate functionality displays a very rich coordination chemistry, and several types of complexes displaying η^3-coordinated[2] or bridging enolate ligands[3] have been reported, although σ coordination, either through its enol oxygen (*O*-enolate) or carbon (*C*-enolate) atoms, predominate by far.[4−7] The coordination mode influences the reactivity of the enolate functionality, and while *C*-enolates often exhibit alkyl-like reactivity (e.g., C−C reductive couplings[5] or migratory insertion[6]), *O*-enolates display a characteristic nucleophilic reactivity, adding to aldehydes and other organic electrophilic reagents.[7] We have recently shown that the incorporation of a nickel enolate functionality into a rigid metallacyclic framework hinders the otherwise facile *C*-/*O*-isomerization and allows the examination of the reactivity of the isomers separatedly.[8,9] In addition, the reactivity of nickelacyclic enolates can be exploited in a number of synthetically useful transformations leading to the formation of different types of cyclic and noncyclic organic products in a highly selective manner.[9,10] Unfortunately, the stabilization of these metallacyclic enolates usually requires the use of chelating ligands,[7b,c,9b] and this may have the undesired effect of blocking some interesting reactions. For example, attempts to produce a cyclic nickel enolate stabilized by PMe_3 led to a dinuclear product as a result of a formal aldol reaction[9b] (eq 1). We were interested in gaining some insight into the mechanism of this uncommon transformation, and to this end, we have studied some further examples. In the course of these studies we have isolated and structurally characterized the different species involved in this process.



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Results and Discussion

As reported previously,[8,9b] the reaction of 2-acetylphenyl complex **1a** with a stoichiometric amount of K^{t}BuO in THF, followed by workup involving simply solvent evaporation and recrystallization from tetrahydrofuran, leads to the dinuclear complex **3a**, isolated as a powdery yellow solid, as shown in Scheme 1. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy reveals that the addition of the base immediately gives rise to a single species characterized by a broad signal located at ca. −20 ppm. On cooling to −80 °C, this signal splits into two resonances, at δ −8.6 and −40.5 ppm, whereas addition

† Dedicated to Dr. J. A. Abad (University of Murcia, Spain) on the occasion of his retirement.

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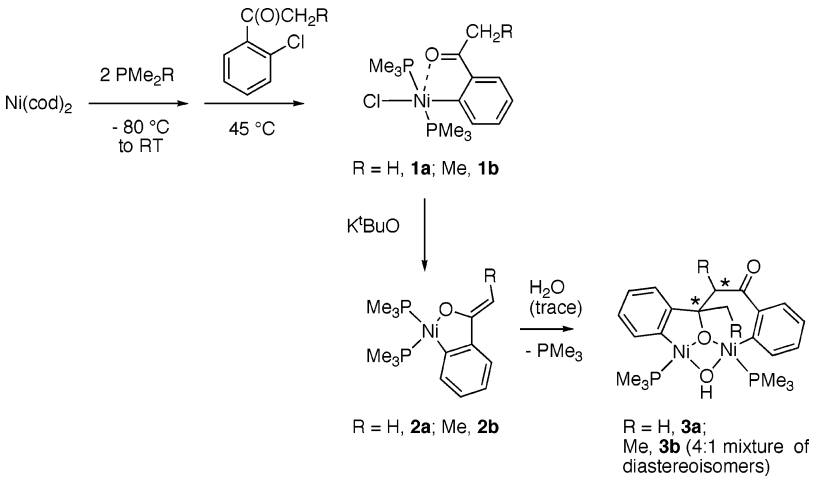
Scheme 1



of HCl to the solution regenerates the starting complex, **1a**, as expected for the enolate complex **2a**.[9b] Attempts to isolate this intermediate invariably result in its transformation into **3a**. Despite the anhydrous conditions employed, the formation of the latter compound can be envisaged as a result of a combination of hydrolysis and aldol addition reactions (Scheme 1). To hinder the addition step, we decided to explore the reactivity of the α-methylated precursor **1b**, which should give rise to a less reactive enolate complex.

Like **1a**, the 2-propionylphenyl derivative **1b** can be readily prepared from $Ni(cod)_2$, PMe_3, and the corresponding aryl chloride. The structure of this compound has been established by X-ray diffraction (see below).

The reaction of **1b** with KO^{t}Bu follows the same path observed for **1a** and affords the corresponding dinuclear compound **3b**, after the usual (nonhydrolytic) workup. The spectroscopic features of **3b** match closely those of **3a**. For instance, the OH and CO functionalities give rise to characteristic absorptions in the IR spectrum at 3400 and 1640 cm^{-1}, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two pairs of singlets (δ −5.9, −10.9, and −6.1, −9.7 ppm, respectively) with intensity ratio 4:1, suggesting that this compound is formed as a diastereomeric pair. This conclusion is further supported by the proton spectrum, where two complete sets of signals with the same relative intensity ratio are observed. The signals corresponding to the CH−CH_3 units were located with the help of the COSY spectrum. In the 2-D NOESY ^1H NMR spectrum, the major isomer displays a NOE cross-peak linking the resonances of the central methyne group and one of the doublet ("*ortho*") aromatic resonances. On this basis and with the help of a DFT (B3LYP/6-31G*) molecular model (Figure 1), the identity of the stereoisomers can be assigned. As can be seen, only one of the two structures (*R,R* or *S,S*) displays an aromatic

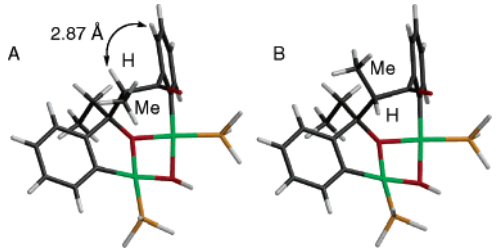


Figure 1. Molecular models of the **3b** diastereomeric pair (PMe_3 ligands have been replaced by PH_3): (A) major isomer (*R,R* or *S,S*), showing the C(Et)H···H(*ortho*) approach; (B) minor isomer (*R,S* or *S,R*).

