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Cyclic Enolates of Ni and Pd: Equilibrium between C- and O-Bound Tautomers and Reactivity Studies

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Abstract: 2-Acylaryl complexes of Ni and Pd containing chelating diphosphines react with K*t*BuO to give metallacyclic enolate complexes. While coordination through the carbon atom is preferred in the case of Pd, the nickel *O*-enolate compounds are formed as the corresponding O-tautomers. Slow equilibration between *O*- and *C*-enolate tautomers is observed for the nickel complex with an unsubstituted enolate function (M–O–C=CH_2). Theoretical DFT calculations suggest that the barrier for the tautomer exchange has its origin in the rigidity of the metallacycle. Whilst the *C*-enolate tautomer is unreactive towards aldehydes, the corresponding *O*-enolate adds to MeCHO and PhCHO, giving rise to products that retain the enolate functionality. The carbonylation of these products cleanly leads to the formation of enol lactones in a highly selective manner.

Keywords: aldol reactions · lactones · metallacycles · nickel · O ligands

Introduction

The chemistry of late-transition-metal enolates is a subject of considerable synthetic interest due to the high levels of selectivity that such compounds introduce in many organic reactions.[1] The detailed study of these complexes is essential for the development of new synthetic applications. Indeed, many of those currently known have emerged as a direct consequence of the work carried out in the last decades. Thus, transition-metal enolates have become indispensable in a number of valuable synthetic methodologies,[2] including some that are effected catalytically.[1e,f,h–k,3] Optimization of these methodologies demands a deeper understanding of their mechanistic details.

Earlier studies have disclosed that the coordination mode of the enolate ligand exerts a strong influence in its reactivity.[2a,4] For instance, in contrast to *O*-enolates, coordination through the carbon atom often causes low enolate-like reactivity and a chemical behaviour more akin to that of metal alkyls, for example, toward migratory insertion.[2e,5] Although some aldol-type additions of C-bound enolates are known,[2f,6] the active participation of the O-bound tautomer in these transformations cannot be ruled out, as the two forms may have similar energies. Both O- and C-binding have been ascertained for late transition metals,[2b–d] but the latter is more common for the softer Lewis acids derived from the heavier elements of these groups.[7,5c] Accordingly, while for nickel *O*- and *C*-enolates are common,[8,2f] in general palladium tends to favour *C*-enolate coordination.[7,5c] In some systems the tautomeric *C*- and *O*-enolate forms have been found to exist.[7,2d]

To gain more insight into the different chemical behaviour of the two isomeric structures, we have prepared Ni and Pd enolate complexes for which interconversion between the O and C isomers is hindered due to their metallacyclic nature. Following Vicente's preparation of cyclic palladium enolates

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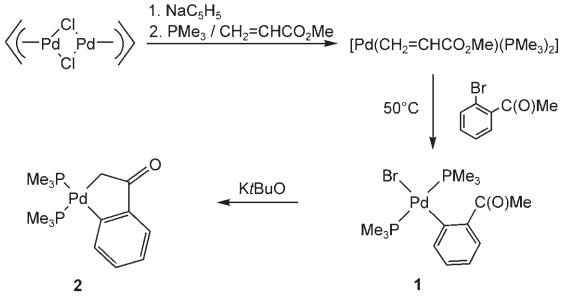
such as $[\overline{Pd\{CH_2C(O)\text{-}2\text{-}C_6H\text{-}3,4,5\text{-}(OMe)_3\}}(tmed)]$[7e] (tmed = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and our own extensive work on metallacycles of nickel and palladium of composition $[\overline{M(CH_2CMe_2\text{-}2\text{-}C_6H_4)}(L)_2]$[9] for different mono- and bidentate neutral L ligands, we have attempted the preparation of related enolate structures using *o*-acetylphenyl derivatives as starting materials. The results of these studies are reported herein. Part of this work has appeared in preliminary form.[10]

Results and Discussion

Palladium compounds: Since experimentally the nickel system involves more difficulties than the palladium complexes, the latter are described first.

Treatment of the chloro-bridged palladium allyl dimer $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ with NaC_5H_5, followed by the addition of PMe_3 and $CH_2{=}CHCO_2Me$ is known to generate the reactive Pd^0 species $[Pd(CH_2{=}CHCO_2Me)(PMe_3)_2]$.[11] This olefin complex is a suitable source of Pd^0 and its use circumvents the experimental complications due to the byproduct contamination commonly associated with the well-known Pd^0/PPh_3, or other related compounds. As represented in Scheme 1, its reaction with 2′-bromoacetophenone at 50 °C,

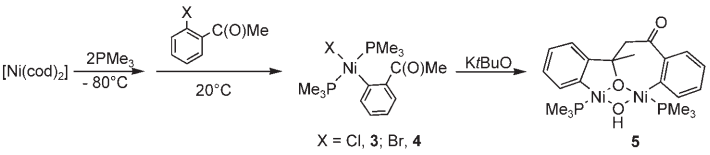


Scheme 1.

allows the isolation of the bromoaryl complex **1** in the form of a colourless crystalline solid. The observation of a $^{31}P\{^1H\}$ singlet at $\delta = -18.4$ ppm and of a virtually coupled triplet in both the ^1H ($\delta = 0.92$; $J_{ap} = 3.6$ Hz) and the $^{13}C\{^1H\}$ (δ=13.9; $J_{ap} = 15$ Hz) NMR spectra is indicative of a *trans*-trimethylphosphine arrangement. Moreover the similarity between the ν(CO) values in the IR spectra of **1** (1665 cm^{-1}) and the starting organic reagent, namely, *o*-bromoacetophenone (ca. 1700 cm^{-1}) suggests little or no apical interaction at all between the metal and the acetyl oxygen atom. This observation is in accord with the strong tendency of Pd^{II} to remain four-coordinate.

Reaction of the bromoaryl compound **1** with K*t*BuO gives the *C*-enolate **2** as air-stable white crystals. The coordination of the carbon atom of the enolate terminus within the metallacyclic structure is supported by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data. Thus, an IR absorption at 1630 cm^{-1} can be attributed to the organic carbonyl unit of **2**, whereas the palladium-bound enolate carbon resonates at $\delta = 52.1$ ppm, as a doublet of doublets, with *trans* and *cis* $^2J_{CP}$ couplings of 71 and 9 Hz, respectively. In the aliphatic region of the ^1H NMR spectrum a triplet due to accidentally equal $^3J_{HP}$ couplings between the Pd-CH_2 protons and the two inequivalent ^{31}P nuclei appears at $\delta = 2.26$ ppm (7.6 Hz). These and other spectroscopic data collected in the Experimental Section are similar to those reported for the related palladacycle $[\overline{Pd(CH_2CMe_2\text{-}2\text{-}C_6H_4)}(PMe_3)_2]$.[9a,b]

Synthesis of nickel enolates: Extension of this chemistry to the analogous nickel compounds is not straightforward. As represented in Scheme 2 the synthesis of chloro- or bro-



Scheme 2.

moaryl compounds related to **1** can be readily accomplished by using $[Ni(cod)_2]$ and the appropriate haloacetophenone substrate. The corresponding complexes, **3** and **4**, are isolated as orange crystalline solids. At variance with IR data for **1**, ν(C=O) data for these compounds (ca. 1630 cm^{-1}) is approximately 70 cm^{-1} lower than in the corresponding organic precursors, suggesting the existence of a weak axial interaction between the acetyl group and the Ni atom, as previously observed in the crystal structure of a related Ni compound.[12] Also in contrast with the Pd complex **1**, treatment of **3** and **4** with K*t*BuO does not afford the expected cyclic enolate with a structure analogous to that of **2**. Instead the dinuclear, sparingly soluble, compound **5** is obtained and isolated in the form of a yellow fine powder. The proposed structure for **5** finds support in microanalytical and spectroscopic data (see Experimental Section). The presence of a coordinated hydroxide ligand is evinced by an IR band at 3300 cm^{-1} and by a ^1H NMR resonance with a chemical shift ($\delta = -5.46$ ppm) similar to that reported for other transition-metal hydroxide compounds.[13] The two inequivalent PMe_3 ligands appear as singlets ($\delta = -10.7$ and -5.0 ppm) in the $^{31}P\{^1H\}$ NMR spectrum, whereas the analysis of the aryl region of the ^1H NMR spectrum reveals the presence of eight multiplets that correspond to two nonequivalent Ni–(*ortho*-substituted)phenyl units, as deduced also from 2D COSY and ^1H-^{13}C one-bond heterocorrelation experiments.

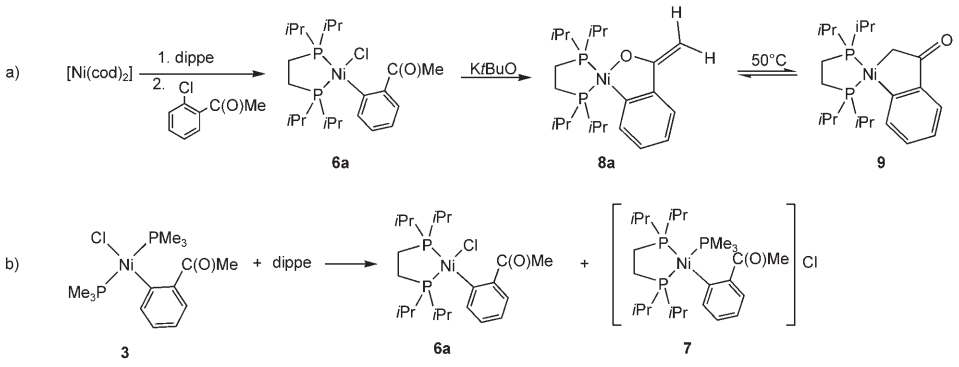
The organic ligand that bridges the two nickel centres of **5** results from the aldolic condensation of the acetylphenyl ligand of two molecules of either **3** or **4**. Even though the formation of **5** requires action of adventitious water, the deliberate addition of H_2O does not improve the yield of **5**. The use of other bases like $Na[N(SiMe_3)_2]$ or TlEtO gives rise to complex reaction mixtures. To gain additional infor-

mation on this complex transformation $^{31}P\{^{1}H\}$ NMR monitoring of the conversion of **3** to **5** was undertaken at −80 °C. Deprotonation appears to be fast and complete under these conditions. Moreover, a new species that gives broad resonances at $\delta = 8.6$ and 40.5 ppm is observed. Quenching the reaction by addition of HCl gives back the starting compound **3**. It thus appears that a highly reactive nickel enolate, possibly analogous to **2**, is initially formed. Nevertheless its lability prevents its isolation as a pure complex. In an attempt to increase the stability of this species the nature of the ancillary ligand has been systematically modified and the effects of this variation monitored.

Treatment of $[Ni(cod)_2]$ with 2′-bromoacetophenone, in the presence of 2,2′-bipyridyl furnishes a complex reaction mixture from which no pure compound can be isolated. The same holds for the analogous reaction with $iPr_2PCH_2CH_2P iPr_2$ (dippe), although useful compounds of this diphosphine may be isolated by a subtle modification of this reaction procedure (see below). At variance with these observations the use of PPh_3 and $Ph_2PCH_2CH_2PPh_2$ (dppe) permits the isolation of the corresponding Ni^{II} aryl compounds (Experimental Section). Nonetheless their reactions with K*t*BuO, or related basic reagents, lead to very unstable and complex reaction mixtures from which no clean products could be separated.

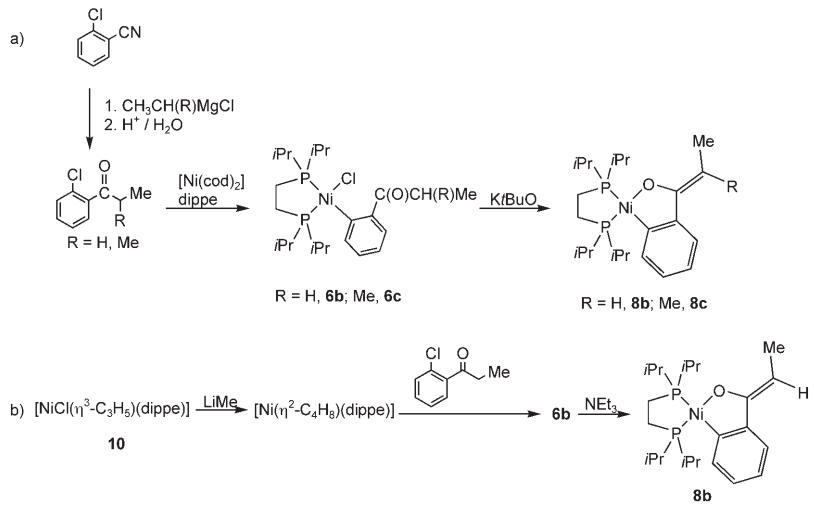
The diphosphine $iPr_2PCH_2CH_2PiPr_2$ (dippe), has proved to be the most suitable auxiliary ligand for the synthesis of aryl–nickel organometallic complexes that would serve as precursors for enolate compounds. While as mentioned above its addition to the $[Ni(cod)_2]$/2′-bromoacetophenone reaction mixture proves fruitless, the use of 2′-chloroacetophenone (Scheme 3a) permits the isolation of the desired chloro–*o*-acetylphenyl–nickel compound **6a**. Long reaction times are needed (3 days, 45 °C), but **6a** can be isolated by this procedure in 70–80 % yield. Alternatively, addition of dippe to **3** gives a mixture of **6a** and the cationic complex **7** (Scheme 3b) when Et_2O is employed as the reaction solvent, whereas the use of toluene produces compound **6a** as the main reaction product.

Treatment of a solution of **6a** in THF with one equivalent of K*t*BuO allows the preparation of the nickel enolate **8a** in good yields (Scheme 3a). At variance with the related Pd enolate **2**, spectroscopic data for the nickel derivative **8a** are consistent with coordination of the oxygen atom of the enolate functionality. For example, the two enolic carbon atoms give ^{13}C resonances at $\delta = 176.1$ and 74.4 ppm, the latter being characterized by a $^{1}J_{CH}$ coupling of 154 Hz, indicative of sp^2 hybridization. Additionally, an IR absorption at 1590 cm^{-1} may be assigned to ν(C=C) of the *O*-enolate ligand, whereas the higher energy band that could be expected for ν(C=O) (at 1630 cm^{-1} in **2**) is conspicuously absent. As reported in a preliminary form, definite structural comfirmation of the proposed *O*-enolate coordination has been provided by X-ray studies, that reveal Ni–O and C=C bond lengths within the metal enolate linkage of 1.857(10) and 1.31(2) Å, respectively.[10] The related enolates **8b** and **8c**, featuring Me substitution at one or the two olefinic sites of **8a** can be prepared by the same methodology (Scheme 4a). The chloroaryl precursors needed for these syntheses are not commercially available, but are obtained by the reaction of 2-chlorobenzonitrile with the appropriate Grignard reagent, followed by acid hydrolysis of the resulting imine.[14] Their oxidative addition to $[Ni(cod)_2]$ in the presence of dippe (45 °C, 24 h) yields the expected nickel *ortho*-substituted aryls **6b** and **6c**, as orange crystalline solids, with spectroscopic properties similar to those of **6a**. Deprotonation of **6b** and **6c** to the enolates **8b** and **8c**, respectively, occurs upon treatment with K*t*BuO. Interestingly, whereas the conversion of **6c** to **8c** requires stirring for 12 h at room temperature, the formation of **8b** is more facile and takes place spontaneously during the synthesis of **6b**, even in the absence of base, although only to a limited extent. Significant decomposition takes place if the heating is prolonged. As represented in Scheme 4b, compound **6b** can also be obtained if a more reactive η^2-butene complex is used as a precursor. This may be generated in situ and then oxidatively reacted with 2′-chloropropiophenone to give **6b**, accompanied with minor amounts of enolate **8b**. The latter becomes the main reaction product when the transformation is performed in the presence of NEt_3. These observations indicate that the ease of deprotonation increase in the order **6c** < **6a** < **6b**. While the formation of **8b** benefits of the stabilizing effect of the alkylation of the double bond, the unfavourable steric interaction of the mutually *cis* aromatic and methyl groups renders the deprotonation of **6c** difficult.



Scheme 3.

