Organometallic Nickelamacrocycles of the Type $[(R_2R'P)Ni(C_2H_4COO)]_n$: Synthesis and Self-Assembly to Form Different Molecular Architectures Tuned by the Phosphine

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The reaction of succinic anhydride with a 1:2 mixture of $(cod)_2Ni$ and a monodentate phosphine generates reactive monomeric nickelalactones, which undergo rapid aggregation to form cyclic oligomers of the composition $[(R_2R'P)Ni(C_2H_4COO)]_n$ ($R_2R'P = EtPh_2P$ (**2**), Me_3P (**4**), $(i\text{-Pr})_3P$ (**5**), Cy_3P (**6**), Et_3P (**7**)). The complexes were fully characterized by elemental analyses (except **4**), NMR and IR spectroscopy, and X-ray crystallography of single crystals. Depending on the bulkiness of the phosphines, three types of nickelamacrocycles with different ring size and different connectivity pattern of the monomeric units are formed. The small Me_3P stabilizes a cyclic tetramer ($n = 4$) in which the units are linked by Ni−O−Ni bonds. This bridge is stable in thf solution. The bulkiest phosphines stabilize another type of cyclotetrameric architecture in **2**, **5**, and **6**, in which the monomeric units are connected by Ni−O−C═O bridges. In contrast, **7**, stabilized by the Et_3P ligand, forms a hexacyclic compound ($n = 6$) with Ni−O−C═O bridges. The IR spectrum of **7** in thf shows two C═O valence frequencies, indicating that at least two species are present in which the carboxylate group is differently coordinated (Ni−O and Ni−O−C═O−Ni coordination).

Introduction

The construction of well-defined supramolecular organometallics of transition metals by self-assembly of reactive monomers is a great challenge in modern organometallic chemistry. Although the formation of supramolecules may dramatically influence the reactivity of organometallics, self-assembly processes of organometallics are not well understood.[1−7]

In previous works we have shown that the composition, structures, and reactivities of alkynol- and alkynediol-nickel(0) complexes depend on the hydrogen-bonded network formed.[8−12] Furthermore, we recently reported the reaction of CO_2 and Schiff bases with $(cod)_2Ni$, resulting in dimeric or cyclic hexameric nickela-azacarboxylates, the structure of which was remarkably influenced by the solvent and the azomethines used for these reactions.[13]

In connection with these surprising results the question arises if compounds of the composition $[(L)_nNi(C_2H_4COO)]$ containing the synthetically valuable nickelalactone fragment can be used for the rational design of supramolecular architectures. Generally, nickelalactones of this type are rather stable monomeric compounds if two ligands L are coordinated or if L is a bidentate chelating ligand. Their preparation is easily possible by different approaches,[14−19] their chemistry is well-investigated,[20−22] and their use as stoichiometric reagents for the synthesis of carboxylic acid derivatives

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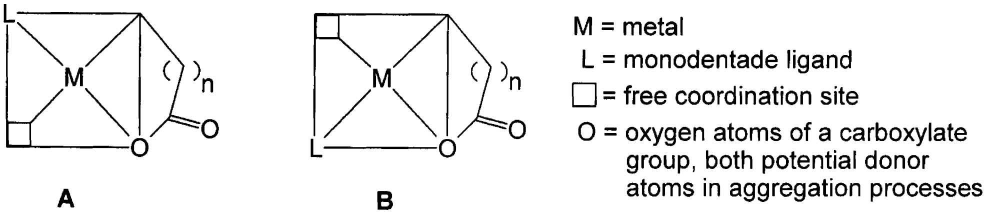
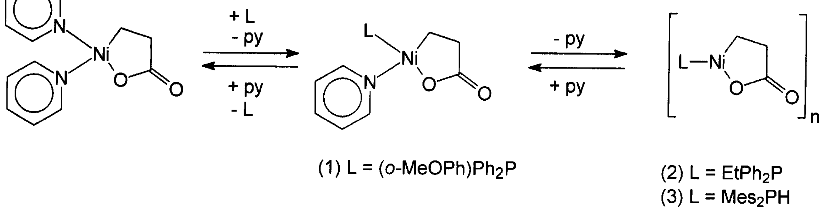
Scheme 1. Two Possible Monomeric Regioisomers "$[(L)Ni(C_2H_4COO)]$"



Scheme 2



offers interesting alternatives to conventional organic synthesis.[18,19,23−25] For example, they were found to be useful reagents for introducing functionalized side chains into steroids[26,27] and for the formation of 3-(arylmercapto)propionic acids.[28]

In contrast to this well-investigated field, the chemistry of nickelalactones containing only one monodentate ligand ($n = 1$) is still underdeveloped. Yamamoto et al. reported so far the only isolated example of such a compound, an oligomeric or polymeric complex of unknown structure containing a Cy_3P ligand per Ni.[15] Furthermore, a related nickelacyclic amide stabilized by Et_3P with a tetrameric structure was also synthesized.[29] In this connection it is interesting to note that a tetrameric palladacyclic carboxylate with Ph_3P as stabilizing ligand is also known.[30]

We describe here a number of new nickelalactones "$[(R_2R'P)Ni(C_2H_4COO)]$" and show that these easily accessible compounds can undergo selective supramolecular aggregation resulting in nickelamacrocycles with different ring size and different connectivity pattern. The molecular architectures of these nickelamacrocycles can be rationalized with respect to the steric properties of the phosphine ligands.