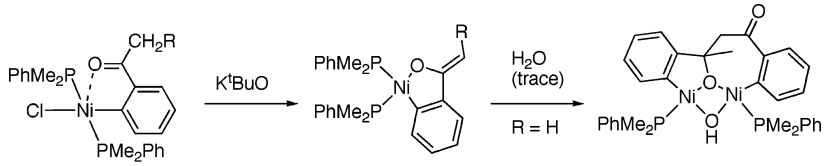
ortho hydrogen in the neighborhood of the central methyne (d(H−H): 2.87 Å), while the other does not (shortest H−H distance, 3.44 Å). The calculation indicates that the energy difference between the two isomers is negligible (less than 0.5 kcal/mol), suggesting a kinetic origin for the observed stereoselectivity.

As found for **1a**, NMR monitoring of the reaction of **1b** with KO^{t}Bu shows the initial formation of a single species, **2b**, characterized by a broad ^{31}P resonance. The position of this signal can vary within a few ppm from one experiment to other, but is similar to that of **2a** (ca. −15 ppm).

Rather surprisingly, the yields obtained for **3a** or **3b** do not improve upon deliberate addition of water to the reaction mixture. In a separate experiment, it was observed that the ^{31}P spectrum of **2b** is not altered by the addition of water. Accordingly, water does not trigger the transformation of **2** into **3**. Indeed, **2b** is fairly stable in THF solution at room temperature, the appearance of significant amounts of **3b** being detected only upon attempted isolation of the product. Thus, removal of the reaction solvent under vacuum followed by extraction of the residue with freshly distilled THF results in an almost complete transformation of **2b** to **3b**. Suspecting that this change is induced by the loss of PMe_3, an extra amount of this ligand was added to the extraction solvent (diethyl ether, in this case). Under these conditions, a significant amount of **2b** remains present and was readily separated from the less soluble complex **3b**. Cooling the ethereal extract led to the isolation of a sample of analytically pure **2b**. The ^1H and ^{13}C NMR spectra of **2b** are analogous to those of analogous complex Ni(OC(=CHMe)-*o*-C_6H_4)(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane),[9b] confirming our previous assumption that this compound has a cyclic *O*-enolate structure. Thus, the vinyl enolate proton gives rise to a quartet resonance at δ 5.21, while the α- and β-olefinic ^{13}C resonances appear at 169.0 and 86.5 ppm, respectively. However, in contrast with the chelating phosphine derivative, **2b** undergoes rapid exchange of the two chemically inequivalent PMe_3 ligands, which give rise to only one signal in the ^1H, ^{13}C, and ^{31}P NMR spectra. The fluxional process removes the $^{13}C-^{31}P$ couplings from the metallacycle signals (clearly observed for the dippe complex), suggesting a dissociative phosphine exchange mechanism.

To avoid phosphine loss by evaporation, we have replaced PMe_3 by the less volatile PMe_2Ph ligand. Treatment of the corresponding precursors, **1c** and **1d**, with KO^{t}Bu leads to different results (Scheme 2). The reaction of the 2-acetyl complex **1c** follows the same course observed for **1a** and **1b**,

Scheme 2



and the initially formed cyclic enolate, **2c** (identified by its characteristic $^{31}P\{^{1}H\}$ spectrum, a broad resonance centered at −13 ppm) is readily transformed into the corresponding dimeric hydroxide **3c** upon the usual workup. However, complex **1d** affords the stable cyclic enolate **2d**, which does not evolve to the corresponding dinuclear species. The stability of **2d** is probably due to the combination of the decreased reactivity of the α-substituted enolate functionality with the lower volatility of the PMe_2Ph ligands. As observed for **2b**, the NMR spectra of **2d** evidence a rapid exchange of the phosphine ligands at room temperature. Compounds **3c** and **2d** have been isolated as crystalline solids, and their X-ray diffraction structures are shown in Figures 3 and 4 (vide infra).

Several features of the self-addition reaction experienced by complexes **2** are mechanistically valuable. The inability of water to trigger this reaction indicates that hydrolysis of the enolate complexes **2** is not involved in the process, or at least does not constitute its rate-limiting step. Even so, the aldol-like structure of the dinuclear complexes **3** suggests the intermediacy of a keto intermediate at some stage. However, although the hydrolysis of **2** would originate a carbonyl functionality amenable to nucleophilic attack, we have observed that **1b** is indefinitely stable in the presence of **2b**. It is also conceivable that a keto group could be generated by the previous isomerization of half of the *O*-enolate molecules to the *C*-form. This is also an unlikely possibility, as we have shown before that *O*-/*C*-enolate isomerization is a very slow process at room temperature in these rigid metallacyclic complexes.[8,9b] Moreover, the *C*-enolate form would be strongly disfavored in the case of the α-methylated complex **2b**.[5]