Compounds **8b** and **8c** exhibit spectroscopic properties similar to those of **8a**. An IR absorption centred around 1600 cm^{-1} may be attributed to the stretching of the C=C bond, while in the ^{1}H NMR spectrum the olefinic proton of **8b** resonates at $\delta = 5.27$ ppm as a quartet, due to coupling with the adjacent methyl protons ($^{3}J_{HH} = 6.7$ Hz). For **8c** the olefinic methyl substituents give



Scheme 4.

rise to singlets at $\delta = 2.40$ and 2.42 ppm. NOESY experiments reveal that the former resonance corresponds to the methyl group *trans* to the oxygen atom. In compound **8b** it is the vinylic H atom that occupies the position in *trans* with respect to the oxygen atom. Since the quality of the X-ray data obtained for **8a** is not very high and therefore a precise analysis of its bonding parameters is not justified, we have also characterized the analogous enolate **8b** by X-ray single-crystal studies. Figure 1 shows an ORTEP view of the structure, which is characterized by a slightly distorted square-planar coordination of the metal. The Ni–P1 distance of 2.163(1) Å is shorter than the Ni–P2 (2.206(1) Å) reflecting the higher *trans* influence of the aryl as compared with the *O*-enolate ligand. The Ni–O bond length of 1.853(3) Å is within the 1.85–2.10 Å range characteristic of Ni–O distances in square-planar alkoxide, aryloxide and hydroxide nickel derivatives with terminal O-bound ligands.[15] The olefinic C7–C8 bond length is normal (1.368(6) Å), being only slightly longer than in ethylene (1.34 Å) and, as expected, much shorter than the C_{sp^2}–C_{sp^3} bond between the olefinic carbon C8 and the methyl substituent (C8–C9 = 1.496(7) Å). These features compare well with those of other nickel compounds containing O-bound enolates[8] or related functionalities.[16]

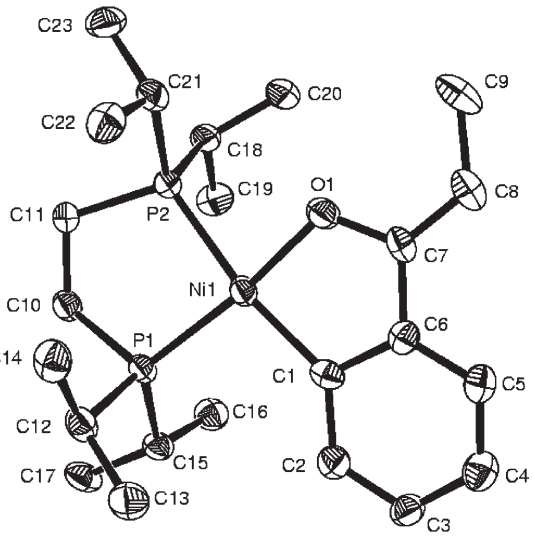
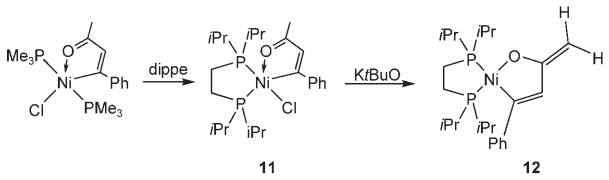


Figure 1. View of the molecular structure of complex **8b** together with the atomic numbering system. Selected bond lengths [Å] and angles [°]: Ni–O1 1.853(3), Ni–C1 1.913(4), Ni–P1 2.1627(12), Ni–P2 2.2064(12), O1–C7 1.342(5), C7–C8 1.368(6), C6–C7 1.464(6), C1–C6 1.398(6), C8–C9 1.496(7); O1-Ni-C1 86.17(15), C1-Ni-P1 99.77(12), O1-Ni-P2 86.10(10), O1-C7-C8 119.7(4), Ni-O1-C7 115.4(2), O1-C7-C6 113.0(3), C6-C7-C8 127.3(4), C7-C8-C9 122.6(5), P1-Ni-P2 88.50(5).

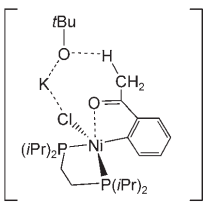
By means of a similar methodology, summarized in Scheme 5, a related nickel *O*-enolate **12** has been prepared. The starting nickel alkenyl can be obtained from *trans*-[Ni-



Scheme 5.

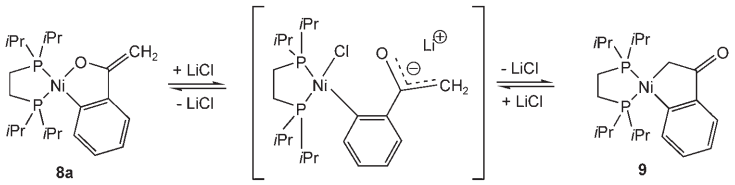
$(CH_3)Cl(PMe_3)_2]$, by successive insertion of CO and PhC≡CH, as reported previously.[12] Whereas its direct reaction with K*t*BuO gives rise to a complex mixture of products, prior PMe_3 substitution by dippe, followed by deprotonation permits isolation of the desired compound **12**. The spectroscopic features of this compound are similar to those of **8a**,**b**. Hence, it is likely that all these compounds show similar chemical reactivity, although that of **12** has not been explored.

Equilibria between C- and O-bound enolates—mechanistic studies on their formation: The preparation of the nickel enolates by the reaction of the appropriate halo aryl precursors with K*t*BuO leads selectively to the O-bound tautomers **8a**–**8c**. Nevertheless at temperatures around 50 °C (Scheme 3a) solutions of compound **8a** in different solvents equilibrate slowly with the *C*-enolate **9**. At room temperature the conversion of **8a** into **9** is very slow, thereby indicating a kinetic control of the selectivity in the formation of the *O*-enolate **8a** by the route depicted in Scheme 3a. A reasonable explanation for this selectivity is that the deprotonation of



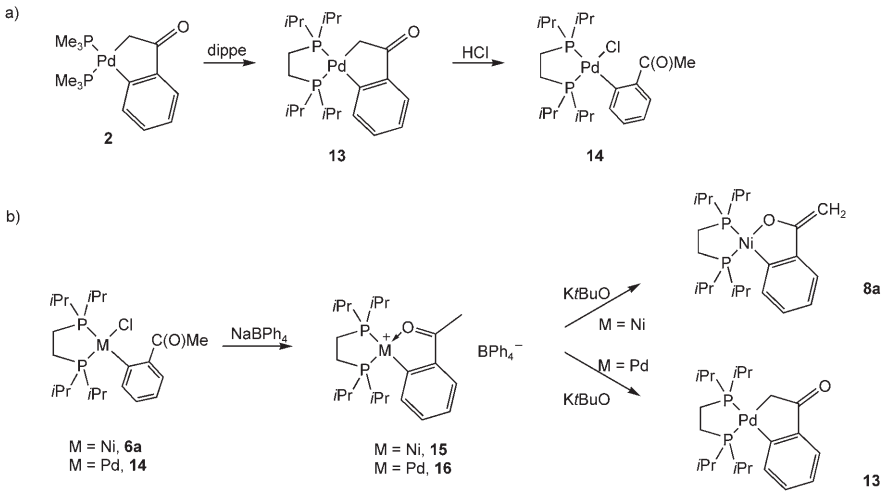
the acetyl group by the base is helped by previous coordination of the oxygen atom to the Ni center, as indicated.[17]

The isomer ratio **8a/9** varies very little in the solvents used (from ca. 3:1 in THF to ca. 1.6:1 in benzene, toluene or cyclohexane, at 50 °C). Measurement of K_{eq} for **8a/9** in toluene at several temperatures in the range 42–112 °C provides the following thermodynamic values: $\Delta G_{298} = -0.31(1)$ kcal mol^{-1}; $\Delta H = -0.28(1)$ kcal mol^{-1} and $\Delta S = +0.12(3)$ cal mol^{-1} K^{-1}, indicating that the reaction is essentially thermoneutral. The equilibration follows first-order kinetics[18] over the temperature range from 52 to 92 °C and it is characterized by activation parameters $\Delta H^{\neq} = 18.5(3)$ kcal mol^{-1}, $\Delta S^{\neq} = -22(1)$ cal mol^{-1} K^{-1}, and $\Delta G^{298}_{\neq} = 25.3(3)$ kcal mol^{-1}. A concerted mechanism, with an ordered η^3-oxoallyl transition state may be suggested. Indeed, η^3-oxoallyl structures have been proposed as intermediates for the interconversion of *C*- and *O*-enolates.[2d] It is worth mentioning in this regard that the deprotonation of **6a** by Li[N(CHMe$_2$)$_2$] yields a 3:1 mixture of **8a/9**. Moreover, the addition of LiCl to solutions of **8a** in THF at room temperature causes an almost instant isomerization of **8a** to a 3:1 mixture of **8a/9**. Accordingly, LiCl is proposed to catalyze the tautomerization as depicted in Scheme 6, that is, via an oxoallyl intermediate structure.



Scheme 6.

Additional experiments on the formation of the nickel and palladium enolates, **8a** and **2**, respectively, were performed with the aim of improving our mechanistic knowledge. Firstly, to check whether the deprotonation of the acetyl group coordinated through the oxygen atom to nickel (and palladium) is feasible, the cationic compounds **15** and **16** (Scheme 7b) were prepared by treatment of the chloroaryl **6a** and **14** with NaBPh$_4$. The chloroaryl palladium complex **14** cannot be obtained directly by oxidative addition of 2′-chloroacetophenone to the zerovalent palladium(0) precursor. Nevertheless, as represented in Scheme 7a, compound **14** is easily obtained from the enolate **2** by means of PMe$_3$ displacement by dippe, followed by HCl addition to



Scheme 7.

the Pd–enolate carbon bond of **13**. Chloride abstraction occurs upon reaction of **6a** and **14** with NaBPh$_4$, yielding the desired cationic derivatives **15** and **16**. Metal coordination of the carbonyl oxygen atom in the two complexes is hinted by the low ν(CO) values of 1575 and 1580 cm^{-1}, found for **15** and **16**, respectively. Note that in the nickel–aryl complexes **3**, **4** and **6a**, *ortho* substituted by an acetyl group, the corresponding ν(CO) IR bands appear around 1630 cm^{-1}, while the frequencies are close to 1700 cm^{-1} in the organic precursors. An X-ray structural determination carried out with the nickel compound **15** (Figure 2) demonstrates the coordination of the acetyl unit. The Ni–O1 bond length of 1.935(2) Å is, as expected, longer than in the nickel enolate **8b**. Also in **15** the Ni–P2 distance of 2.1425(7) Å is shorter than the Ni–P1 (2.2202(6) Å), reflecting the higher *trans* influence of the aryl as compared with the *O*-carbonyl of the acetyl ligand. The bond length of the carbonyl O1–C2 1.259(3) is quite normal. Compound **15** reacted with K*t*BuO to yield the O-bound nickel enolate **8a**, but the Pd complex gave the C-bound palladium analogue, **13**, as the only observable product. This result illustrates once more the strong preference of Pd for the C-bound configuration.

Secondly, if the formation of the *O*-enolate **8a** is the result of an intermolecular attack by *t*BuO$^-$ onto the acetyl group, (vide supra) then an intramolecular version of this process, whereby an alkoxide or aryloxide base has been incorporated to the metal coordination sphere, could be feasible, although alcohol elimination should give rise to the *C*-enolate isomer **9**. With this aim in mind the *trans*-nickel–aryl–aryloxide complexes **17a** and **17b** were synthesized (Scheme 8). Both react rapidly with dippe at room temperature and while partial decomposition occurs, one of the

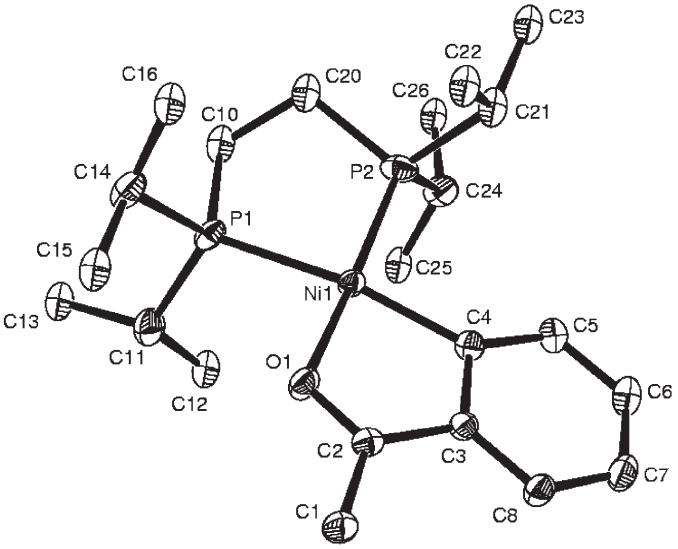
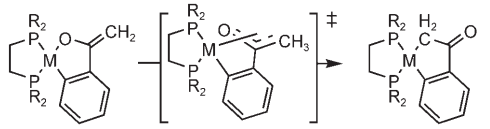


Figure 2. View of the structure of the cationic portion of compound **15** together with the atomic numbering system. Selected bond lengths [Å] and angles [°]: Ni–O1 1.935(2), Ni–C4 1.939(2), Ni–P1 2.2202(6), Ni–P2 2.1425(7), O1–C2 1.259(3), C1–C2 1.482(3), C2–C3 1.463(3), C3–C4 1.420(3); O1-Ni-C4 85.25(9), C4-Ni-P2 96.96(8), O1-Ni-P1 89.87(6), O1-C2-C1 118.9(2), Ni-O1-C2 114.0(2), O1-C2-C3 117.1(2), C1-C2-C3 124.02(2), P1-Ni-P2 88.97(3).

major species of both reactions is the expected *C*-enolate **9**, while the *O*-enolate **8a** was not observed.

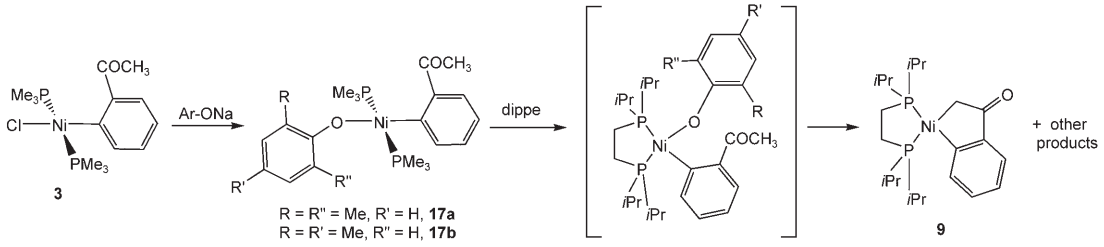
DFT study of the interconversion of *C*- and *O*-enolate tautomers: To provide theoretical support to the mechanism proposed for the exchange between the tautomeric enolate forms, and to gain a better understanding of the properties of these complexes, DFT calculations were performed on model complexes of the simplified diphosphine ligand $H_2PCH_2CH_2PH_2$ (from now on dpe) by using the BP86 functional and the numerical basis set DN*, as implemented in the Spartan Pro package. For Ni complexes, this study has been further expanded to the methyl and isopropyl P-substituted complexes, the latter corresponding to the full representation of the real compounds. In the case of the simple model containing the dpe ligand, the calculation of the stationary points was verified with a frequency calculation. The structures of the models containing substituted diphosphines were built from those of the dpe complexes and optimized with the same DFT method, although a frequency calculation was not attempted in these cases. Since the *i*Pr groups allow for a number of conformers, the calculation of the structures of these compounds was initiated by a molecular mechanics conformational analysis, by using the Merck Molecular Force Field. The positions of the atoms in the metallacyclic unit were fixed, and the structures of the five more stable conformers were optimized with the DFT without imposed restrictions. The results of this study are summarized in Table 1.

Table 1. Results of the theoretical study.



M	R	*O*-Enolate	TS	*C*-Enolate	ΔE(O→C) [kcal mol^{-1}]	Barrier(O→C) [kcal mol^{-1}]
Ni	H	***O*-Ni**	**TS**	***C*-Ni**	+2.07	25.2
Pd	H	***O*-Pd**	–	***C*-Pd**	+7.23	–
Ni	Me	***O*-Ni′**	**TS′**	***C*-Ni′**	+2.11	25.4
Ni	*i*Pr	***O*-Ni″**	**TS″**	***C*-Ni″**	+0.03	25.4

Figure 3 shows the structures calculated for the model complexes ***O*/*C*-Ni**, ***O*/*C*-Pd**, and **TS**. Some key distances and angles are shown in the figure. The geometric parameters of substituted model compounds ***O*/*C*-Ni′** and ***O*/*C*-Ni″** show no significant differences to those of the dpe models and have been omitted for the sake of simplicity. The availability of the crystal structures of compounds **8a** and **8b** allow for some interesting comparisons. In general, the structural features of these compounds are well reproduced in the model complexes. As in the experimental structure, the metallacyclic unit is essentially planar. The calculated Ni–O bond length (1.859 Å) matches well the experimental values (**8a**: 1.857(10); **8b**: 1.853(3) Å). Other important parameters are also correctly reproduced. For example, the Ni–O–C (**8a**: 118.0(8)°; **8b**: 115.4(2)°) and O–C=C (**8a**: 119(1)°; **8b**: 119.7(4)°) angles are close to the calculated values, 115.9 and 121.2°, respectively. The exocyclic double bond is slightly bent out of the plane of the metallacycle, in order to avoid the nearby aromatic hydrogen atom. This small distortion is also found in the real complexes. The Pd *O*-enolate displays very similar features. In contrast with the



Scheme 8.