Results and Discussion

Synthesis of the Nickelamacrocycles. Our strategy was to generate reactive monomeric complexes of the type "$[(L)Ni(C_2H_4COO)]$" in a first step which would be able to undergo fast aggregation to form supramolecular compounds by self-assembly. Tuning this reaction is a synthetic challenge, as typical organometallic decomposition pathways such as β-hydride elimination or the reductive decoupling of the organic moiety are expected to be competitive reactions. Furthermore, monomeric species of the above composition may, in principle, exist in two regioisomeric forms, **A** and **B**, which are different in the arrangement of the monodentate ligand (Scheme 1). Whereas **B** tends to produce polymers rather than macrocyclic species by aggregation processes, the isomer **A** is expected to give highly ordered, regularly repeating molecular architectures, e.g., cyclic oligomers.

To examine which monodentate ligands L stabilize **A** rather than **B**, we investigated the reaction of different ligands L with the monomeric complex $[(py)_2Ni(C_2H_4COO)]$. We found that phosphines $R_2R'P$ are suitable ligands for stabilizing **A**. For example, the reaction with $(o\text{-MeOPh})Ph_2P$ resulted in the formation of mixed ligand complex $[(o\text{-MeOPh})Ph_2P)(py)Ni(C_2H_4COO)]$ (**1**) according to Scheme 2.

The isolated yellow crystalline compound **1** was characterized by elemental analysis and NMR measurements. Furthermore, its solid-state structure was elucidated by X-ray crystallography of single crystals. Figure 1 displays the molecular structure, which shows that the phosphine is indeed in *trans* position to the oxygen atom of the carboxylate group. As expected, the metal is in a square-planar environment and the bond lengths and angles, listed in the caption, fall within usual values. NMR measurements in thf-d_8 gave no evidence for the presence of isomer **B** in solution on the NMR scale. To the best of our knowledge, **1** is the first isolated example of a nickelactone bearing two different monodentate ligands.

$EtPh_2P$ reacted with $[(py)_2Ni(C_2H_4COO)]$ under substitution of both pyridine ligands, resulting in the formation of the compound $[(EtPh_2P)Ni(C_2H_4COO)]_4$ (**2**), and Mes_2PH reacts analogously to form $[(Mes_2PH)Ni(C_2H_4COO)]_4$ (**3**). The X-ray structures of both componds will be discussed below.

Having established this reaction for generating some suitable complexes for investigation of aggregation reactions, we turned our attention to a more general synthesis. We found that the reaction of succinic anhy-

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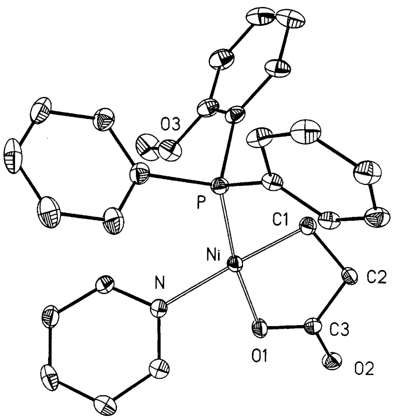
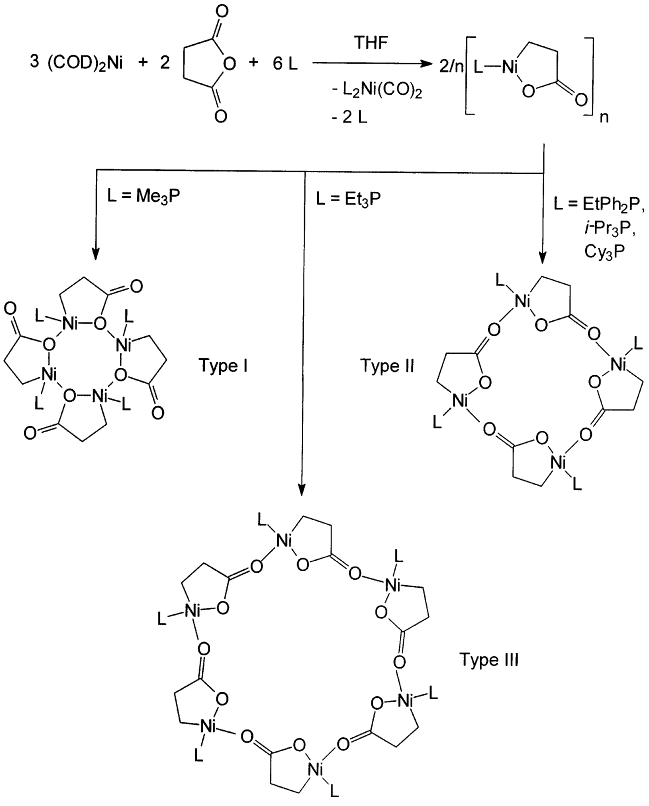