The dissociable phosphine ligands play an important role in this reaction. The overall stoichiometry of the addition process involves the net loss of one phosphine unit per Ni atom. Thus, it is not surprising that the transformation of the relatively stable enolate **2b** is favored when the volatile PMe_3 ligand is removed by evaporation and hindered by addition of extra amounts of this ligand. The low volatility of PMe_2Ph prevents the transformation of **2d**, and, in general, the use of the chelating diphosphine dippe allows the isolation of both substituted and nonsubstituted ($Ni-O-C(R)=CH_2$) cyclic enolates.[8,9b] Hence, it appears likely that phosphine dissociation may occur at the initial stages of the self-addition reaction. The highly fluxional behavior of compounds **2** is also consistent with facile phosphine dissociation. Nickel hydroxides and alkoxides stabilized by monodentate phosphine ligands display a strong tendency to form oxygen-bound dimers of type **D**[11] (Scheme 3), and

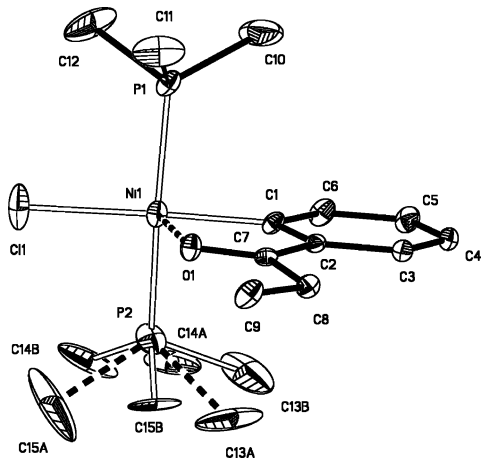


Figure 2. ORTEP view of **1b**. Selected bond lengths (Å) and angles (deg): Ni1−C1, 1.885(3); Ni1−P1, 2.1907(10); Ni1−P2, 2.1775(10); Ni1−Cl1, 2.2375(11); Ni1−O1, 2.472(2); C7−O1, 1.222(4); C1−Ni1−O1, 77.60(11); Ni1−C1−C2, 118.5(2); P1−Ni1−P2, 169.15(4).

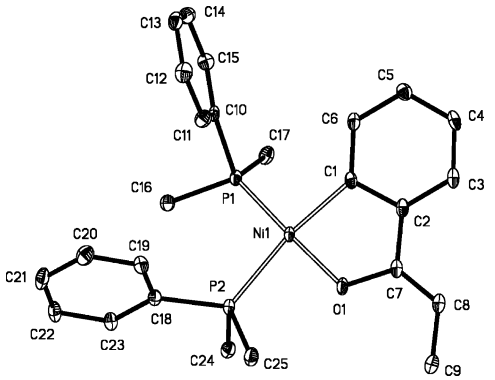


Figure 3. ORTEP perspective of compound **2d**. Selected bond distances (Å) and angles (deg): Ni1−C1, 1.932(2); Ni1−O1, 1.8595(15); Ni−P1, 2.1391(6); Ni1−P2, 2.2400(7); O1−C(7), 1.347(3); C7−C8, 1.337(3); C1−Ni1−O1, 85.76(8); P1−Ni1−P2, 89.90(3).

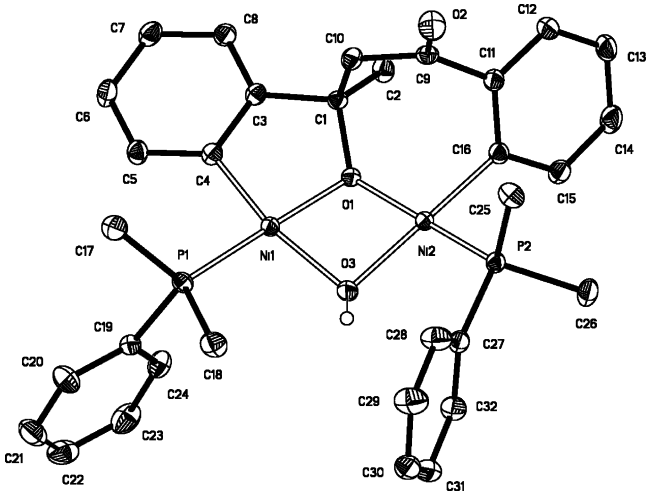
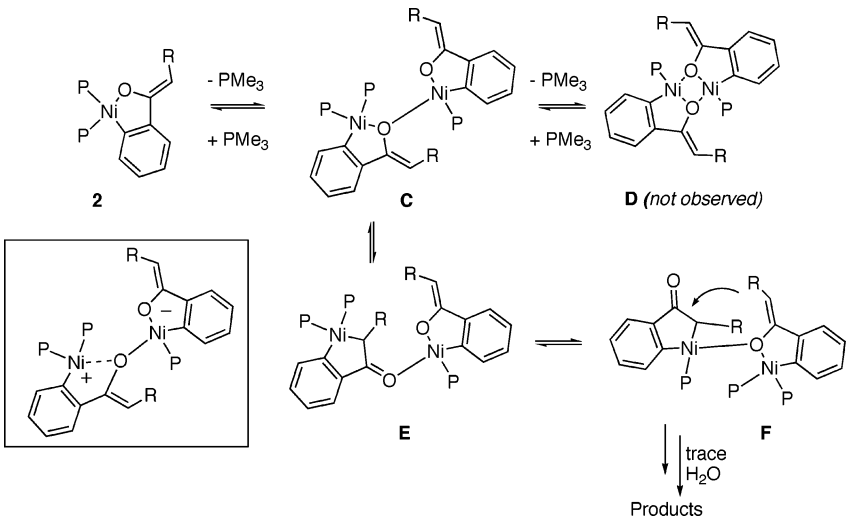