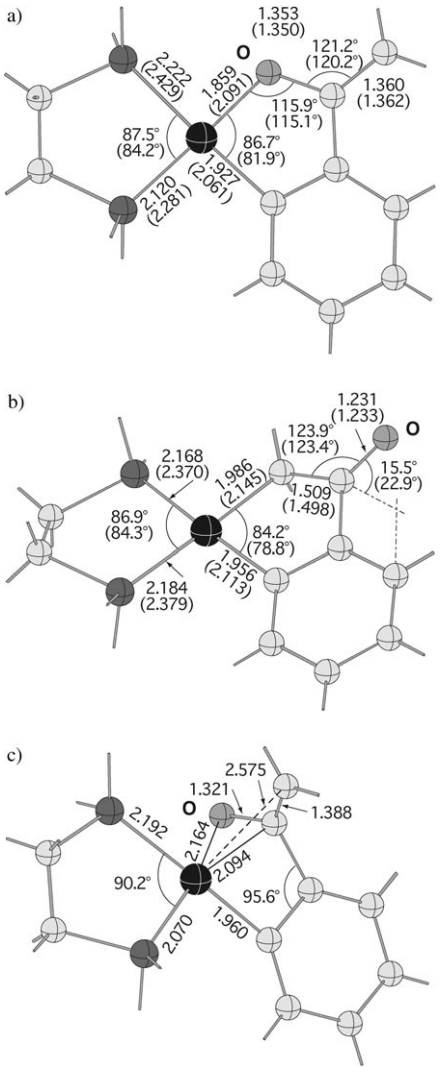


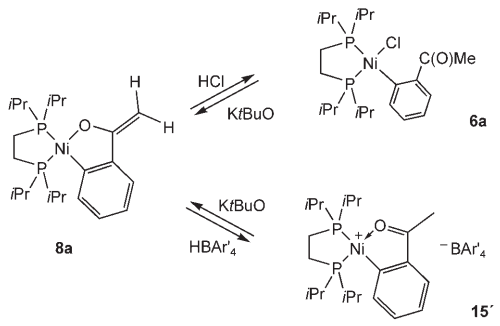
Figure 3. Schematic representation of the calculated geometries of simplified O- and C-cyclic enolates showing some selected geometric parameters for Ni and Pd (in parenthesis): a) [M(*o*-$C_6H_6C(=CH_2)O)(H_2PCH_2CH_2PH_2)$], M = Ni (***O*-Ni**) and Pd (***O*-Pd**); b) [M(*o*-$C_6H_6C(=O)CH_2)(H_2PCH_2CH_2PH_2)$], M = Ni (***C*-Ni**) and Pd (***C*-Pd**) (top view); c) transition state (TS).

flat structure exhibited by the ***O*-M** models, the metallacycle ring of the *C*-enolates shows a significant puckering. A similar conformation is found in the Pd *C*-enolate complex [Pd-($CH_2C(=O)$-2-C_6H-3,4,5-$(OMe)_3$(tmed)], but the different co-ligands present in this compound prevents a more precise comparison with their structural features.

The relative energies of the model complexes are shown in Table 1. As expected, the C-tautomeric form is strongly favored for Pd. For Ni, the *C*-enolate is favored by only about 2 kcal mol^{-1}. This difference further diminishes to 1.7 kcal mol^{-1} if the zero-point energy (ZPE) correction is taken into account. The introduction of carbon substituents on the P atoms of the phosphine does not change significantly the energy balance, although there seems to be a tendency to favor the *O*-enolate form when electron-donor alkyl groups replace the hydrogen atoms. Since the energy calculation does not take into account the solvation effects, it can be concluded that the calculation reasonably reproduces the thermoneutral character of the ***O*-Ni**/***C*-Ni** equilibrium.

As discussed previously, the experimental data suggest that for the Ni derivatives the equilibration of the tautomers could involve an intermediate η^3-enolate species. Accordingly, we have searched for such an intermediate. Starting with the more simple dpe ligand, two stationary points were located in the energy surface, each of them characterized by one imaginary frequency. They correspond to transition states in which the Ni atom interacts simultaneously with the C and O atoms of the enolate fragment, and differ only in the conformation of the Ni–dpe chelate. These transition states were used as a starting point to build the structures corresponding to the methyl and isopropyl derivatives, and in the latter case the structures of the ten ($=2\times5$) more stable conformers were fully optimized. Since the conformational change of the diphosphine ligand is thought to be facile, we have selected the lower energy transition states for the calculation of the energy barrier. The structure of the transition state corresponding to the dpe ligand is shown in Figure 3. As can be seen, the O-C-CH_2 unit is approximately perpendicular to the coordination plane (93.3°), allowing a π-interaction with the Ni atom. The lengths of the Ni–O and Ni–C bonds suggest that the interaction is not symmetrical, and can be considered closer to η^2-C=O than a η^3-pseudoallylic interaction. The relatively long C=O and short C=C bonds further support this view; hence, an early transition state in the O→C reaction coordinate is indicated.[19] The energy difference between **TS** and ***O*-Ni** (ca. 25.2 kcal mol, 24.5 kcal mol with ZPE correction) is in good accord with the experimental $\Delta G^{\neq}$ for **8a**→**9** (25.3 kcal mol^{-1}), although it is somewhat higher than the activation enthalpy ($\Delta H^{\neq}=18.5$ kcal mol). The introduction of methyl or *i*Pr substituents in the diphosphine does not alter significantly the relative energy of the corresponding transition states (**TS′** and **TS″**, respectively). Therefore, the origin of the relatively high barrier to the tautomeric exchange does not reside in the steric hindrance caused by the dippe ligand, but in the distortion of the metallacyclic ring during the process. As can be seen in Figure 3, the aryl–C(O) bond has to bend noticeably (the angle formed by this bond and the aromatic ring is close to 90°), in order to maintain the M–enolate interaction. This restriction is absent in open-chain enolates, where the interconversion is facile. It is also worth to recall that the presence of bulky substituents on the diphosphine ligand seems to have a small influence on the equilibrium constant or the exchange rate between the two tautomers.

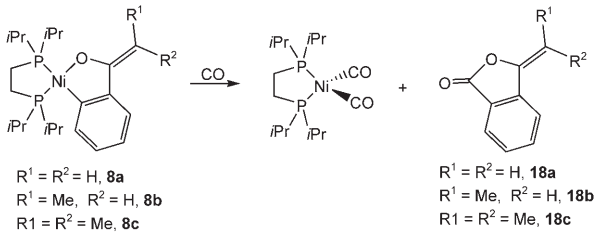
Reactions of enolates and Brønsted acids: As represented in Scheme 9 the reaction of **8a** with HCl reverts enolate formation and regenerates the starting chloroaryl compound **6a**. The analogous reaction with $[H(OEt_2)_2][BAr'_4]$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$) also occurs with protonation of the enolate



Scheme 9.

functionality and yields the cationic aryl compound **15** as the corresponding $BAr'_4{}^-$ salt, **15′**. The palladium enolates **2** and **13** also react with HCl with selective cleavage of the Pd–CH_2 bond (see Scheme 7a for the reaction of the dippe derivative **13**).

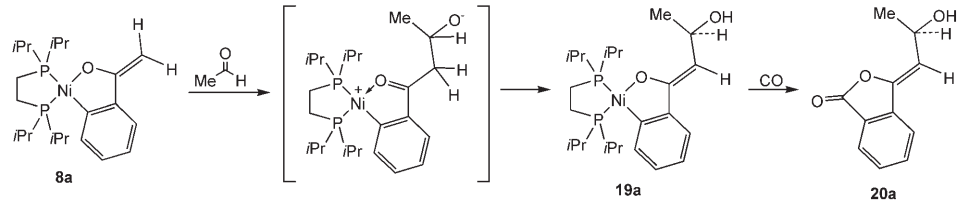
Reactions with carbon monoxide: Upon bubbling CO through a solution of **8a**, reductive carbonylation to $[Ni(CO)_2(dippe)]$ occurs (Scheme 10) with concomitant for-



Scheme 10.

mation of lactone **18a**. The related enolates **8b** and **8c** react similarly producing the analogous lactones **18b** and **18c**. The organic compounds can be separated from the Ni^0 organometallic product by standard chromatographic techniques. They have been characterized by high-resolution mass spectrometry and by IR and NMR spectroscopy (see Experimental Section). It is worth pointing out that the selectivity of this reaction provides additional support for the structure of the parent enolates. Thus, the carbonylation of **8b** (R^1 = Me, R^2 = H) yields a single isomer, **18b**, for which NOESY experiments reveal the same *Z* configuration of the C=C bond present in **8b**. This selectivity contrasts with previous results on the generation of related lactones, obtained as mixtures of their *Z* and *E* isomers,[20] and has been used as structural probe for the nature of the products resulting from the reactions of **8a** with MeC(O)H and PhC(O)H, to be discussed below.

Reactions with aldehydes: Despite the fact that enolizable carbonylic compounds like MeC(O)H may undergo acid–base reactions with metal enolates, giving rise to equilibrium mixtures of different enolates, we considered this mode of reactivity unlikely for **8a**, as the Ni–C_{aryl} bond of the putative protonation product would keep the carbonylic functionality in the vicinity of the metal coordination environment. In accord with expectations, compound **8a** and MeC(O)H react at room temperature with formation of the condensation product **19a**, resulting from nucleophilic attack of the enolate carbon atom onto the carbonylic aldehyde carbon atom (Scheme 11). Most remarkably, **19a** is an



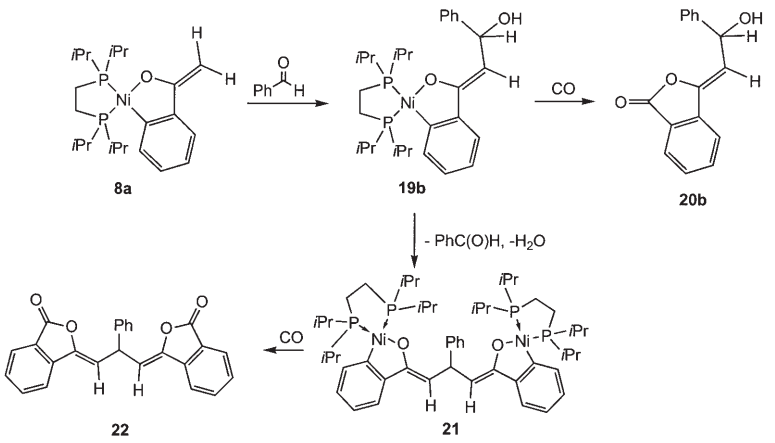
Scheme 11.

enolate related to **8a**, formally derived from the addition of one of the enolate C–H bonds to the carbonyl group. Further reaction of **19a** with an excess of MeC(O)H does not take place, possibly due to steric hindrance. In agreement with this assumption, the methyl-substituted enolates **8b** and **8c** do not react with acetaldehyde. Although it is widely accepted that aldehyde coordination precedes the C–C bond-forming step in aldol transformation induced by transition metals,[2a,4c,5a–5f] this mechanistic hypothesis appears doubtful in the present case due to the rigid nature of the enolate fragment. Instead, aldehyde attack by the enolate carbon and a prototropic shift (rather than Ni^{2+} shift) seems more likely.

The NMR spectra of **19a** are very similar to those of the parent enolate **8a**. The =CH part of the new enolate ligand gives ^1H and ^{13}C signals at $\delta = 4.73$ and 97.3 ppm ($^1J_{CH} = 153$ Hz), respectively, while the hydroxyl group is responsible for an IR absorption around 3200 cm^{-1} and a proton resonance at $\delta = 5.77$ ppm. The low thermal stability of this product has precluded characterization by microanalysis. However, in the presence of CO it is quantitatively converted into the lactone **20a** (Scheme 11), that has been isolated in a pure form.

Similarly to acetaldehyde, the non-enolizable aldehyde PhCHO reacts with **8a** giving rise to a new β-hydroxyenolate complex **19b**, which is structurally similar to **19a**. In contrast with the latter, **19b** is stable enough to allow its isolation in analytically pure form. It can also be carbonylated in situ, to afford the corresponding lactone in good isolated yield (Scheme 12).

Experimental conditions prove to be important for the successful preparation of **19b**. Thus, relatively concentrated reaction mixtures (ca. 0.16 M in each reactant) lead to full conversion within approximately 4 h, but the reaction be-



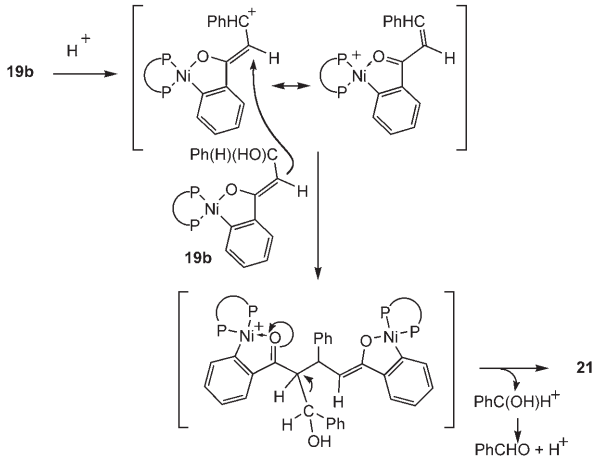
Scheme 12.

comes too slow when more diluted solutions are used. In practice, **19b** is best obtained using a large excess of PhCHO (1:10). Under these conditions, the product is cleanly formed within 5 min, but on standing for longer periods of time, it slowly converts into a second product (**21**) the transformation being complete after about 48 h. The NMR spectra of **21** are strikingly similar to those of its precursor (**19b**), both showing almost the same number of signals located at very close positions. The main differences are found in the ^{1}H spectrum of the former, which lacks the hydroxyl resonance and displays an apparently anomalous CH signal with a relative intensity of 0.5 H. These features suggest that **21** has the binuclear structure shown in Scheme 12. This proposal was confirmed by the EI-MS spectrum of the corresponding carbonylation product **22**, which shows the expected molecular ion at m/z 380.

The formation of **21** from two molecules of **19b** requires the release of two molecules of water and one of PhCHO, therefore an excess of the latter is not needed. Indeed, it has been observed that pure samples of **19b** dissolved in THF evolve into **21**, albeit much more slowly (ca. 10 days) than observed in the reaction of **8a** with an excess of benzaldehyde. The apparent catalytic effect of PhCHO is probably due to traces of benzoic acid, which are difficult to remove. In fact, the formation of **21** was retarded when the benzaldehyde was distilled immediately prior to use. However, the presence of small amounts of benzoic acid can be considered unavoidable, since this could be formed from the well-known autoxidation reaction of benzaldehyde (Cannizzaro reaction), catalyzed by the basic Ni enolate complexes.

Scheme 13 shows a likely mechanism for the acid-catalyzed formation of compound **21**. Protonation of **19b**, followed by loss of water produces a very reactive enone, activated by coordination to the metal center. This intermediate readily undergoes the addition of a second molecule of **19b**. The species formed is sterically crowded and readily eliminates PhCHO (in the form of $PhC(OH)H^{+}$), to give the final product. Our observation that related nickel enolates react with α,β-unsaturated ketones gives some support to this mechanistic proposal.[8a]

One final comment which is worthy of note concerns the reactivity of the enolate tautomers **8a** and **9** (Scheme 3a) towards aldehydes. Only the O-bound structure **8a** exhibits the enolate reactivity presented in Scheme 11 and 12. Thus when an approximate 2:1 mixture of **8a**/**9** is treated at room temperature with either MeC(O)H or PhC(O)H, $^{31}P\{^{1}H\}$ NMR monitoring reveals consumption of **8a**, while **9** remains unaltered (20 °C, 24 h). Hence under these conditions only the *O*-enolate is sufficiently nucleophilic to add to aldehydes.



Scheme 13.

Conclusion

Cyclic palladium enolates stabilized by either PMe_3 or $iPr_2PCH_2CH_2PiPr_2$ (dippe) auxiliary ligands can be prepared following a conventional organometallic synthetic methodology. Only the *C*-enolate isomers are observed. Isolation of analogous nickel enolates has only been possible when the chelating diphosphine dippe is employed. The failure to obtain nickel enolates containing monodentate phosphine ligands could be due to the formation of binuclear oxygen-bridged species by means of phosphine dissociation. This would facilitate an intramolecular aldol condensation, ultimately leading to compound **5**.

While C-coordination is favored for the Pd enolate complex, O-coordination is preferred by the nickel complexes. Nonetheless for compound **8a**, which features primary alkyl coordination in the C-bound form (compound **9**, see Scheme 3a), equilibrium mixtures of the two tautomers may be generated. Still, the *O*-enolate predominates. DFT calculations suggest that the tautomeric exchange is hindered by

the incorporation of the enolate functionality into a rigid metallacyclic fragment. The parent *O*-enolate complex **8a** reacts with enolizable and non-enolizable aldehydes, giving products that retain the enolate functionality. Interestingly, the *C*-enolate tautomer **9** does not react with aldehydes, illustrating the relationship between coordination mode and reactivity in this class of compounds.

Experimental Section

Microanalyses were performed by the Analytical Service of the Instituto de Investigaciones Químicas. The spectroscopic instruments used were Bruker Model Vector 22 for IR spectra, and Bruker DPX-300, DRX-400 and DRX-500 for NMR spectroscopy. The ^{13}C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to $SiMe_4$. The $^{13}C\{^1H\}$ NMR assignments were helped in most cases with the use of gate-decoupling techniques. $^{31}P\{^1H\}$ NMR shifts are referenced to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a b.p. of 40–60 °C. The compound $[Ni(\eta^3\text{-}C_3H_5)Cl(PMe_3)_2]$ was prepared by oxidative addition of allyl chloride to $[Ni(cod)_2]$ in the presence of PMe_3. The Grignard reagents Mg(R)Cl (R = Et, *i*Pr) and the sodium salts NaArO (Ar = 2,4-dimethylphenoxide and 2,6-dimethylphenoxide) were prepared following the conventional methodologies. The ligands PMe_3 and $iPr_2PCH_2CH_2iPr_2$ (dippe), the acid $[H(OEt_2)][BAr'_4]$ ($BAr'_4 = B[3,5\text{-}C_6H_3\text{-}(CF_3)_2]_4$) and its salt $NaBAr'_4$,[21] and the complexes $[Ni(cod)_2]$,[22] $[Pd(\eta^2\text{-}CH_2{=}CH{-}CO_2Me)(PMe_3)_2]$[11] and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$[23] were prepared according to literature methods. The nickel compounds $[Ni(CH_2Ph)Cl(PMe_3)_2]$[24] and $[Ni(C(Ph){=}CH{-}CO{-}CH_3)Cl(PMe_3)_2]$[12] were previously prepared in our laboratories.

Synthesis of $[Pd(C_6H_4\text{-}o\text{-}C(O)CH_3)Br(PMe_3)_2]$ (1): 2′-Bromoacetophenone (0.27 mL, 2 mmol) was added to a solution of $[Pd(\eta^2\text{-}CH_2{=}CH{-}CO_2Me)(PMe_3)_2]$ (340 mg, 1 mmol) in Et_2O (40 mL). The mixture was stirred and heated to 50 °C for 14 h. The solution was evaporated under vacuum and the residue extracted with CH_2Cl_2 (30 mL). After partial evaporation of the solvent and cooling at −20 °C, complex **1** was isolated as white crystals in 65% yield. ^1H NMR (C_6D_6, 20 °C): $\delta = 0.92$ (t, $^*J_{HP} = 3.6$ Hz, 18H; $P(CH_3)_3$), 2.41 (s, 3H; CH_3), 6.84 (t, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 6.97 (t, $^3J_{HH} = 7.3$ Hz, 1H; CH_{ar}), 7.50 (d, $^3J_{HH} = 7.7$ Hz, 1H; CH_{ar}), 7.63 ppm (d, $^3J_{HH} = 7.5$ Hz, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = -18.4$ ppm (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 13.9$ (t, $^1J_{CP} = 15$ Hz; $P(CH_3)_3$), 28.1 (s, CH_3), 122.2 (s, CH_{ar}), 129.9 (s, CH_{ar}), 130.3 (s, CH_{ar}), 136.8 (m, CH_{ar}), 143.5 (s, C_{ar}–C=O), 162.0 (t, $^2J_{CP} = 6$ Hz; C_{ar}–Pd), 200.0 ppm (s, C=O); IR (Nujol): $\tilde{\nu} = 1665\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{25}BrP_2OPd$: C 36.7, H 5.5; found: C 36.4, H 5.6.

Synthesis of $[Pd(CH_2C(O)\text{-}o\text{-}C_6H_4)(PMe_3)_2]$ (2): K*t*BuO (123 mg, 1.1 mmol) was added to a cold solution (−80 °C) of **1** (457 mg, 1 mmol) in THF (40 mL). The mixture was stirred at room temperature for 1 h and then taken to dryness. The residue was extracted with CH_2Cl_2 (25 mL) and the resulting solution was centrifuged. After concentration, addition of some Et_2O and cooling to −20 °C, enolate **2** was obtained as colourless crystals. Yield: 75%; ^1H NMR (C_6D_6, 20 °C): $\delta = 0.75$ (d, $^2J_{HP} = 7.3$ Hz 9H; $P(CH_3)_3$), 0.88 (d, $^2J_{HP} = 7.3$ Hz, 9H; CH_3), 2.26 (t, $^2J_{HH} = 7.6$ Hz, 2H; CH_2), 7.20 (m, 2H; CH_{ar}), 7.71 (m, 1H; CH_{ar}), 8.20 ppm (m, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = -23.1$ (A, AX spin system), −23.9 ppm (X, AX spin system; $J_{AX} = 30$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 16.1$ (d, $^1J_{CP} = 22$ Hz; $P(CH_3)_3$), 17.5 (d, $^1J_{CP} = 21$ Hz; $P(CH_3)_3$), 52.1 (dd, $^2J_{CP} = 71$, 9 Hz; CH_2), 124.1 (s, CH_{ar}), 124.6 (d, $J_{CP} = 4$ Hz; CH_{ar}), 126.7 (d, $J_{CP} = 9$ Hz; CH_{ar}), 136.4 (m, CH_{ar}), 149.0 (s, C_{ar}–C=O), 164.1 (dd, $^2J_{CP} = 125$, 9 Hz; C_{ar}–Pd), 202.9 ppm (t, $^3J_{CP} = 8$ Hz; C=O). IR (Nujol): $\tilde{\nu} = 1630\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{24}P_2OPd$: C 44.6, H 6.4; found: C 44.5, H 6.2.

Synthesis of $[Ni(C_6H_4\text{-}o\text{-}C(O)CH_3)X(PMe_3)_2]$ (X = Cl, 3; X = Br, 4): A suspension of $[Ni(cod)_2]$ (275 mg, 1 mmol) in toluene (50 mL) was cooled at −80 °C and a solution of PMe_3 in toluene (1 M, 2 mL, 2 mmol) was added. The mixture was warmed to room temperature, stirred for 15 min, and then cooled to −80 °C. 2′-Chloroacetophenone (0.13 mL, 1 mmol) was then added, and the mixture was stirred at RT for 24 h and then evaporated under reduced pressure. The residue was extracted with Et_2O (40 mL) and filtered. The solution was concentrated and cooled to −20 °C furnishing compound **3** as orange crystals in 85% yield. ^1H NMR (C_6D_6, 20 °C): $\delta = 0.76$ (t, $^*J_{HP} = 3.5$ Hz, 18H; $P(CH_3)_3$), 2.38 (s, 3H; CH_3), 6.71 (pseudo-t, $J = 7.5$ Hz, 1H; CH_{ar}), 6.88 (pseudo-t, $J = 7.5$ Hz, 1H; CH_{ar}), 7.41 (d, $^3J_{HH} = 7.6$ Hz, 1H; CH_{ar}), 7.76 ppm (d, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = -16.2$ ppm (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 12.7$ (t, $^1J_{CP} = 13$ Hz; CH_3), 26.3 (s, CH_3), 120.8 (s, CH_{ar}), 128.7 (s, CH_{ar}), 130.4 (s, CH_{ar}), 136.9 (t, $^5J_{CP} = 4$ Hz; CH_{ar}), 142.8 (s, C_{ar}–C=O), 171.8 (t, $^2J_{CP} = 35$ Hz; C_{ar}–Ni), 199.1 ppm (s, C=O); IR (Nujol): $\tilde{\nu} = 1635\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{25}ClP_2ONi$: C 46.0, H 6.9; found: C 45.6, H 7.3.

The bromide derivative **4** was similarly prepared, although in this case the oxidative addition of the 2′-bromoacetophenone to $[Ni(cod)(PMe_3)_2]$ requires only 3 h. Yield: 80%; ^1H NMR (C_6D_6, 20 °C): $\delta = 0.81$ (t, $^*J_{HP} = 3.8$ Hz, 18H; $P(CH_3)_3$), 2.35 (s, 3H; CH_3), 6.70 (t, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 6.88 (t, $^3J_{HH} = 7.2$ Hz, 1H; CH_{ar}), 7.40 (d, $^3J_{HH} = 7.7$ Hz, 1H; CH_{ar}), 7.74 ppm (d,; $^3J_{HH} = 7.5$ Hz, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = -16.4$ ppm (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 13.6$ (t, $^1J_{CP} = 14$ Hz; $P(CH_3)_3$), 26.4 (s, CH_3), 121.0 (s, CH_{ar}), 129.0 (s, CH_{ar}), 130.7 (s, CH_{ar}), 136.5 (t, $^5J_{CP} = 4$ Hz; CH_{ar}), 142.8 (s, C_{ar}–C=O), 173.7 (t, $^2J_{CP} = 35$ Hz; C_{ar}–Ni), 199.3 (s, C=O); IR (Nujol): $\tilde{\nu} = 1635\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{25}BrP_2ONi$: C 41.0, H 6.2, found: C 41.4, H 5.8.

Synthesis of compound 5: K*t*BuO (112 mg, 1 mmol) was added to a solution of **4** (410 mg, 1 mmol) in THF (50 mL) at −80 °C. After stirring the mixture at room temperature for 4 h, the solvent was removed in vacuum. The resulting yellow solid was extracted with CH_2Cl_2 (20 mL) and the suspension was centrifuged to separate the KCl and partially concentrated. After addition of some petroleum ether and cooling at −20 °C, compound **5** was obtained as a yellow powder. Yield: 55%; ^1H NMR (C_6D_6, 20 °C): $\delta = -5.46$ (s, 1H; O*H*), 0.53 (s, 3H; CH_3), 0.93 (d, $^2J_{HP} = 10.0$ Hz, 9H; $P(CH_3)_3$), 1.27 (d, $^2J_{HP} = 9.3$ Hz, 9H; $P(CH_3)_3$), 3.00 (d, $^2J_{HH} = 18.1$ Hz, 1H; CH_2), 4.85 (d, $^2J_{HH} = 18.1$ Hz, 1H; CH_2), 6.37 (dm, $^3J_{HH} = 7.5$ Hz, 1H; CH_{ar}), 6.42 (d, $^3J_{HH} = 7.6$ Hz, 1H; CH_{ar}), 6.62 (tm, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 6.79 (tm, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 6.87 (tm, $^3J_{HH} = 7.2$ Hz, 1H; CH_{ar}), 6.92 (tm, $^3J_{HH} = 7.3$ Hz, 1H; CH_{ar}), 7.07 (dm, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 7.67 ppm (d, $^3J_{HH} = 7.6$ Hz, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = -10.7$ (s, PMe_3), −5.9 ppm (s, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 13.4$ (d, $^1J_{CP} = 30$ Hz; $P(CH_3)_3$), 14.3 (d, $^1J_{CP} = 28$ Hz; $P(CH_3)_3$), 26.6 (s, CH_3), 63.9 (s, CH_2), 82.6 (s, C-O), 121.3 (s, CH_{ar}), 123.0 (s, CH_{ar}), 123.5 (s, CH_{ar}), 124.4 (s, CH_{ar}), 125.7 (s, CH_{ar}), 126.7 (s, CH_{ar}), 137.3 (s, CH_{ar}), 138.4 (d, $J_{CP} = 9$ Hz; CH_{ar}), 141.7 (d, $^2J_{CP} = 33$ Hz; C_{ar}–Ni), 148.2 (d, $^2J_{CP} = 45$ Hz, C_{ar}–Ni), 149.5 (s, C_{ar}–C–O), 168.3 (s, C_{ar}–C=O), 206.9 ppm (s, C=O); IR (Nujol): $\tilde{\nu} = 3300$ (OH), 1655 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{22}H_{32}P_2O_3Ni$: C 50.4, H 6.2; found: C 50.6, H 6.0.

Synthesis of $[Ni(C_6H_4\text{-}o\text{-}C(O)CH_3)Br(dppe)]$: The ligand dppe (398 mg, 1 mmol) was added to a suspension of $[Ni(cod)_2]$ (275 mg, 1 mmol) in toluene (50 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 15 min, cooled to −80 °C and 2′-bromoacetophenone (0.14 mL, 1 mmol) was added. The resulting solution was then stirred at RT for 1.5 h, during which time the initial yellow colour due to $[Ni(cod)(PMe_3)_2]$ turned red-brown. The solvent was evaporated under vacuum and the residue extracted with of toluene (80 mL). After partial concentration of the solution and cooling to −30 °C, the product was isolated as an orange solid. Yield: 85%; ^1H NMR (C_6D_6, 20 °C): $\delta = 2.10$ (s, 3H; CH_3), 2.14–2.34 (m, 4H; CH*H*), 6.73 (t, $^3J_{HH} = 7.4$ Hz, 1H; CH_{ar}), 6.93 (t, $^3J_{HH} = 7.0$ Hz, 1H; CH_{ar}), 7.14–7.64 (m, 20H; CH_{ar}), 7.76 (d, $^3J_{HH} = 6.4$ Hz, 1H; CH_{ar}), 8.02 ppm (m, 1H; CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 41.8$ (A, AX spin system), 54.3 ppm (X, AX spin system; $J_{AX} = 34$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): $\delta = 25.2$ (dd, $^1J_{CP} = 26$ Hz, $^2J_{CP} = 14$ Hz; CH_2), 26.2 (s, CH_3), 30.6 (dd, $^1J_{CP} = 27$ Hz, $^2J_{CP} = 23$ Hz; CH_2), 121.9 (s, CH_{ar}), 128.4–134.2 (m, CH_{ar}), 129.9 (d, $J_{CP} = 5$ Hz; CH_{ar}), 130.7

(s, CH_{ar}), 139.2 (s, CH_{ar}), 143.8 (s, C_{ar}–C=O), 174.7 (dd, $^2J_{CP}=85$, 36 Hz; C_{ar}–Ni), 205.9 ppm (d, $^4J_{CP}=6$ Hz, *C*=*O*); IR (Nujol): $\tilde{\nu}=1640\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{44}H_{37}BrP_2ONi$: C 67.6, H 4.8; found: C 67.9, H 5.0.

Synthesis of [Ni(C_6H_4-*o*-C(O)CH_3)Br(PPh_3)$_2$]: This complex was prepared by a analogous route to that employed for the related dppe complex, although it was extracted with CH_2Cl_2 and crystallized from a CH_2Cl_2/Et_2O mixture. Yield: 85%. ^{1}H NMR (C_6D_6, 20°C): $\delta=1.94$ (s, 3H; CH_3), 6.41 (t, $^3J_{HH}=7.4$ Hz, 1H; CH_{ar}), 6.52 (t, $^3J_{HH}=7.5$ Hz, 1H; CH_{ar}), 6.66 (d, $^3J_{HH}=6.9$ Hz, 1H; CH_{ar}), 7.73 (m, 1H; CH_{ar}), 6.78–7.70 ppm (m, 30H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=25.9$ ppm (s); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=25.9$ (s, CH_3), 121.5 (s, CH_{ar}), 125.6–132.4 (m, CH_{ar}), 129.1 (s, CH_{ar}), 132.7 (s, CH_{ar}), 136.9 (s, CH_{ar}), 143.5 (s, C_{ar}–C=O), 168.6 (m, C_{ar}–Ni), 200.6 ppm (m, *C*=*O*);. IR (Nujol): $\tilde{\nu}=1640\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{34}H_{31}BrP_2ONi$: C 62.2, H 4.8; found: C 62.6, H 5.2.