Figure 4. ORTEP perspective of compound **3c**. Selected bond distances (Å) and angles (deg): Ni1−O1, 1.8945(10); Ni1−O3, 1.8986(11); Ni2−O1, 1.9060(10); N1−P1, 2.1436(4); Ni2−P2, 2.1221(4); Ni1−C4, 1.8790(14); Ni2−C16, 1.8839(14); C9−O2, 1.2227(18); C1−O1, 1.4665(16); Ni1···Ni2, 2.8312(3); Ni1−O1−Ni2, 96.31(4); Ni−O3−Ni2, 96.08(5); Ni1−O1−Ni2−O3, 21.15-(5).

Scheme 3



although such compounds have not been observed in our system, association of complexes **2** in solution through their enolate oxygen atoms appears likely. The associative process brings two enolate fragments into proximity and favors the addition process. Obviously, the structure of the doubly bridged species **D** is too rigid to allow any interaction, but a singly bridged intermediate, **C**, may be flexible enough to allow the addition reaction. Self-addition of enolates is a highly unusual process, and we are unaware of any literature precedent. Therefore, we consider likely that the C−C bond formation step may actually be preceded by the tautomerization of one of the enolate units within the dimeric species **C** to the *C*-coordination mode. The interaction of the enolate oxygen with a second metal center may facilitate the opening and the subsequent reorganization of the metallacycle, as indicated in Scheme 3 (inset). In our previous work on the dippe-based system, we observed that lithium salts efficiently induce the *C*-/*O*-enolate tautomerization, probably due to the same kind of effect. In the resulting intermediate **E**, the nucleophilic and electrophilic centers are too far apart to interact, but simple ligand reorganization to **F** would enable the aldol addition to proceed, the initial addition products being rapidly trapped by traces of water present in the reaction medium.

X-ray Crystal Structures of Complexes 1b, 2d, and 3c. The crystal structures of the title compounds are shown in Figures 2, 3, and 4. As can be seen in Figure 2, compound **1b** displays a pentacoordinated structure, with the carbonyl oxygen atom occupying the apical position of a distorted square-planar coordination polyhedron. The coordination of the carbonyl group causes a decrease of ca. 60 cm^{-1} of the IR frequency of the ν(C═O) band, relative to the organic precursor. The Ni−O bond length (2.472(2) Å) is somewhat shorter than in the previously reported complex Ni(C(Ph)═C(H)$COCH_2SiMe_3$)(Cl)$(PMe_3)_2$,[12] which displays a similar interaction, characterized by a Ni−O distance of 2.535 Å. The configuration of the propionyl fragment is highly reminiscent of that observed in the enolate **2d** (vide infra). Notwithstanding its weakness, the nickel−carbonyl interaction may play a role in the deprotonation of the acyl functionality, by increasing its Brönsted acidity of the α-H atoms and favoring the selective formation of the *O*-bound enolate tautomer.

The molecules of **2d** display a slightly distorted square-planar geometry (Figure 3). The Ni−O distance, 1.8595(15) Å, is somewhat shorter than in the complexes Ni(R)(OAr)(dippe) (1.907 Å),[11a] despite the similar coordination environment of the enolate and aryloxide moieties. However, it is comparable to those of terminal nickel hydroxides and methoxides[13] and identical, within the experimental error, to that found in the dippe-containing analogue of **2d**.[9b] Noteworthy, the enolate C═C bond length (1.337(3) Å) is shorter than in the dippe complex (1.368(6) Å) and approaches that of a typical C═C bond. Other metrical parameters associated with the metallacyclic unit are very similar in the PMe_2Ph and the dippe compounds. As expected, the P−Ni−P (98.90(3)°) is somewhat wider in **2d** than in the diphosphine derivative (88.49(6)°).

The crystal structure of **3c** confirmed our structural proposal and shows essentially the same features anticipated by the DFT models discussed above (Figure 4). This unusual molecule displays a bridging tridentate organic ligand, which originates five- and seven-membered metallacyclic moieties. The largest one adopts a boat conformation, with the keto group pointing away from the nickel center. The Ni−OH and Ni−OR bonds display similar lengths (ca. 1.9 Å), comparable to those found in dinuclear hydroxo[14] and alkoxo[15] nickel complexes. The central Ni_2O_2 core is not planar, but slightly puckered (dihedral angle: 21.13(5)°), and the Ni−Ni distance (2.8312(3) Å) can be considered normal, very likely not involving any metal−metal bonding interaction.

Conclusions

2-Acylaryl derivatives **1a**−**d** are cleanly deprotonated by potassium *tert*-butoxide, leading to the metallacyclic enolate complexes **2a**−**d**. Unlike the analogous complexes containing

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the chelating diphosphine dippe, complexes **2** experience an unusual self-addition reaction leading to the dinuclear alkoxo-hydroxide complexes **3**. This transformation can be envisaged as a combination of hydrolysis and aldol reaction. The latter process is not initiated by the presence of water, but it is facilitated by the release of the monodentate phosphine ligand, especially in the case of the volatile PMe_3. It is likely that the mechanism of this reaction is facilitated by the formation of a dinuclear intermediate bridged through an *O*-enolate functionality.