Synthesis of [Ni(C_6H_4-*o*-C(O)CHR^{1}R^2)Cl(dippe)] (R^1=R^2=H, 6a; R^1=H, R^2=Me, 6b; R^1=R^2=Me, 6c): The compounds **6b** and **6c** were prepared from 2-chloropropiophenone and 2-chloroisobutirophenone. These precursors were previously synthesized by treating 2-chlorobenzonitrile with Mg(Br)Et or Mg(Br)*i*Pr followed by acid hydrolysis with H_2SO_4. 2-Chloropropiophenone: 79% yield; ^{1}H NMR (C_6D_6, 20°C): $\delta=1.18$ (t, $^3J_{HH}=7.3$ Hz, 3H; CH_3), 2.93 (q, 2H; CH_2), 7.29, 7.35, 7.39, 7.42 ppm (m, 1H; CH_{arom}). 2-Chloroisobutirophenone: 43% yield; ^{1}H NMR (C_6D_6, 20°C): $\delta=1.03$ (d, $^3J_{HH}=7.3$ Hz, 3H; CH_3), 3.03 (sept, 1H; CH); 6.98 (m, 1H; CH_{arom}), 6.98 (m, 2H; CH_{arom}), 7.14 ppm (m, 1H; CH_{arom}).

A suspension of [Ni(cod)$_2$] (275 mg, 1mmol) in toluene (40 mL) was cooled at −80°C, and treated with dippe (0.31 mL, 1 mmol). The mixture was warmed to RT, stirred for 15 min and then 2′-chloroacetophenone (0.13 mL, 1 mmol) was added. The mixture was stirred at 45°C for 3 d, after which time the solvent was removed in vacuo. The resulting orange solid was extracted with CH_2Cl_2 (30 mL) and this solution was filtered. The volume was reduced and cooled to −30°C to provide complex **6a** as orange crystals. Yield: 75%; ^{1}H NMR (C_6D_6, 20°C): $\delta=0.87$ (dd, $^3J_{HP}=13.7$ Hz, $^3J_{HH}=6.9$ Hz, 12H; CH_3), 1.21 (dd, $^3J_{HP}=12.4$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 1.33 (dd, $^3J_{HP}=15.2$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 1.46 (m, 2H; CH_2), 1.64 (m, 2H; CH_2), 2.01 (m, 2H; *CH*), 2.29 (m, 2H; *CH*), 2.53 (s, 3H; CH_3), 6.80 (tm, $^3J_{HH}=7.4$ Hz, 1H; CH_{ar}), 6.97 (tm, $^3J_{HH}=7.3$ Hz, 1H; CH_{ar}), 7.49 (t, $^3J_{HH}\approx{}^3J_{HP}=6.3$ Hz, 1H; CH_{ar}), 7.56 ppm (dm, $^3J_{HH}=7.7$ Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=65.9$ (A, AX spin system), 71.9 ppm (X, AX spin system; $J_{AX}=32$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=17.2$ (s, CH_3), 17.5 (dd, $^1J_{CP}=20$ Hz, $^2J_{CP}=12$ Hz; CH_2), 18.1 (s, CH_3), 19.4 (s, CH_3), 23.4 (t, $J_{CP}=23$ Hz; CH_2), 24.0 (d, $^1J_{CP}=17$ Hz; *CH*), 24.5 (d, $^1J_{CP}=22$ Hz; *CH*), 27.2 (s, CH_3), 121.9 (s, CH_{ar}), 130.0 (d, $J_{CP}=6$ Hz; CH_{ar}), 130.7 (s, CH_{ar}), 138.3 (s, CH_{ar}), 146.1 (s, *C*–C=O), 173.7 (dd, $^2J_{CP}=82$, 37 Hz; C_{ar}–Ni), 203.2 ppm (d, $^4J_{CP}=4$ Hz; *C*=O); IR (Nujol): $\tilde{\nu}=1630\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{22}H_{39}ClP_2ONi$: C 55.6, H 8.3; found: C 55.4, H 8.3.

Compounds **6b** and **6c** were prepared according to the same procedure, although in both cases the oxidative addition only requires 24 h. Both products are crystallized from THF in 80% (**6b**) and 65% (**6c**) yields.

[Ni(C_6H_4-*o*-C(O)CH_2CH_3)Cl(dippe)] (6b): ^{1}H NMR (C_6D_6, 20°C): $\delta=0.98$ (dd, $^3J_{HP}=13.7$ Hz, $^3J_{HH}=7.0$ Hz, 12H; CH_3), 1.29 (t,; $^3J_{HH}=7.3$ Hz, 3H CH_3), 1.35 (dd, $^3J_{HP}=12.5$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 1.46 (dd, $^3J_{HP}=15.3$ Hz, $^3J_{HH}=7.2$ Hz, 6H; CH_3), 1.50 (m, 2H; CH_2), 1.78 (m, 2H; CH_2), 2.15 (m, 2H; *CH*), 2.43 (m, 2H; *CH*), 3.09 (quart, $^3J_{HH}=7.3$ Hz, 2H; CH_2), 6.91 (tm, $^3J_{HH}=7.3$ Hz, 1H; CH_{ar}), 7.08 (tm, $^3J_{HH}=7.3$ Hz, 1H; CH_{ar}), 7.58 (t, $^3J_{HH}\approx{}^3J_{HP}=6.4$ Hz, 1H; CH_{ar}), 7.68 ppm (dm, $^3J_{HH}=7.7$ Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=72.8$ (A, AX spin system), 77.4 ppm (X, AX spin system; $J_{AX}=21$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=8.7$ (s, CH_3), 17.2 (s, CH_3), 17.4 (dd, $^1J_{CP}=20$ Hz, $^2J_{CP}=12$ Hz; CH_2), 17.9 (s, CH_3), 19.3 (s, CH_3), 19.4 (s, CH_3), 23.6 (t, $J_{CP}=23$ Hz; CH_2), 24.0 (d, $^1J_{CP}=18$ Hz; *CH*), 24.6 (d, $^1J_{CP}=25$ Hz; *CH*), 31.8 (s, CH_2), 121.9 (s, CH_{ar}), 129.5 (m, CH_{ar}), 130.0 (d, $J_{CP}=6$ Hz; CH_{ar}), 138.4 (s, CH_{ar}), 145.7 (s, C_{ar}–C=O), 173.5 (dd, $^2J_{CP}=85$, 37 Hz; *C*–Ni), 206.2 (d, $^4J_{CP}=4$ Hz; *C*=O); IR (Nujol): $\tilde{\nu}=1645\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{23}H_{41}ClP_2ONi$: C 56.4, H 8.4; found: C 56.4, H 8.4.

[Ni(C_6H_4-*o*-C(O)$CH(CH_3)_2$)Cl(dippe)] (6c): ^{1}H NMR (C_6D_6, 20°C): $\delta=0.99$ (dd, $^3J_{HP}=13.6$ Hz, $^3J_{HH}=7.0$ Hz, 12H; CH_3), 1.28 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.34 (dd, $^3J_{HP}=12.5$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 1.44 (dd, $^3J_{HP}=15.3$ Hz, $^3J_{HH}=7.2$ Hz, 6H; CH_3), 1.49 (m, 2H; CH_2), 1.78 (m, 2H; CH_2), 2.15 (m, 2H; *CH*), 2.43 (m, 2H; *CH*), 3.66 (sept, $^3J_{HH}=6.4$ Hz, 1H; *CH*), 6.92 (tm, $^3J_{HH}=7.7$ Hz, 1H; CH_{ar}), 7.08 (tm, $^3J_{HH}=7.3$ Hz, 1H; CH_{ar}), 7.58 (t, $^3J_{HH}\approx J_{HP}=6.3$ Hz, 1H; CH_{ar}), 7.70 ppm (dm, $^3J_{HH}=7.8$ Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=65.6$ (A, AX spin system), 73.0 ppm (X, AX spin system, $J_{AX}=33$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=17.3$ (s, CH_3), 17.3 (t, $J_{CP}=16$ Hz; CH_2), 17.9 (s, CH_3), 19.3 (s, CH_3), 19.8 (s, CH_3), 23.6 (partially hidden dd, CH_2), 23.9 (d, $^1J_{CP}=23$ Hz; *C*H), 24.6 (d, $^1J_{CP}=22$ Hz; *C*H), 34.7 (s, *C*H), 121.8 (s, CH_{ar}), 129.7 (m, CH_{ar}), 130.0 (d, $J_{CP}=6$ Hz; CH_{ar}), 138.6 (s, CH_{ar}), 144.6 (s, C_{ar}–C=O), 175.1 (dd, $^2J_{CP}=85$, 36 Hz; C_{ar}–Ni), 209.8 ppm (m, *C*=O). IR (Nujol): $\tilde{\nu}=1625\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{24}H_{43}ClP_2ONi$: C 57.2, H 8.6; found: C 57.1, H 8.7.

Synthesis for the complexes [Ni{*o*-C_6H_4–C=C(HR)O}(dippe)] (R=H, 8a; R=Me, 8b): KO*t*Bu (123 mg, 1.1 mmol) was added to a cooled (−78°C) solution of [Ni(C_6H_4-*o*-C(O)CH_3)(Cl)(dippe)], **6a**, (475 mg, 1 mmol) in anhydrous THF (80 mL) under N_2. After stirring at room temperature for 1 h, the solvent was removed in vacuo. The resulting yellow solid was extracted with toluene (100 mL) and this solution was centrifuged to remove the KCl. Recrystallization from THF provided 277 mg (65%) of the enolate **8a** as yellow crystals. ^{1}H NMR (C_6D_6, 20°C): $\delta=0.77$ (dd, $^3J_{HP}=11.8$ Hz, $^3J_{HH}=7.0$ Hz, 6H; CH_3), 0.94 (dd, $^3J_{HP}=13.0$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 0.98 (m, 2H; CH_2), 1.10 (m, 2H; CH_2), 1.13 (dd, $^3J_{HP}=17.4$ Hz, $^3J_{HH}=7.3$ Hz, 6H; CH_3), 1.34 (dd, $^3J_{HP}=15.4$ Hz, $^3J_{HH}=7.2$ Hz, 6H; CH_3), 1.99 (m, 2H; CH_2), 2.07 (m, 2H; *CH*), 4.62 (s, 1H; *CH*H), 4.79 (d, $^2J_{HH}=1.7$ Hz, 1H; CH*H*), 7.14 (m, 2H; CH_{ar}), 7.73 (pseudo-t, $^3J_{HH}=6.6$ Hz, 1H; CH_{ar}), 7.74 ppm (m, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=72.3$ (A, AX spin system), 78.1 ppm (X, AX spin system, $J_{AX}=25$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=16.0$ (dd, $^1J_{CP}=20$ Hz, $^2J_{CP}=10$ Hz; CH_2), 18.1 (d, $^2J_{CP}=5$ Hz; CH_3), 18.1 (s, CH_3), 19.2 (d, $^2J_{CP}=4$ Hz; CH_3), 21.1 (d, $^2J_{CP}=6$ Hz; CH_3), 22.4 (dd, $^1J_{CP}=26$ Hz, $^2J_{CP}=23$ Hz; CH_2), 24.0 (d, $^1J_{CP}=17$ Hz; *CH*), 25.2 (d, $^1J_{CP}=21$ Hz; *CH*), 75.9 (s, CH_2), 122.9 (s, CH_{ar}), 123.4 (s, CH_{ar}), 124.9 (d, $J_{CP}=7$ Hz; CH_{ar}), 137.4 (m, CH_{ar}), 156.2 (s, C_{ar}–C–O), 158.6 (dd, $^2J_{CP}=27$, 87 Hz; C_{ar}–Ni), 176.1 (d, $^3J_{CP}=14$ Hz; *C*–O); IR (Nujol): $\tilde{\nu}=1590\ cm^{-1}$ (C=C); elemental analysis calcd (%) for $C_{22}H_{38}P_2ONi$: C 60.2, H 8.7; found: C 60.0, H 8.3.

Complex **8b** can be prepared according to the same methodology (yield: 65%) or, alternatively, by the following procedure: a solution of LiMe was added (0.63 mL of 1.6 M solution in hexane, 1 mmol) to a solution of complex **10** (199 mg, 0.5 mmol) in THF (40 mL) at −78°C. The mixture was stirred at RT during 20 min, after which time $SiMe_3Cl$ (0.63 mL) was added to neutralize the LiMe excess. 2′-Chlorophenylethylcetone (0.07 mL, 0.5 mmol) and NEt_3 (0.70 mL) were then added at −80°C and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and the residue extracted with toluene (100 mL) and the solution centrifuged and taken to dryness. The residue was recrystallized from THF. Yield: 65%; ^{1}H NMR (C_6D_6, 20°C): $\delta=0.75$ (dd, $^3J_{HP}=11.8$ Hz, $^3J_{HH}=7.0$ Hz, 6H; CH_3), 0.80 (m, 2H; CH_2), 0.94 (dd, $^3J_{HP}=12.9$ Hz, $^3J_{HH}=7.1$ Hz, 6H; CH_3), 1.05 (m, 2H; CH_2), 1.14 (dd, $^3J_{HP}=17.1$ Hz, $^3J_{HH}=7.3$ Hz, 6H; CH_3), 1.38 (dd, $^3J_{HP}=15.4$ Hz, $^3J_{HH}=7.2$ Hz, 6H; CH_3), 2.00 (m, 2H; *CH*), 2.10 (m, 2H; *CH*), 2.36 (d, $^3J_{HH}=6.7$ Hz, 3H; CH_3), 5.27 (quart, $^3J_{HH}=6.7$ Hz, 1H; =*CH*), 7.17 (m, 2H; CH_{ar}), 7.37 (m, 1H; CH_{ar}), 7.73 ppm (m, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): $\delta=65.4$ (A, AX spin system), 72.5 ppm (X, AX spin system, $J_{AX}=32$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): $\delta=11.4$ (s, CH_3), 16.2 (dd, $^1J_{CP}=20$ Hz, $^2J_{CP}=11$ Hz; CH_2), 18.1 (d, $^2J_{CP}=4$ Hz; CH_3), 18.2 (s, CH_3), 19.2 (d, $^2J_{CP}=4$ Hz; CH_3), 21.1 (d, $^2J_{CP}=6$ Hz; CH_3), 22.4 (t, $^1J_{CP}=24.2$ Hz; CH_2), 24.0 (d, $^1J_{CP}=17$ Hz; *CH*), 25.2 (d, $^1J_{CP}=21$ Hz; *CH*), 86.1 (s, =*CH*), 121.3 (s, CH_{ar}), 123.3 (s, CH_{ar}), 123.9 (d, $J_{CP}=7$ Hz; CH_{ar}), 137.5 (m, CH_{ar}), 156.5 (s, C_{ar}–C–O), 158.0 (dd, $^2J_{CP}=27$, 88 Hz; C_{ar}–Ni), 169.7 ppm (d, $^3J_{CP}=13$ Hz, *C*–O); IR (Nujol): $\tilde{\nu}=1610\ cm^{-1}$ (C=C); elemental analysis calcd (%) for $C_{23}H_{40}P_2ONi$: C 61.0, H 8.9; found: C 60.8, H 8.9.

Synthesis of [Ni{*o*-C_6H_4−C=$C(CH_3)_2$O}(dippe)] (8c): K*t*BuO (123 mg, 1.1 mmol) was added to a solution of complex **6c** (504 mg, 1 mmol) in THF (80 mL) at −78 °C. After stirring the mixture at RT for 24 h, the solvent was removed under vacuum. The yellow residue was extracted with toluene (100 mL) and the resulting solution was centrifuged to separate the KCl. The solution was evaporated and the residue recrystallized from THF providing the enolate **8c** as yellow crystals in 65% yield. ^{1}H NMR (C_6D_6, 20 °C): δ = 0.76 (dd, $^3J_{HP}$ = 11.8 Hz, $^3J_{HH}$ = 7.0 Hz, 6H; CH_3), 0.80 (m, 2H; CH_2), 0.92 (dd, $^3J_{HP}$ = 12.7 Hz, $^3J_{HH}$ = 7.1 Hz, 6H; CH_3), 1.09 (m, 2H; CH_2), 1.14 (dd, $^3J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.3 Hz, 6H; CH_3), 1.39 (dd, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.2 Hz, 6H; CH_3), 1.98 (m, 2H; C*H*), 2.11 (m, 2H; C*H*), 2.40 (s, 3H; CH_3), 2.42 (s, 3H; CH_3), 7.14 (m, 1H; CH_{ar}), 7.23 (t, $^3J_{HH}$ = 7.5 Hz, 1H; CH_{ar}), 7.43 (t, $^3J_{HH}$ = 7.0 Hz, 1H; CH_{ar}), 7.93 ppm (d, $^3J_{HH}$ = 7.9 Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 72.4 (A, AX spin system), 72.7 ppm (X, AX spin system, J_{AX} = 19 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 16.7 (dd, $^1J_{CP}$ = 20 Hz, $^2J_{CP}$ = 10 Hz; CH_2), 18.8 (d, $^2J_{CP}$ = 5 Hz, 4C; CH_3), 19.8 (d, $^2J_{CP}$ = 5 Hz; CH_3), 20.7 (s, CH_3), 21.1 (s, CH_3), 21.8 (d, $^2J_{CP}$ = 6 Hz; CH_3), 23.0 (dd, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 22 Hz, 1C; CH_2), 24.5 (d, $^1J_{CP}$ = 17 Hz; C*H*), 25.9 (d, $^1J_{CP}$ = 21 Hz; C*H*), 97.7 (s, =C), 122.6 (s, CH_{ar}), 123.1 (d, J_{CP} = 6 Hz; CH_{ar}), 124.0 (s, CH_{ar}), 138.2 (m, CH_{ar}), 155.0 (s, C_{ar}−C−O), 160.5 (dd, $^2J_{CP}$ = 87, 25 Hz; C_{ar}–Ni), 162.9 ppm (d, $^3J_{CP}$ = 14 Hz; *C*−O); IR (Nujol): $\tilde{\nu}$ = 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{24}H_{42}P_2ONi$: C 61.7, H 9.1; found: C 62.0, H 8.9.

Synthesis of [Ni(η^3-C_3H_5)Cl(dippe)] (10): A solution of the complex [Ni(η^3-C_3H_5)Cl(PMe_3)$_2$] (278 mg, 1 mmol) in Et_2O (40 mL) was cooled to −80 °C and treated with dippe (0.31 mL, 1 mmol). After the solution was warmed to room temperature, it was pumped to dryness and the remaining solid was dissolved in Et_2O (50 mL) and filtered. Its concentration and cooling to −20 °C produced orange crystals in quantitative yield. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 1.14 (brs, 14H; CH_3, CH_2), 1.26 (brs, 12H; CH_3, CH_2), 2.05 (brs, 2H; C*H*), 2.37 (brs, 1H; C*H*), 2.70 (d, $^2J_{HH}$ = 8.2 Hz, 2H; CH*H*), 4.37 (brs, 2H; CH*H*), 5.05 ppm (q, $^3J_{HH}$ = 10.8 Hz, 1H; C*H*); ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 81.6 ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 18.9 (s, CH_3), 19.6 (m, CH_3), 21.9 (m, CH_2), 26.5 (d, $^1J_{CP}$ = 25 Hz; C*H*), 63.4 (d, $^2J_{CP}$ = 13 Hz; CH_2), 113.5 ppm (s, C*H*).

Synthesis of [Ni(C(Ph)=CH−CO−Me)Cl(dippe)] (11): A solution of the complex [Ni(C(Ph)=CH−CO−Me)Cl(PMe_3)$_2$], (392 mg, 1 mmol) in Et_2O (50 mL), cooled to −80 °C, was treated with dippe (0.31 mL, 1 mmol). After the solution was warmed to room temperature, it was pumped to dryness and the remaining solid was dissolved in Et_2O (50 mL). The solvent was again evaporated to remove the PMe_3. The extraction with toluene (60 mL), filtration, partial concentration and addition of some Et_2O, furnished the desired complex as an orange solid. Yield: 70%; ^{1}H NMR (C_6D_6, 20 °C): δ = 0.41 (dd, $^3J_{HP}$ = 11.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H; CH_3), 0.82 (m, 6H; CH_3), 0.86 (m, 2H; CH_2), 0.95 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.2 Hz, 3H; CH_3), 1.09 (dd, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.0 Hz, 3H; CH_3), 1.11 (m, 2H; CH_2), 1.49 (m, 8H; 2CH_3, 2C*H*), 1.67 (dd, $^3J_{HP}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 3H; CH_3), 2.00 (m, 1H; C*H*), 2.15 (s, 3H; CH_3), 2.78 (m, 1H; C*H*), 6.52 (dd, $^4J_{HP}$ = 14.8, 4.3 Hz, 1H; =C*H*), 7.11 (t, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 2H; CH_{ar}), 8.17 (d, $^3J_{HH}$ = 8.0 Hz, 2H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 66.4 (A, AX spin system), 73.2 ppm (X, AX spin system, J_{AX} = 33 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ = 16.0 (d, $^2J_{CP}$ = 7 Hz; CH_3), 16.8 (d, $^2J_{CP}$ = 6 Hz; CH_3), 17.1 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 12 Hz; CH_2), 17.6 (s, CH_3), 18.0 (d, $^2J_{CP}$ = 3 Hz; CH_3), 18.5 (d, $^2J_{CP}$ = 3 Hz; CH_3), 18.6 (d, $^2J_{CP}$ = 3 Hz; CH_3), 20.1 (d, $^2J_{CP}$ = 4 Hz; CH_3), 20.2 (d, $^2J_{CP}$ = 4 Hz; CH_3), 22.2 (d, $^1J_{CP}$ = 22 Hz; C*H*), 22.5 (t, J_{CP} = 24 Hz; CH_2), 23.1 (d, $^1J_{CP}$ = 23 Hz; C*H*), 25.6 (d, $^1J_{CP}$ = 17 Hz; C*H*), 27.3 (d, $^1J_{CP}$ = 23 Hz; C*H*), 29.7 (s, CH_3), 126.6 (s, CH_{ar}), 127.5 (s, CH_{ar}), 134.1 (s, =CH), 149.7 (s, C_{ar}), 199.4 (d, $^4J_{CP}$ = 5 Hz; *C*=O), 209.5 (dd, $^2J_{CP}$ = 84, 31 Hz; =C−Ni); IR (Nujol): $\tilde{\nu}$ = 1635 (C=O), 1505 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{24}H_{41}ClP_2ONi$: C 57.5, H 8.2; found: C 57.3, H 8.1.

Synthesis of [Ni{CH(Ph)=CH−C(=CH_2)O}(dippe)] (12): Following the same methodology than for **8c**, the enolate **12** was prepared from complex **11**, although in this case, only one hour was required for the deprotonation. It was isolated as brown crystals after recrystallization from Et_2O. Yield: 35%; ^{1}H NMR (C_6D_6, 20 °C): δ = 0.57 (m, 6H; CH_3), 0.68 (m, 2H; CH_2), 0.96 (dd, $^3J_{HP}$ = 13.0 Hz, $^3J_{HH}$ = 7.1 Hz, 6H; CH_3), 0.96 (m, 2H; C*H*), 0.97 (m, 2H; CH_2), 1.33 (m, 12H; CH_3), 2.07 (m, 2H; C*H*), 4.34 (t, $^2J_{HH}$ = 1.5 Hz, 1H; C*H*H), 4.58 (d, $^2J_{HH}$ = 1.1 Hz, 1H; CH*H*), 6.77 (dd, $^4J_{HP}$ = 8.3, 6.1 Hz, 1H; =C*H*), 7.02 (t, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 7.13 (t, $^3J_{HH}$ = 7.3 Hz, 2H; CH_{ar}), 7.33 ppm (d, $^3J_{HH}$ = 7.1 Hz, 2H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 73.5 (A, AX spin system), 76.1 ppm (X, AX spin system, J_{AX} = 29 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ = 15.4 (dd, $^1J_{CP}$ = 20 Hz, $^2J_{CP}$ = 11 Hz; CH_2), 17.6 (d, $^2J_{CP}$ = 6 Hz; CH_3), 18.3 (s, CH_3), 19.4 (d, $^2J_{CP}$ = 4 Hz; CH_3), 20.1 (t, J_{CP} = 23 Hz; CH_2), 23.9 (d, $^1J_{CP}$ = 22 Hz; C*H*), 24.2 (d, $^1J_{CP}$ = 17 Hz; C*H*), 80.4 (s, CH_2), 122.8 (s, C_{ar}), 123.7 (s, CH_{ar}), 126.4 (d, J_{CP} = 2 Hz; CH_{ar}), 127.1 (s, CH_{ar}), 146.6 (d, $^3J_{CP}$ = 4 Hz; =CH), 166.4 (dd, $^2J_{CP}$ = 83, 26 Hz; =C−Ni), 178.7 ppm (dd, $^3J_{CP}$ = 16, 2 Hz; *C*−O); IR (Nujol): $\tilde{\nu}$ = 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{26}H_{40}P_2ONi$: C 62.0, H 8.7; found: C 61.3, H 8.6.

Synthesis of [Pd(CH_2C(O)-*o*-C_6H_4)(dippe)] (13): The ligand dippe (0.31 mL, 1 mmol) was added to a cooled (−80 °C) solution of complex **2** (376 mg, 1 mmol) in THF (30 mL), and the mixture warmed slowly to room temperature. The solvent was then evaporated and the residue extracted with toluene (30 mL) and filtered. After concentration and the addition of some Et_2O complex **13** was obtained as colourless crystals. Yield: 90%; ^{1}H NMR (C_6D_6, 20 °C): δ = 0.69 (m, 12H; CH_3), 0.91 (m, 12H; CH_3), 1.08 (m, 2H; CH_2), 1.18 (m, 2H; CH_2), 1.77 (m, 2H; C*H*), 1.92 (m, 2H; C*H*), 3.44 (dd, $^3J_{HP}$ = 7.3, 6.2 Hz, 2H; CH_2), 7.26 (m, 2H; CH_{ar}), 7.88 (m, 1H; CH_{ar}), 8.32 ppm (m, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 68.4 (A, AX spin system), 72.9 ppm (X, AX spin system, J_{AX} = 15 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ = 17.9 (s, CH_3), 19.1 (d, $^2J_{CP}$ = 6 Hz; CH_3), 19.8 (d, $^2J_{CP}$ = 8 Hz; CH_3), 20.0 (dd, $^1J_{CP}$ = 39 Hz, $^2J_{CP}$ = 18 Hz; CH_2), 24.8 (d, $^1J_{CP}$ = 15 Hz; C*H*), 25.0 (d, $^1J_{CP}$ = 12 Hz; C*H*), 47.0 (dd, $^2J_{CP}$ = 66,8 Hz; CH_2), 124.1 (s, CH_{ar}), 124.9 (d, J_{CP} = 4 Hz; CH_{ar}), 126.5 (d, J_{CP} = 8 Hz; CH_{ar}), 138.6 (dd, J_{CP} = 10, 5 Hz; CH_{ar}), 149.2 (s, C_{ar}–C=O), 163.3 (dd, $^2J_{CP}$ = 21, 8 Hz; C_{ar}–Pd), 201.7 ppm (t, $^3J_{CP}$ = 7 Hz; *C*=O); IR (Nujol): $\tilde{\nu}$ = 1625 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{22}H_{38}P_2OPd$: C 54.3, H 7.9; found: C 54.1, H 7.9.

Synthesis of [Pd(C_6H_4-*o*-C(O)CH_3)Cl(dippe)] (14): A solution of complex **13** (487 mg, 1 mmol) in THF (30 mL), cooled to −80 °C, was treated with HCl (10 mL of a 0.1 M solution in THF, 1 mmol). The mixture was stirred at RT for 15 min, and the solvent evaporated. The resulting white solid was extracted with CH_2Cl_2 and the solution centrifuged. Concentration of this solution and cooling to −20 °C furnished white crystals in quantitative yield. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 1.03 (dd, $^3J_{HP}$ = 14.8 Hz, $^3J_{HH}$ = 7.0 Hz, 12H; CH_3), 1.20 (dd, $^3J_{HP}$ = 13.4 Hz, $^3J_{HH}$ = 7.1 Hz, 6H; CH_3), 1.34 (dd, $^3J_{HP}$ = 16.1 Hz, $^3J_{HH}$ = 7.2 Hz, 6H; CH_3), 1.59 (m, 2H; CH_2), 1.87 (m, 2H; CH_2), 2.32 (m, 2H; C*H*), 2.53 (m, 2H; C*H*), 2.53 (s, 3H; CH_3), 6.94 (tm, $^3J_{HH}$ = 7.4 Hz, 1H; CH_{ar}), 7.07 (tm, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 7.47 (t, $^3J_{HH} \approx J_{HP}$ = 7.6 Hz, 1H; CH_{ar}), 7.63 ppm (dd, $^3J_{HH}$ = 7.6 Hz, J_{HP} = 1.6 Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 70.3 (A, AX spin system), 73.5 ppm (X, AX spin system, J_{AX} = 15 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 16.7 (s, CH_3), 18.0 (s, CH_3), 18.3 (dd, $^1J_{CP}$ = 20 Hz, $^2J_{CP}$ = 10 Hz; CH_2), 19.1 (d, $^2J_{CP}$ = 4 Hz; CH_3), 23.6 (dd, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 22 Hz; CH_2), 24.2 (d, $^1J_{CP}$ = 18 Hz; C*H*), 28.9 (s, CH_3), 122.4 (s, CH_{ar}), 129.7 (d, J_{CP} = 8 Hz; CH_{ar}), 130.2(d, J_{CP}=7 Hz; CH_{ar}), 137.0 (d, J_{CP} = 3 Hz; CH_{ar}), 146.3 (s, C_{ar}–C=O), 167.4 (d, $^2J_{CP}$ = 135 Hz; C_{ar}–Pd), 202.2 ppm (d, $^4J_{CP}$ = 3 Hz; *C*=O); IR (Nujol): $\tilde{\nu}$ = 1675 cm^{-1} (C=O); no analytical data available.

Synthesis of [M{C_6H_4-*o*-C(O)CH_3}(dippe)]$^+$[BAr_4]$^-$ (M=Ni, Ar=Ph, 15; Ar=3,5-$C_6H_3(CF_3)_2$, 15′; M=Pd, Ar=Ph, 16): These compounds were prepared following the same procedure. Compound **15**: $NaBPh_4$ (171 mg, 0.5 mmol) was added to a solution of complex **6a** (238 mg, 0.5 mmol) in THF (50 mL) cooled to −80 °C. The mixture was stirred at room temperature for 1 h after which time the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and centrifuged. After removal of the solvent in vacuo, the product was crystallized from a mixture of acetone/Et_2O as yellow crystals in 90% yield. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 1.38 (m, 12H; CH_3), 1.49 (m, 12H; CH_3), 1.62 (m, 2H; CH_2), 1.90 (m, 2H; CH_2), 2.40 (m, 2H; C*H*), 2.56 (m, 2H; C*H*), 2.65 (s, 3H; CH_3), 7.30 (tm, $^3J_{HH}$ = 7.5 Hz, 1H; CH_{ar}), 7.38 (tm, $^3J_{HH}$ = 6.4 Hz, 1H; CH_{ar}), 7.51 (t, $^3J_{HH} \approx {}^3J_{HP}$ = 7.5 Hz, 1H; CH_{ar}), 7.66 ppm (dm, $^3J_{HH}$ = 7.7 Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 75.4 (A, AX spin system), 84.4 ppm (X, AX spin system, J_{AX} = 30 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 16.6 (dd, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 7 Hz; CH_2), 18.8 (d, $^2J_{CP}$ = 5 Hz; CH_3), 19.0 (s,

*C*H$_3$), 19.8 (d, $^2J_{CP}$=3 Hz; *C*H$_3$), 22.1 (d, $^2J_{CP}$=4 Hz; *C*H$_3$), 22.3 (dd, $^1J_{CP}$=29 Hz, $^2J_{CP}$=18 Hz; *C*H$_2$), 24.5 (s, *C*H$_3$), 24.8 (d, $^1J_{CP}$=19 Hz; *C*H), 26.7 (d, $^1J_{CP}$=24 Hz; *C*H), 126.6 (s, *C*H$_{ar}$), 131.9 (s, *C*H$_{ar}$), 136.7 (d, J_{CP}= 6 Hz; *C*H$_{ar}$), 138.5 (d, J_{CP}=3 Hz, *C*H$_{ar}$), 148.4 (s, *C*$_{ar}$–C=O), 165.9 (dd, $^2J_{CP}$=77, 28 Hz; *C*$_{ar}$–Ni), 222.1 ppm (t, $^3J_{CP}$=10 Hz; *C*=O); IR (Nujol): $\tilde{\nu}$=1575 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{46}H_{59}BP_2ONi$: C 72.8, H 7.8; found: C 72.4, H 7.9.