Experimental Section

All preparations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were rigorously dried under nitrogen 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 ^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. The compound 2-chloropropiophenone was prepared as described previously.[9b] Molecular modeling was carried out with the Spartan 04 package.[16]

Synthesis of Ni(C_6H_4-*o*-C(O)CH_2CH_3)(Cl)(PMe_3)$_2$ (1b). A 1 M solution of PMe_3 in toluene (6 mL, 6 mmol) was added to a suspension of Ni(cod)$_2$ (825 mg, 3 mmol) in toluene (50 mL) at −78 °C. The mixture was allowed to warm to room temperature, and 2-chloropropiophenone (0.41 mL, 3 mmol) was added. The resulting solution was stirred at 45 °C for 4 h, and the initial yellow color turned dark red. The solvent was evaporated under vacuum and the residue extracted with Et_2O (20 mL). After partial concentration of the solution and cooling to −20 °C, the product was isolated as a red-brown solid. Yield: 75%. IR (Nujol mull): ν(C═O), 1639 cm^{-1}. Anal. Calcd for $C_{15}H_{27}ClNiOP_2$: C, 47.48; H, 7.17. Found: C, 48.18; H, 7.14. ^1H NMR (C_6D_6, 20 °C, 300 MHz): δ 0.78 (t, 18H, *J_{HP} = 3.8 Hz, PMe_3), 1.24 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 2.76 (q, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 6.73 (m, 1H, $C_{ar}H$), 6.89 (dt, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, $C_{ar}H$), 7.44 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, $C_{ar}H$), 7.80 (dd, 1H, $^3J_{HH}$ =7.5 Hz, $^4J_{HH}$ = 1.0 Hz, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75 MHz): δ 8.9 (s, CH_2CH_3), 12.7 (t, $^1J_{CP}$ = 13 Hz, PMe_3), 31.5 (s, CH_2CH_3), 120.7 (s, $C_{ar}H$), 128.7 (s, $C_{ar}H$), 129.5 (s, $C_{ar}H$), 137.0 (t, J_{CP} = 4 Hz, $C_{ar}H$), 142.4 (s, C_{ar}-CO), 171.4 (t, $^2J_{CP}$ = 35 Hz, C_{ar}-Ni), 201.9 (s, CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, 121 MHz): δ −16.2 (PMe_3).

Synthesis of Ni(C_6H_4-*o*-C(O)CH_3)(Cl)(PMe_2Ph)$_2$ (1c). Dimethylphenylphosphine (1.42 mL, 10 mmol) was added to a cooled solution (−78 °C) of 1.37 g (5 mmol) of Ni(cod)$_2$ in 50 mL of toluene. The mixture was allowed to reach room temperature, and 0.65 mL (5 mmol) of 2-chloroacetophenone was added. The reaction mixture was heated at 45 °C for 4 h. The solvent was removed under vacuum and the residue extracted with 10 mL of THF. Dark red crystals of the pure product were obtained after adding some diethyl ether and cooling at −20 °C. Yield: 50%. Anal. Calcd for $C_{24}H_{29}ClNiOP_2$: C, 58.88; H, 5.97. Found: C, 58.40; H, 6.07. IR (Nujol mull): ν(C═O) 1642 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 0.87 (bs, 6H, PMe_2Ph), 1.40 (bs, 6H, PMe_2Ph), 2.43 (s, 3H, CH_3), 6.75 (td, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, $C_{ar}H$), 6.82 (td, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, $C_{ar}H$), 7.18 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ =1.4 Hz, $C_{ar}H$), 7.27−7.34 (m, 5H, $C_{ar}H$), 7.37−7.46 (m, 5H, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75 MHz): δ 11.4 (bs, P*Me*MePh), 13.0 (bs, *P*Me*MePh*), 26.3 (s, CH_3), 121.6 (s, $C_{ar}H$), 128.2 (s, $C_{ar}H$), 129.2 (s, $C_{ar}H$), 129.5 (s, $C_{ar}H$), 131.0 (s, $C_{ar}H$), 135.8 (t, J_{CP} = 18 Hz, C_{ar}), 137.8 (s, $C_{ar}H$), 143.2 (s, C_{ar}), 168.2 (t, J_{CP} = 36 Hz, C_{ar}Ni), 200.9 (s, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121 MHz): δ 9.8.

Synthesis of Ni(C_6H_4-*o*-C(O)CH_2CH_3)(Cl)(PMe_2Ph)$_2$ (1d). To a cooled solution (−78 °C) of 1.1 g (4 mmol) of Ni(cod)$_2$ in 50 mL of toluene was added 1.14 mL (8 mmol) of dimethylphenylphosphine. The mixture was allowed to reach room temperature, and 0.54 mL (4 mmol) of 2-chloropropiophenone was added. The reaction mixture was heated at 45 °C for 4 h. The solvent was removed under vacuum and the residue extracted with 10 mL of THF. Dark red crystals of the pure product were isolated after crystallization at −20 °C. Yield: 58%. Anal. Calcd for $C_{25}H_{31}ClNiOP_2$: C, 59.62; H, 6.20. Found: C, 59.74; H, 6.21. IR (Nujol mull): ν(C═O), 1644 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C, 400 MHz): δ 0.89 (bs, 6H, P*Me*MePh), 1.19 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 1.39 (s, 6H, PMe*Me*Ph), 2.79 (q, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 6.74 (t, 1H, $^3J_{HH}$ = 7.4 Hz, $C_{ar}H$), 6.82 (t, 1H, $^3J_{HH}$ = 7.1 Hz, $C_{ar}H$), 7.20 (d, 1H, $^3J_{HH}$ = 7.4 Hz, $C_{ar}H$), 7.26−7.35 (m, 6H, $C_{ar}H$), 7.44 (bs, 4H, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75 MHz): δ 8.8 (s, CH_2CH_3), 11.5 (t, J_{CP} = 14 Hz, P*Me*MePh), 12.9 (t, J_{CP} = 13 Hz, PMe*Me*Ph), 31.4 (s, CH_2CH_3), 121.6 (s, $C_{ar}H$), 128.2 (s, $C_{ar}H$), 129.2 (s, $C_{ar}H$), 129.4 (s, $C_{ar}H$), 130.1 (s, $C_{ar}H$), 135.9 (t, J_{CP} = 19 Hz, C_{ar}), 138.0 (s, $C_{ar}H$), 142.8 (s, C_{ar}), 167.9 (t, $^2J_{CP}$ = 36 Hz, C_{ar}Ni), 203.5 (s, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121 MHz): δ −9.9 (s).

Synthesis of 2b. Potassium *tert*-butoxide (57 mg, 0.5 mmol) was dissolved in 3 mL of THF and added to a cooled solution (−78 °C) of 190 mg of complex **1b** (0.5 mmol) in 10 mL of THF. After reaching room temperature, the solvent was removed under reduced pressure, and 8 mL of a solution of PMe_3 (0.1 mmol) in Et_2O was added to afford an orange solution. The solution was filtered from a yellow precipitate of compound **3b** and cooled to −20 °C to give **2b** as orange crystals. Yield: 15%. Anal. Calcd for $C_{15}H_{26}NiOP_2$: C, 52.52; H, 7.64. Found: C, 52.99; H, 7.89. IR (Nujol mull): ν(C═C), 1614 cm^{-1}. ^1H NMR (C_6D_6, 20 °C, 400 MHz): δ 0.87 (d, 18H, $^2J_{HP}$ = 7.7 Hz, PMe_3), 2.29 (d, 3H, $^3J_{HH}$ = 6.7 Hz, ═CHCH_3), 5.21 (q, 1H, $^3J_{HH}$ = 6.7 Hz, ═C*H*CH_3), 7.05 (m, 1H, $C_{ar}H$), 7.10 (m, 2H, $C_{ar}H$), 7.58 (d, 1H, $^3J_{HH}$ = 7.3 Hz, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 100 MHz): δ 11.8 (s, CHCH_3), 16.3 (d, J_{CP} = 22 Hz, PMe_3), 86.5 (s, *C*HCH_3), 121.6 (s, $C_{ar}H$), 123.9 (s, $C_{ar}H$), 124.2 (s, $C_{ar}H$), 136.7 (s, $C_{ar}H$), 155.8 (bs, C_{ar}-Ni), 157.4 (s, C_{ar}-CO), 169.0 (s, CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, 162 MHz): δ −13.7 (bs, PMe_3).

Synthesis of 2d. A solution of 0.27 g (2.3 mmol) of K^{t}BuO in 5 mL of THF was added to a cooled solution (−78 °C) of 1.05 g of **1d** (2.1 mmol) dissolved in 10 mL of THF. After reaching room temperature, solvent was removed in vacuo, and 20 mL of toluene was added. After centrifugation, the solution was taken to dryness and the residue extracted with 10 mL of THF. Concentration of this solution and cooling at −20 °C afforded the product as red crystals. Yield: 42%. Anal. Calcd for $C_{25}H_{30}NiOP_2$: C, 64.28; H, 6.47. Found: C, 63.90; H, 6.44. IR (Nujol mull): ν(C═C), 1573 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 1.49 (d, 12 H, $^2J_{HP}$ = 8.0 Hz, P*Me*$_2$Ph), 1.81 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 4.72 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*CH_3), 6.55−6.62 (m, 2H, $C_{ar}H$), 6.79 (m, 2H, $C_{ar}H$), 7.10 (m, 1H, $C_{ar}H$), 7.34−7.43 (m, 5H, $C_{ar}H$), 7.76 (t, 4H, $^3J_{HP}$ = 6.8 Hz, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75 MHz): δ 10.9 (s, CH*C*H$_3$), 15.3 (d, $^1J_{CP}$ = 24 Hz, P*Me*$_2$Ph), 87.0 (s, *C*HCH$_3$), 120.6 (s, $C_{ar}H$), 123.4 (s, $C_{ar}H$), 124.2 (s, $C_{ar}H$), 128.9 (d, $^2J_{CP}$ = 9 Hz, $C_{ar}H$), 130.2 (s, $C_{ar}H$), 131.6 (d, $^2J_{CP}$ = 11 Hz, $C_{ar}H$), 137.7 (s, $C_{ar}H$), 154.4 (s, C_{ar}), 155.9 (s, C_{ar}), 167.9 (s,O*C*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121 MHz): δ 0.4 (bs).