The same procedure was employed for the synthesis of **15′** and **16**, but using NaBAr′$_4$, for the former. Compound **15′** was crystallized from Et$_2$O and **16** from CH$_2$Cl$_2$/Et$_2$O, both in approximately 80–85% yield.

[Ni(C$_6$H$_4$-*o*-C(O)CH$_3$)(dippe)]$^+$[BAr′$_4$]$^-$ (15′): ^{1}H NMR (CD$_2$Cl$_2$, 20°C): δ=1.23 (dd, $^3J_{HP}$=13.3 Hz, $^3J_{HH}$=7.0 Hz, 6H; C*H*$_3$), 1.23 (dd, $^3J_{HP}$= 14.2 Hz, $^3J_{HH}$=7.1 Hz, 6H; C*H*$_3$), 1.32 (dd, $^3J_{HP}$=16.4 Hz, $^3J_{HH}$=7.3 Hz, 6H; C*H*$_3$), 1.37 (dd, $^3J_{HP}$=18.7 Hz, $^3J_{HH}$=7.3 Hz, 6H; C*H*$_3$), 1.67 (m, 2H; C*H*$_2$), 1.94 (m, 2H; C*H*$_2$), 2.28 (m, 2H; C*H*), 2.46 (m, 2H; C*H*), 2.55 (s, 3H; C*H*$_3$), 7.10 (tm, $^3J_{HH}$=7.4 Hz, 1H; C*H*$_{ar}$), 7.26 (tm, $^3J_{HH}$=6.4 Hz, 1H; C*H*$_{ar}$), 7.34 (t, $^3J_{HH}\approx{}^3J_{HP}$=7.5 Hz, 1H; C*H*$_{ar}$), 7.53 ppm (dm, $^3J_{HH}$= 7.6 Hz, 1H; C*H*$_{ar}$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20°C): δ=75.1 (A, AX spin system), 84.4 ppm (X, AX spin system, J_{AX}=30 Hz); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20°C): δ=16.2 (dd, $^1J_{CP}$=26 Hz, $^2J_{CP}$=7 Hz; *C*H$_2$), 18.3 (d, $^2J_{CP}$=5 Hz; *C*H$_3$), 18.5 (s, *C*H$_3$), 19.5 (d, $^2J_{CP}$=3 Hz; *C*H$_3$), 21.8 (dd, $^1J_{CP}$=29 Hz, $^2J_{CP}$=18 Hz; *C*H$_2$), 21.9 (d, $^2J_{CP}$=4 Hz; *C*H$_3$), 23.9 (s, *C*H$_3$), 24.6 (d, $^1J_{CP}$=19 Hz; *C*H), 26.6 (d, $^1J_{CP}$=24 Hz; *C*H), 126.5 (s, *C*H$_{ar}$), 131.6 (s, *C*H$_{ar}$), 136.6 (d, J_{CP}=6 Hz; *C*H$_{ar}$), 138.4 (s, *C*H$_{ar}$), 148.4 (s, *C*$_{ar}$–C=O), 165.7 (dd, $^2J_{CP}$=77, 28 Hz; *C*$_{ar}$–Ni), 222.5 (d, $^3J_{CP}$=9 Hz; *C*=O); IR (Nujol): $\tilde{\nu}$=1580 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{54}H_{51}BF_{24}P_2ONi$: C 49.8, H 3.9; found: C 49.3, H 4.4.

[Pd(C$_6$H$_4$-*o*-C(O)CH$_3$)(dippe)]$^+$[BPh$_4$]$^-$ (16): ^{1}H NMR (CD$_2$Cl$_2$, 20°C): δ=1.24 (m, 24H; C*H*$_3$), 1.63 (m, 2H; C*H*$_2$), 1.96 (m, 2H; C*H*$_2$), 2.31 (m, 2H; C*H*), 2.47 (m, 2H; C*H*), 2.65 (s, 3H; C*H*$_3$), 7.22 (t, $^3J_{HH}$=8.1 Hz, 1H; C*H*$_{ar}$), 7.39 (m, 2H; C*H*$_{ar}$), 7.71 ppm (m, 1H; C*H*$_{ar}$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20°C): δ=77.6 (A, AX spin system), 87.7 ppm (X, AX spin system, J_{AX}=20 Hz); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20°C): δ=16.6 (dd, $^1J_{CP}$= 24 Hz, $^2J_{CP}$=6 Hz; *C*H$_2$), 18.1 (d, $^2J_{CP}$=3 Hz; *C*H$_3$), 18.5 (s, *C*H$_3$), 19.0 (d, $^2J_{CP}$=4 Hz; *C*H$_3$), 20.9 (d, $^2J_{CP}$=3 Hz; *C*H$_3$), 23.8 (dd, $^1J_{CP}$=31 Hz, $^2J_{CP}$= 19 Hz; *C*H$_2$), 24.9 (d, $^1J_{CP}$=19 Hz; *C*H), 25.4 (d, J_{CP}=3 Hz; *C*H$_3$), 26.1 (d, $^1J_{CP}$=27 Hz; *C*H), 125.9 (s, *C*H$_{ar}$), 132.9 (s, *C*H$_{ar}$), 133.0 (s, *C*H$_{ar}$), 137.4 (s, *C*H$_{ar}$), 147.8 (s, *C*$_{ar}$–C=O), 173.4 (d, $^2J_{CP}$=118 Hz; *C*$_{ar}$–Pd), 221.9 ppm (dd, $^3J_{CP}$=8, 3 Hz; *C*=O); IR (Nujol): $\tilde{\nu}$=1580 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{46}H_{59}BP_2OPd$: C 68.5, H 7.4; found: C 68.4, H 7.4.

Synthesis of [Ni(C$_6$H$_4$-*o*-C(O)CH$_3$)(OAr)(PMe$_3$)$_2$] (17a and 17b): Sodium 2,6-dimethylphenoxide (2.1 mL of a 0.48 M solution in THF, 1 mmol) was added to a solution of complex **3** (365 mg, 1 mmol) in THF (50 mL) cooled to −80°C. The mixture was stirred for one hour at room temperature, and the solvent was pumped off. The residue was extracted with Et$_2$O (30 mL) and the solution centrifuged. Reduction of the volume and cooling to −20°C produced yellow-green crystals of complex **17a** in essentially quantitative yield. ^{1}H NMR (C$_6$D$_6$, 20°C): δ=0.52 (brs, 18H; C*H*$_3$), 2.38 (s, 3H; C*H*$_3$), 2.72 (s, 3H; C*H*$_3$), 3.36 (s, 3H; C*H*$_3$), 6.82 (t, $^3J_{HH}$=7.3 Hz, 1H; C*H*$_{ar}$), 6.69 (m, 2H; C*H*$_{ar}$), 7.24 (m, 2H; C*H*$_{ar}$), 7.35 (d, $^3J_{HH}$=7.8 Hz, 1H; C*H*$_{ar}$), 7.82 ppm (d, $^3J_{HH}$=7.5 Hz, 1H; C*H*$_{ar}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=−20.4 ppm (s); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=11.8 (brs, *C*H$_3$), 18.6 (s, *C*H$_3$), 19.1 (s, *C*H$_3$), 26.4 (s, *C*H$_3$), 112.4 (s, *C*H$_{ar}$), 120.7 (s, *C*H$_{ar}$), 122.5 (s, *C*H$_{ar}$), 127.9 (s, *C*H$_{ar}$), 128.6 (s, *C*H$_{ar}$), 130.2 (s, *C*H$_{ar}$), 137.6 (s, *C*H$_{ar}$), 143.5 (s, *C*$_{ar}$–CH$_3$), 166.3 (s, *C*$_{ar}$–O), 167.9 (t, $^2J_{CP}$=45 Hz; *C*$_{ar}$–Ni), 198.8 ppm (s, *C*=O); IR (Nujol): $\tilde{\nu}$= 1645 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{22}H_{34}P_2O_2Ni$: C 58.6, H 7.6; found: C 58.8, H 7.4.

The related complex **17b** was obtained also in quantitative yield following the same preparation, but using 2,4-dimethylphenoxide. ^{1}H NMR (C$_6$D$_6$, 20°C): δ=0.59 (brs, 18H; C*H*$_3$), 2.38 (s, 3H; C*H*$_3$), 2.41 (s, 3H; C*H*$_3$), 2.53 (s, 3H; C*H*$_3$), 6.70 (t, $^3J_{HH}$=7.4 Hz, 1H; C*H*$_{ar}$), 6.87 (t, $^3J_{HH}$= 7.5 Hz, 1H; C*H*$_{ar}$), 7.07 (brs, 1H; C*H*$_{ar}$), 7.26 (brs, 2H; C*H*$_{ar}$), 7.37 (d, $^3J_{HH}$=7.7 Hz, 1H; C*H*$_{ar}$), 7.85 ppm (brs, 1H; C*H*$_{ar}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=−18.2 ppm (s); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=11.9 (t, $^1J_{CP}$= 12 Hz *C*H$_3$), 18.1 (s, *C*H$_3$), 20.7 (s, *C*H$_3$), 26.2 (s, *C*H$_3$), 118.7 (s, *C*H$_{ar}$), 119.8 (s, *C*$_{ar}$–C=O), 120.6 (s, *C*H$_{ar}$), 127.1 (s, *C*$_{ar}$–CH$_3$), 127.6 (s, *C*H$_{ar}$), 128.1 (s, *C*H$_{ar}$), 130.2 (s, *C*H$_{ar}$), 130.6 (s, *C*H$_{ar}$), 137.7 (s, *C*H$_{ar}$), 143.5 (s, *C*$_{ar}$–CH$_3$), 165.2 (s, *C*$_{ar}$–O), 170.9 (m, *C*$_{ar}$–Ni), 199.2 ppm (s, *C*=O); IR (Nujol): $\tilde{\nu}$=1655 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{22}H_{34}P_2O_2Ni$: C 58.6, H 7.6; found: C 58.2, H 7.5.

Synthesis of O=C[C$_6$H$_4$-*o*-C(=CR^{1}R^2)O] (R^1=R^2=H, 18a; R^1=H, R^2= Me, 18b; R^1=R^2=Me, 18c): CO was bubbled for 5 min at room temperature through a solution of complex **8a** (100 mg, 0.1 mmol) in THF (15 mL). After this time the initial orange solution turned pale yellow. The solvent was evaporated under vacuum and the oily residue was extracted with petroleum ether (30 mL) and filtered. Compound **18a** was separated from the complex [Ni(dippe)(CO)$_2$] by spinning band chromatography, with petroleum ether as eluent. Yield: 60%; ^{1}H NMR (C$_6$D$_6$, 20°C): δ=4.61 (d, $^2J_{HH}$=2.8 Hz, 1H; =C*H*H), 4.82 (d, $^2J_{HH}$=2.8 Hz, 1H; =CH*H*), 6.80 (t, $^3J_{HH}$=6.7 Hz, 1H; C*H*$_{ar}$), 6.91 (m, 2H; C*H*$_{ar}$), 7.48 ppm (d, $^3J_{HH}$=8.2 Hz, 1H; C*H*$_{ar}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=90.0 (s, *C*H$_2$), 120.1 (s, *C*H$_{ar}$), 124.8 (s, *C*H$_{ar}$), 125.2 (s, *C*$_{ar}$–C=O), 129.9 (s, *C*H$_{ar}$), 133.6 (s, *C*H$_{ar}$), 138.7 (s, *C*$_{ar}$–C–O), 151.9 (s, *C*–O), 165.9 ppm (s, *C*=O); IR (Nujol): $\tilde{\nu}$=1770 (C=O), 1660 cm^{-1} (C=C); HREIMS: *m*/*z* calcd for $C_9H_6O_2$: 146.0368; found: 146.0369.

Compounds **18b** and **18c** were prepared in the same manner. The former was purified by spinning band chromatography using a 4:1 mixture of petroleum ether/Et$_2$O as eluent, while the latter was crystallized from petroleum ether.

Compound 18b: ^{1}H NMR (C$_6$D$_6$, 20°C): δ=1.67 (d, $^4J_{HH}$=7.2 Hz, 3H; C*H*$_3$), 4.99 (quart, $^4J_{HH}$=7.2 Hz, 1H; =C*H*), 6.83 (t, $^3J_{HH}$=7.4 Hz, 1H; C*H*$_{ar}$), 6.98 (m, 2H; C*H*$_{ar}$), 7.56 ppm (d, $^3J_{HH}$=7.7 Hz, 1H; C*H*$_{ar}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=10.8 (s, *C*H$_3$), 102.9 (s, =CH), 119.1 (s, *C*H$_{ar}$), 124.6 (s, *C*$_{ar}$–C=O), 124.8 (s, *C*H$_{ar}$), 128.8 (s, *C*H$_{ar}$), 133.4 (s, *C*H$_{ar}$), 139.3 (s, *C*$_{ar}$–C–O), 146.4 (s, *C*–O), 166.0 ppm (s, *C*=O); IR (Nujol): $\tilde{\nu}$=1770 (O–C=O) 1685 cm^{-1} (C=C); HR EIMS: *m*/*z* calcd for $C_{10}H_8O_2$: 160.0524; found: 160.0524.

Compound 18c: ^{1}H NMR (C$_6$D$_6$, 20°C): δ=1.54 (s, 3H; C*H*$_3$), 1.77 (s, 3H; C*H*$_3$), 6.83 (t, $^3J_{HH}$=7.5 Hz, 1H; C*H*$_{ar}$), 7.02 (t, $^3J_{HH}$=7.6 Hz, 1H; C*H*$_{ar}$), 7.15 (d, $^3J_{HH}$=7.5 Hz, 1H; C*H*$_{ar}$), 7.69 ppm (d, $^3J_{HH}$=7.7 Hz, 1H; C*H*$_{ar}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=17.9 (s, *C*H$_3$), 19.6 (s, *C*H$_3$), 117.7 (s, =C-(CH$_3$)$_2$), 122.2 (s, *C*H$_{ar}$), 125.2 (s, *C*H$_{ar}$), 127.8 (s, *C*H$_{ar}$), 128.2 (s, *C*$_{ar}$–C=O), 133.2 (s, *C*H$_{ar}$), 138.5 (s, *C*$_{ar}$–C–O), 141.4 (s, *C*–O), 165.9 ppm (s, *C*=O); IR (Nujol): $\tilde{\nu}$=1770 (O–C=O), 1695 cm^{-1} (C=C); HR EIMS: *m*/*z* calcd for $C_{11}H_{10}O_2$: 174.0681; found: 174.0680.

Synthesis of [Ni{*o*-C$_6$H$_4$–C(=CHCHOHMe)O}(dippe)] (19a): Acetaldehyde in CH$_2$Cl$_2$ (2 mL of a 0.17 M solution) was added to complex **8a** (150 mg, 0.34 mmol), which was placed in a Schlenck tube, at −78°C. The mixture was stirred at room temperature for 30 min, and the solvent was evaporated under reduced pressure, to give a red solid. This solid was washed twice with petroleum ether (2×10 mL) and was judged pure by 1H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. No satisfactory analytical data could be obtained for this complex, which decomposed upon attempted recrystallization, even under an inert atmosphere. ^{1}H NMR (C$_6$D$_6$, 20°C): δ=1.18 (m, 12H; C*H*$_3$), 1.18 (s, 3H; C*H*$_3$), 1.33 (m, 12H; C*H*$_3$), 1.45 (m, 2H; C*H*$_2$), 1.75 (m, 2H; C*H*$_2$), 2.21 (m, 2H; C*H*), 2.37 (m, 2H; C*H*), 4.70 (m, 1H; =C*H*), 4.73 (m, 1H; C*H*-OH), 5.77 (brs, 1H; O*H*), 6.76 (t, $^3J_{HH}$=7.1 Hz, 1H; C*H*$_{ar}$), 6.81 (t, $^3J_{HH}$=7.3 Hz, 1H; C*H*$_{ar}$), 7.09 (d, $^3J_{HH}$=7.4 Hz, 1H; C*H*$_{ar}$), 7.13 ppm (t, $^3J_{HH}\sim{}^3J_{HP}\sim$6.6 Hz, 1H; C*H*$_{ar}$); ^{31}P{^{1}H} NMR (C$_6D_6$, 20°C): δ=73.0 (A, AX spin system), 78.7 ppm (X, AX spin system, J_{AX}=24 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20°C): δ=16.7 (dd, $^1J_{CP}$=22 Hz, $^2J_{CP}$=10 Hz;, *C*H$_2$), 18.6 (s, *C*H$_3$), 18.7 (d, $^2J_{CP}$=5 Hz; *C*H$_3$), 18.8 (d, $^2J_{CP}$=5 Hz; *C*H$_3$), 19.0 (s, *C*H$_3$), 19.6 (d, $^2J_{CP}$= 4 Hz; *C*H$_3$), 19.9 (d, $^2J_{CP}$=5 Hz; *C*H$_3$), 21.9 (d, $^2J_{CP}$=6 Hz; *C*H$_3$), 22.0 (d, $^2J_{CP}$=6 Hz; *C*H$_3$), 22.4 (dd, $^1J_{CP}$=27 Hz, $^2J_{CP}$=21 Hz; *C*H$_2$), 24.2 (d, $^1J_{CP}$=17 Hz; *C*H), 24.5 (s, *C*H$_3$), 24.7 (d, $^1J_{CP}$=17 Hz; *C*H), 26.0 (d, $^1J_{CP}$= 23 Hz; *C*H), 26.1 (d, $^1J_{CP}$=22 Hz; *C*H), 66.4 (s, *C*H-OH), 97.4 (s, =CH), 121.1 (s, *C*H$_{ar}$), 123.6 (s, *C*H$_{ar}$), 125.3 (d, J_{CP}=6 Hz, *C*H$_{ar}$), 138.1 (s, *C*H$_{ar}$), 154.3 (s, *C*$_{ar}$–C–O), 158.1 (dd, $^2J_{CP}$=28, 85 Hz; *C*$_{ar}$–Ni), 169.8 ppm (d, $^3J_{CP}$=14 Hz; *C*–O); IR (Nujol): $\tilde{\nu}$=3200 (OH), 1605 cm^{-1} (C=C).