Synthesis of the Dinuclear Complex 3b. Potassium *tert*-butoxide (115 mg, 1 mmol) was dissolved in 5 mL of THF and added to a cooled solution (−78 °C) of 370 mg of complex **1b** (1 mmol) in 20 mL of THF. After reaching room temperature, the solvent was removed under vacuum, 10 mL of THF was added,

(16) *Spartan 04*; Wavefunction, Inc.: Irvine, CA, 2004.

and the solution was concentrated, affording **3b** as a powdery yellow solid. This solid retains variable amounts of solvent, preventing good analytical data from being collected. Yield: 50%. IR (Nujol mull): ν(OH), 3397 cm^{-1}; ν(C═O), 1639 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C, 300 MHz) 8:2 mixture of isomers; major isomer: δ −5.65 (s, 1H, OH), 0.27 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 0.69 (m, 1H, $CHHCH_3$), 0.90 (d, 9H, $^2J_{HP}$ = 9.9 Hz, PMe_3), 0.95 (m, obscured by resonance at 0.90 ppm, 1H, $CHHCH_3$), 1.24 (d, 9H, $^2J_{HP}$ = 9.2 Hz, PMe_3), 2.71 (q, 1H, $^3J_{HH}$ = 7.5 Hz, $CHCH_3$), 3.21 (d, 3H, $^3J_{HH}$ = 7.5 Hz, $CHCH_3$), 6.27 (d, 1H, $^3J_{HH}$ = 7.4 Hz, $C_{ar}H$), 6.35 (d, 1H, $^3J_{HH}$ = 7.5 Hz, $C_{ar}H$), 6.63 (td, 1H, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.1 Hz, $C_{ar}H$), 6.74−6.90 (m, 3H, $C_{ar}H$), 7.07 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz, $C_{ar}H$), 7.62 (d, 1H, $^3J_{HH}$ = 7.3 Hz, $C_{ar}H$); minor isomer: δ −5.58 (s, 1H, OH), 0.41 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 0.92 (d, 9 H, $^2J_{HP}$ = 10.2 Hz, PMe_3), 1.24 (d, 9 H, $^2J_{HP}$ = 10.2 Hz, PMe_3), 1.08 (d, 3H, $^3J_{HH}$ = 7.7 Hz, $CHCH_3$), 3.62 (q, 1H, $^3J_{HH}$ = 7.7 Hz, $CHCH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 121 MHz) major isomer: δ −5.9, −10.9; minor isomer: δ −6.1, −9.7.

Synthesis of the Dinuclear Complex 3c. Potassium *tert*-butoxide (168 mg, 1.4 mmol) was added to a solution of **1c** (632 mg, 1.3 mmol) in THF (50 mL) at −78 °C. After stirring the mixture at room temperature for 4 h, the solvent was removed under reduced pressure. The resulting yellow solid was extracted with THF (10 mL), the suspension centrifuged to separate the KCl, and the solution partially concentrated. After addition of some diethyl ether and cooling at −20 °C, compound **3c** was obtained as yellow crystals. Yield: 40%. Anal. Calcd for $C_{32}H_{36}Ni_2O_3P_2$: C, 59.32; H, 5.60. Found: C, 59.20; H, 5.72. IR (Nujol mull): ν(OH) 3639 cm^{-1}; ν(C═O) 1652 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C, 500 MHz): δ −5.76 (s, 1H, OH), 0.63 (s, 3H, CH_3), 0.94 (bs, 3H, P*Me*MePh), 1.00 (d, 3H, $^2J_{HP}$ = 9.8 Hz, PMe_2Ph), 1.19 (d, 3H, $^2J_{HP}$ = 9.9 Hz, P*Me*MePh), 1.32 (d, 3H, $^2J_{HP}$ = 7.6 Hz, PMe*Me*Ph), 3.10 (d, 1H, $^2J_{HH}$ = 18.2 Hz, CH*H*), 5.11 (d, 1H, $^2J_{HH}$ = 18.2 Hz, *CH*H), 5.95 (d, 1H, $^3J_{HH}$ = 7.2 Hz, $C_{ar}H$), 6.37 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, $C_{ar}H$), 6.42 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, $C_{ar}H$), 6.71 (t, 1H, $^3J_{HH}$ = 7.4 Hz, $C_{ar}H$), 6.93 (m, 2H, $C_{ar}H$), 7.19 (dd, 1H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.2 Hz, $C_{ar}H$), 7.44 (bs, 6H, $C_{ar}H$), 7.68 (d, 1H, $^3J_{HH}$ = 6.7 Hz, $C_{ar}H$), 7.85 (m, 2H, $C_{ar}H$), 7.99 (bs, 2H, $C_{ar}H$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, 75 MHz): δ 10.58 (d, $^1J_{CP}$ = 29 Hz, P*Me*MePh), 10.68 (d, $^1J_{CP}$ = 29 Hz, *P*Me*MePh*), 13.7 (bs, P*Me*MePh), 14.3 (d, $^1J_{CP}$ = 6 Hz, *P*Me*MePh*), 26.4 (s, CH_3), 64.2 (s, CH_2), 82.9 (s, C−O), 121.3 (s, $C_{ar}H$),123.2 (s, $C_{ar}H$), 123.5 (s, $C_{ar}H$), 124.2 (s, $C_{ar}H$), 126.1 (s, $C_{ar}H$), 127.0 (s, $C_{ar}H$), 128.8 (s, $C_{ar}H$), 129.2 (d, $^1J_{CP}$ = 9 Hz, C_{ar}), 130.4 (s, CH_{ar}), 130.7 (s, CH_{ar}), 132.0 (bs, CH_{ar}), 133.9 (d, $^1J_{CP}$ = 39 Hz, C_{ar}), 137.9 (s, CH_{ar}), 138.3 (bs, CH_{ar}), 141.2 (bs, C_{ar}-Ni), 147.2 (d, $^2J_{CP}$ = 44 Hz, C_{ar}-Ni), 149.3 (s, C_{ar}-C−O), 168.3 (s, C_{ar}-C═O), 206.5 (s, C═O). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 202 MHz): δ 9.5 (s), −0.3 (s).

X-ray Crystallography. Crystals coated with dry perfluoropolyether were mounted on a glass fiber and fixed in a cold nitrogen stream (T = 100(2) K). Intensity data were collected on a Bruker-Nonius ×8Apex-II CCD diffractometer (**1b** and **3c**) or a Bruker SMART Apex CCD diffractometer (**2d**), both equipped with a Mo Kα_1 radiation (λ = 0.71073 Å) source and graphite monochromator. The data were reduced (SAINT)[17] and corrected for Lorentz polarization and absorption effects by a multiscan method (SADABS).[18] The structure was solved by direct methods (SIR-2002)[19] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[20] minimizing $w[F_o^2 - F_c^2]^2$. The methyl groups of a phosphine ligand in the structure of **1b** were found disordered. Therefore a model was included, and the occupancy factors for the methyl groups on that phosphine were fixed to 0.5. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (except for those in compound **2d**, which were included in the refinement from observed positions and fully isotropically refined) and were calculated and allowed to ride on the attached carbon atoms with the isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} values of the corresponding carbon atoms.

Crystal data for 1b: $C_{15}H_{27}ClNiOP_2$, M_r = 379.47, orange needle (0.48 × 0.16 × 0.14 mm^3) from diethyl ether, orthorhombic, space group $Pca2_1$ (no. 29), a = 18.8920(6) Å, b = 9.2032(3) Å, c = 10.5612(3) Å, V = 1836.24(10) Å^3, Z = 4, ρ_{calcd} = 1.373 g cm^{-3}, λ(Mo Kα_1) = 0.71073 Å, F(000) = 800, μ = 1.370 mm^{-1}, T = 100(2) K; 21 331 reflections were collected in the range 5.78° < 2θ < 61.06°, index ranges −26 ≤ h ≤ 25, −13 ≤ k ≤ 9, −14 ≤ l ≤ 15, of which 5477 were independent [R(int) = 0.0365] and 5103 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.0455, wR_2 (all data) = 0.1084, $w = [\sigma^2(F_o^2) + (0.0348P)^2 + 2.74P]^{-1}$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; no. of data/restraints/parameters 5477/64/195; goodness of fit on (F^2) = 1.106. In the final difference map, the highest peaks (to ca. 0.97 e Å^{-3}) were close to disordered methyl groups of one phosphine ligand.

Crystal data for 2d: $C_{25}H_{30}NiOP_2$, M_r = 467.14, red block (0.36 × 0.26 × 0.24 mm^3) from tetrahydrofuran, monoclinic, space group $P2_1/n$ (no. 14), a = 10.8446(9) Å, b = 16.8315(14) Å, c = 12.7181(11) Å, β = 102.542(2)°, V = 2266.0(3) Å^3, Z = 4, ρ_{calcd} = 1.369 g cm^{-3}, λ(Mo Kα_1) = 0.71073 Å, F(000) = 984, μ = 1.011 mm^{-1}, T = 100(2) K; 14 369 reflections were collected in the range 4.08° < 2θ < 56.92°, index ranges −14 ≤ h ≤ 12, −22 ≤ k ≤ 20, −16 ≤ l ≤ 16, of which 5223 were independent [R(int) = 0.0311] and 4099 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.0390, wR_2 (all data) = 0.0884, $w = [\sigma^2(F_o^2) + (0.0454P)^2 + 0.0000P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$; no. of data/restraints/parameters 5223/0/382; goodness of fit on (F^2) = 0.972. In the final difference map, the highest peaks (to ca. 0.84 e Å^{-3}) were close to the nickel atom.

Crystal data for 3c: $C_{32}H_{36}Ni_2O_3P_2P_2$, M_r = 647.97, prism yellow (0.20 × 0.20 × 0.11 mm^3) from diethyl ether, triclinic, space group $P\bar{1}$ (no. 2), a = 11.6560(6) Å, b = 12.2387(6) Å, c = 12.8339(7) Å, α = 66.2720(10)°, β = 63.7110(10)°, γ = 69.2970(10)°, V = 1468.02(13) Å^3, Z = 2, ρ_{calcd} = 1.466 g cm^{-3}, λ(Mo Kα_1) = 0.71073 Å, F(000) = 676, μ = 1.423 mm^{-1}, T = 100(2) K; 31 912 reflections were collected in the range 5.98° < 2θ < 61.04°, index ranges −16 ≤ h ≤ 16, −17 ≤ k ≤ 17, −18 ≤ l ≤ 18, of which 8891 were independent [R(int) = 0.0261] and 7513 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.0281, wR_2 (all data) = 0.0715, $w = [\sigma^2(F_o^2) + (0.0353P)^2 + 0.5261P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$; no. of data/restraints/parameters 8891/1/363; goodness of fit on (F^2) = 1.057. In the final difference map, the highest peaks (to ca. 0.65 e Å^{-3}) were close to nickel 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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