Synthesis of [Ni{*o*-C$_6$H$_4$–C(=CHCHOHPh)O}(dippe)] (19b): Complex **8a** (160 mg, 0.36 mmol) was dissolved in THF (2 mL). PhCHO (0.37 mL, 3.6 mmol) was added at room temperature. After 10 min the solvent was removed under reduced pressure. An oily residue was obtained that was

washed twice with petroleum ether (20 mL), and then recrystallized from toluene/Et_2O to afford **19b** (112 mg, 55% yield) as yellow crystals. ^{1}H NMR (C_6D_6, 20°C): δ = 0.76 (m, 14H; 4CH_3 and 1CH_2), 1.01 (m, 2H; CH_2), 1.10 (m, 6H; CH_3), 1.34 (m, 6H; CH_3), 2.03 (m, 4H; CH), 5.48 (dd, $^5J_{HP}$ = 4.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; =CH), 6.91 (d, $^4J_{HH}$ = 3.4 Hz, 1H; OH), 7.10 (m, 4H; CH_{ar}), 7.28 (m, 3H; CH_{ar}), 7.48 (d, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 7.93 ppm(d, $^3J_{HH}$=7.9 Hz, 1H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): δ = 73.3 (A, AX spin system), 78.1 ppm (X, AX spin system, J_{AX} = 22 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): δ = 15.1 (dd, $^1J_{CP}$ = 21 Hz, $^2J_{CP}$ = 10 Hz; CH_2), 17.9 (s, CH_3), 18.0 (d, $^2J_{CP}$ = 4 Hz; CH_3), 18.1 (d, $^2J_{CP}$ = 5 Hz; CH_3), 18.3 (s, CH_3), 19.4 (d, $^2J_{CP}$ = 5 Hz; CH_3), 19.5 (d, $^2J_{CP}$ = 5 Hz; CH_3), 21.2 (s, CH_3), 21.3 (s, CH_3), 21.9 (dd, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 22 Hz; CH_2), 23.8 (d, $^1J_{CP}$ = 16 Hz; CH), 24.2 (d, $^1J_{CP}$ = 16 Hz; CH), 25.2 (d, $^1J_{CP}$ = 22 Hz; CH), 25.4 (d, $^1J_{CP}$ = 22 Hz; CH), 73.2 (s, CH–OH), 97.3 (s, =CH), 122.0 (s, CH_{ar}), 123.8 (s, CH_{ar}), 124.9 (d, J_{CP} = 7 Hz; CH_{ar}), 125.9 (s, CH_{ar}), 126.8 (s, C_{ar}H), 127.9 (s, C_{ar}H), 137.4 (m, C_{ar}H), 148.5 (s, C_{ar}), 155.1 (s, C_{ar}), 157.9 (dd, $^2J_{CP}$ = 28, 85 Hz; C_{ar}–Ni), 169.8 ppm (d, $^3J_{CP}$ = 14 Hz; C–O); IR (Nujol): $\tilde{\nu}$ = 3250 (OH), 1605 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{29}H_{44}P_2O_2Ni$: C 63.9, H 8.1; found: C 64.2, H 7.8.

Synthesis of O=C-*o*-C_6H_4C(=CHCHOHR)O (R=Me, 20a; R=Ph, 20b): CO was bubbled through a solution of **19a** (100 mg, 0.18 mmol) in THF (15 mL). After 5 min the initial light orange solution turned pale yellow. The solvent was evaporated under vacuum and the resulting oil was extracted with petroleum ether (30 mL) and filtered. Compound **20a** was separated from the complex [Ni(dippe)(CO)$_2$] by spinning band chromatography with Et_2O as eluent. Yield: 76 mg, 40%; ^{1}H NMR (C_6D_6, 20°C): δ = 1.26 (d, $^3J_{HH}$ = 6.4 Hz, 3H; CH_3), 3.89 (br s, 1H; OH), 4.94 (m, 1H; CH-OH), 5.35 (d, $^3J_{HH}$ = 8.3 Hz, 1H; =CH), 6.78 (t, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 6.90 (m, 2H; CH_{ar}), 7.53 ppm (d, $^3J_{HH}$ = 7.5 Hz, 1H; CH_{ar}); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): δ = 23.7 (s, CH_3), 63.04 (s, CH–OH), 112.6 (s, =CH), 120.2 (s, CH_{ar}), 125.1 (s, C_{ar}-C=O), 125.4 (s, CH_{ar}), 129.9 (s, CH_{ar}), 134.0 (s, CH_{ar}), 139.7 (s, C_{ar}–C–O), 144.8 (s, C–O), 166.2 ppm (s, C=O); IR (Nujol): $\tilde{\nu}$ = 3250 (OH), 1785 (O–C=O), 1690 cm^{-1} (C=C); HR EIMS: *m*/*z* calcd for $C_{10}H_8O_2$: 190.0630; found: 190.0631.

Compound **20b** was prepared in a similar way. A 3:2 mixture of Et_2O/petroleum ether was used as eluent. (45% yield). ^{1}H NMR (C_6D_6, 20°C): δ = 4.42 (s, 1H; OH), 5.60 (d, $^3J_{HH}$ = 9.0 Hz, 1H; =CH), 6.02 (d, $^3J_{HH}$ = 9.0 Hz, 1H; CHOH), 6.75 (m, 1H; CH_{ar}), 6.76 (d, $^3J_{HH}$ = 6.9 Hz, 1H; CH_{ar}), 6.85 (t, $^3J_{HH}$ = 7.5 Hz, 1H; CH_{ar}), 7.06 (t, $^3J_{HH}$ = 7.1 Hz, 1H; CH_{ar}), 7.18 (t, $^3J_{HH}$ = 7.4 Hz, 2H; CH_{ar}), 7.50 (d, $^3J_{HH}$ = 7.8 Hz, 1H; CH_{ar}), 7.55 ppm (d, $^3J_{HH}$ = 7.5 Hz, 2H; CH_{ar}); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): δ = 68.1 (s, CH–OH), 110.9 (s, =CH), 119.9 (s, CH_{ar}), 124.7 (s, C_{ar}–C=O), 124.9 (s, CH_{ar}), 126.0 (s, CH_{ar}), 128.0 (s, CH_{ar}), 128.4 (s, CH_{ar}), 129.4 (s, CH_{ar}), 133.5 (s, CH_{ar}), 139.1 (s, C_{ar}–C–O), 143.5 (s, C_{ar}), 144.8 (s, C–O), 165.8 ppm (s, C=O); IR (Nujol): $\tilde{\nu}$ = 3330 (OH), 1785 (O–C=O), 1685 cm^{-1} (C=C); HR EIMS: *m*/*z* calcd for $C_{16}H_{12}O_3$: 252.0786; found: 252.0780.

Synthesis of binuclear complex 21

Method a: Enolate **8a** (160 mg, 0.36 mmol) was disso1ved in THF (2 mL). Freshly distilled $C_6H_5C(O)H$ (0.37 mL, 3.6 mmol) was added to this solution at −78°C. The mixture was stirred for 48 h at room temperature, after which time the solvent was removed under reduced pressure. The residue was washed twice with petroleum ether (20 mL) and then recrystallized from Et_2O to afford **21** as yellow crystals.

Method b: A solution of complex **19b** (100 mg, 0.18 mmol) in THF (2 mL) was stirred for 48 h to effect dimerization to **21** in quantitative yield. ^{1}H NMR (C_6D_6, 20°C): δ = −0.81 (m, 16H; 4CH_3, 2CH_2), 0.88 (m, 4H; CH_2), 0.96 (m, 12H; CH_3), 1.18 (m, 12H; CH_3), 1.38 (m, 12H; CH_3), 1.94 (m, 2H; CH), 2.04 (m, 6H; CH), 5.56 (d, $^3J_{HH}$ = 6.8 Hz, 1H; CH), 5.65 (t, $^3J_{HH}$ = 7.2 Hz, 2H; =CH), 7.05 (t, $^3J_{HH}$ = 7.4 Hz, 1H; CH_{ar}), 7.11 (m, 4H; CH_{ar}), 7.31 (t, $^3J_{HH}$ = 7.4 Hz, 2H; CH_{ar}), 7.37 (s, 2H; CH_{ar}), 7.65 (s, 2H; CH_{ar}), 7.92 ppm (d, $^3J_{HH}$ = 7.5 Hz, 2H; CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C): δ = 73.7 (A, AX spin system), 77.2 ppm (X, AX spin system, J_{AX} = 23 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): δ = 15.7 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 10 Hz; CH_2), 18.1 (s, CH_3), 18.2 (s, CH_3), 18.7 (s, CH_3), 19.6 (d, $^2J_{CP}$ = 4 Hz; CH_3), 20.2 (d, $^2J_{CP}$ = 5 Hz; CH_3), 21.3 (s, CH_3), 22.8 (t, J_{CP} = 24 Hz; CH_2), 23.5 (d, $^1J_{CP}$ = 17 Hz; CH), 24.2 (d, $^1J_{CP}$ = 17 Hz; CH), 25.3 (d, $^1J_{CP}$ = 21 Hz; CH), 25.4 (d, $^1J_{CP}$ = 21 Hz; CH), 39.8 (s, CH), 100.3 (s, =CH), 121.9 (s, CH_{ar}), 122.8 (s, CH_{ar}), 123.3 (s, CH_{ar}), 123.5 (d, J_{CP} = 7 Hz; CH_{ar}), 127.1 (s, CH_{ar}), 129.2 (s, CH_{ar}), 137.6 (s, CH_{ar}), 152.5 (s, C_{ar}), 157.4 (s, C_{ar}), 159.0 (dd, $^2J_{CP}$ = 88, 26 Hz; C_{ar}–Ni), 167.6 ppm (d, $^3J_{CP}$ = 15 Hz; C–O); IR (Nujol): $\tilde{\nu}$ = 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{51}H_{80}P_4O_2Ni_2$: C 63.4, H 8.3; found: C 62.9, H 8.5.

Synthesis of [O=C-*o*-C_6H_4C(=CH−)O)]$_2$CHPh (22): This compound was prepared by the procedure given for **18a**, starting from complex **21** and using a 3:1 mixture of petroleum ether/Et_2O as eluent. Yield: 45%. ^{1}H NMR (C_6D_6, 20°C): δ = 5.63 (t, $^3J_{HH}$ = 9.7 Hz, 1H; Ph-CH), 6.01 (d, $^3J_{HH}$ = 9.7 Hz, 2H; =CH), 7.29 (t, $^3J_{HH}$ = 7.3 Hz, 1H; CH_{ar}), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 2H; CH_{ar}), 7.48 (d, $^3J_{HH}$ = 7.7 Hz, 2H; CH_{ar}), 7.58 (m, 2H; CH_{ar}), 7.74 (m, 4H; CH_{ar}), 7.91 ppm (d, $^3J_{HH}$ = 7.6 Hz, 2H; CH_{ar}); ^{13}C{^{1}H} NMR (C_6D_6, 20°C): δ = 39.3 (s, Ph–CH), 108.5 (s, =CH), 120.4 (s, CH_{ar}), 125.0 (s, C_{ar}–C=O), 125.6 (s, CH_{ar}), 127.4 (s, CH_{ar}), 127.9 (s, CH_{ar}), 129.3 (s, CH_{ar}), 130.4 (s, CH_{ar}), 134.8 (s, CH_{ar}), 139.7 (s, C_{ar}), 142.1 (s, C_{ar}–C–O), 146.2 (s, =C–O), 166.7 ppm (s, C=O); IR (Nujol): $\tilde{\nu}$ = 1775 (O–C=O), 1695 cm^{-1} (C=C); HREIMS: *m*/*z* calcd for $C_{25}H_{16}O_4$: 380.1049; found: 380.1045.

Computational details: All calculations were performed using the package Spartan Pro.[25] Initial guess of the molecular geometry was obtained with the semiempirical PM3 method, and the resulting structures were fully optimized without restrictions with DFT methods, using the BP86 functional and the numerical basis set DN*, which includes *d*-type polarization functions for all non-hydrogen atoms. The gradient correction was included in a perturbative manner only after convergence on a local potential was achieved (pBP method). The geometry of the minima and saddle-points of the potential surface were checked with a frequency calculation, only for the more simple models with H substituents on the phosphine ligand. For the calculation of the geometry of "real" molecules containing isopropyl substituents, a guess model of the molecular geometry was built starting from result of a previous calculation on the simplified molecules, and those were subjected to a molecular mechanics conformational analysis (MMFF, Merck Molecular Force Field), while maintaining fixed the positions of the core atoms. The geometries of the five most stable conformers were subjected to full optimization without restraints by using the DFT method, and the lower computed energies were used in the thermochemical and activation barrier calculations.

X-ray structure determination of 8b and 15: A summary of the fundamental crystal and refinement data are given in Table 1 in the Supporting Information. CCDC-273534 (**8b**) and CCDC 273533 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 8b: The intensity data of compounds **8b** were collected at 173 K on a ENRAF Nonius CAD4 single-crystal diffractometer equipped with a fine-focus sealed tube graphite monochromated radiation source (radiation type $Cu_{K\alpha}$, λ = 1.54180 Å), using a $\theta/2\theta$ scan method. To determine the cell parameters 24 reflections between 24 and 35° were used; one standard reflection every 100 counts was measured to monitor crystal decay.

The structure was solved by Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2)[26] with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The data were corrected empirically[27] by absorption effect. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2 F_o^2 + (0.0891P)^2 + 4.4001P]$, in which $P = (F_o^2 + 2F_c^2)/3$, was used.

Compound 15: A crystal with well-defined faces was coated with a polyfluoroether oil coated and cooled at 173 K. It was mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected by a combination of two frame sets covering more than a hemisphere of the reciprocal space. The cell parameters were determined and refined by a least-squares fit of all reflection collected. Each frame exposure time was of 20 s covering 0.3° in ω. The crystal to detector distance was 5.02 cm. Coverage of the unique set was over 94% complete to at least 30° in θ. The first 50

frames were recollected at the end of the data collection to monitor crystal decay. A multiscan absorption correction (SADABS[26]) was applied. The structure was solved by Multan and Fourier methods using SHELXS.[26] Full-matrix least-square refinement was carried out using SHELXTL[26] minimizing $w(F_o^2-F_c^2)^2$. Weighted R factors (Rw) and all goodness-of-fit (S) values are based on F^2, conventional R factors (R) are based on F.

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[17] As observed for the PMe_3 derivatives **3** and **4**, the frequency of the ν(C=O) band of the acetyl group of **6a–c** is about 70 cm^{-1} lower than in the corresponding organic precursors, suggesting the existence of a Ni···O interaction in these molecules. However, if this interaction exists, it must be weak, as ^1H and ^{13}C NMR spectra of the these compounds indicate free rotation of the aryl group relative to the Ni–C bond.

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