Figure 1. ORTEP drawing of complex **1** (50% probability level, H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg): Ni−O1 1.899(3), Ni−C1 1.939(5), Ni−N 1.950(4), Ni−P 2.1323(13), O1−C3 1.295(6), O2−C3 1.236(6), C1−C2 1.518(7), C2−C3 1.522(6), N−Ni−P 99.77(13), N−Ni−O1 87.35(16), P−Ni−C1 88.00(15), C1−Ni−O1 85.35(17).

Scheme 3. Tuning the Type of Nickelmacrocycles by Monodentate Phosphines



dride with (cod)$_2$Ni in the presence of a monodentate phosphine in thf using a modified method developed by Uhlig et al.[14] is a simple way for synthesizing a great number of complexes of the type [(R$_2$R′P)Ni(C$_2$H$_4$-COO)]$_n$. Scheme 3 shows that three different types of nickelamacrocycles were found to be formed by self-assembly of the monomeric compounds "[(R$_2$R′P)Ni(C$_2$H$_4$-COO)]". Size and connectivity patterns of these cyclic compounds are affected by the nature of the phosphines.

Structures of the Nickelamacrocycles. With L = Me$_3$P complex **4** is generated in good yield (78%). Its ^{1}H NMR spectrum (in toluene-d_8) exhibits a doublet for the CH$_3$ groups at $\delta = 1.10$ ppm and a multiplet for the Ni-CH$_2$ group at $\delta = 0.09$ ppm. The H atoms of the second CH$_2$ group are magnetically unequal, so for each H atom a separate multiplet at 1.92 and 2.47 ppm was observed, suggesting the formation of an oligomeric assembly. Only one ^{31}P signal at −3.5 ppm in benzene-d_6 was observed, confirming the symmetrical structure of the complex. The C=O stretching frequency at 1646 cm^{-1} in Nujol suspension is comparable with those of complexes where the COO group is coordinated only via the C−O group.[14,16] This assumption is confirmed by X-ray diffraction analysis of a single crystal, grown from toluene. Figure 2 shows that **4** forms a tetrameric nickelamacrocycle in the solid state, containing an inner eight-membered Ni$_4$O$_4$ ring. The square-planar coordination sphere of each nickel center is formed by a phosphorus atom, one oxygen atom of the COO group, a carbon atom of the cyclic propionate, and the endocyclic oxygen atom of the neighboring nickelacyclic unit. The bond lengths and angles, listed in the caption, lie in the range of typical values and therefore need no further discussion.

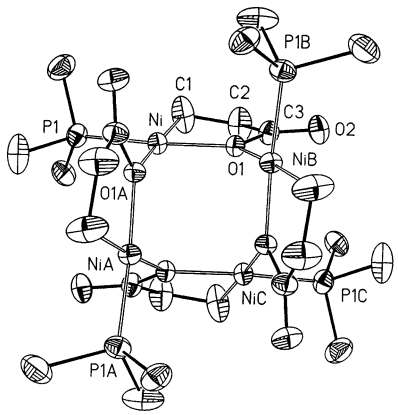


Figure 2. ORTEP drawing of complex **4** (50% probability level, H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg): Ni−O1 1.926(3), Ni−C1 1.913(5), Ni−P1 2.1216(12), Ni−O1A 1.974(3), O1−C3 1.310(5), O2−C3 1.218(5), C1−C2 1.469(8), C2−C3 1.485(6), Ni···NiC 3.781(2), P1···P1A 6.157(2), P1−Ni−O1A 96.34(8), O1−Ni−O1A 89.29(11), P1−Ni−C1 88.45(16), C1−Ni−O1 85.85(17). Symmetry transformations used to generate equivalent atoms: #A $z-1/2$, $-y+1/2$, $x+1/2$.

If EtPh$_2$P is used as supporting ligand, another type of cyclic oligomers is generated. This is indicated by a strongly shifted C=O stretching frequency at 1558 cm^{-1} of the isolated compound **2**, suggesting the coordination of the C=O group. The molecular structure of **2**, determined by X-ray diffraction analysis of single crystals, shows a tetrameric complex with a pattern of connection that is different from that of **4** (Figure 3, Scheme 3).

In contrast to **4**, in compound **2** the fourth donor atom of the square-planar coordinated nickel is not the endocyclic but the exocyclic oxygen atom of the neighboring nickelalactone unit. This results in the formation of a larger, 16-membered macrocycle containing the inner unit [−Ni−O−C−O−]$_4$ (type II in Scheme 3). A noteworthy feature of the macrocycles of type II is seen in a view of the lattice along the *c* axis in Figure 4, which shows (for **2** as an example) that the packing results in the formation of channels.

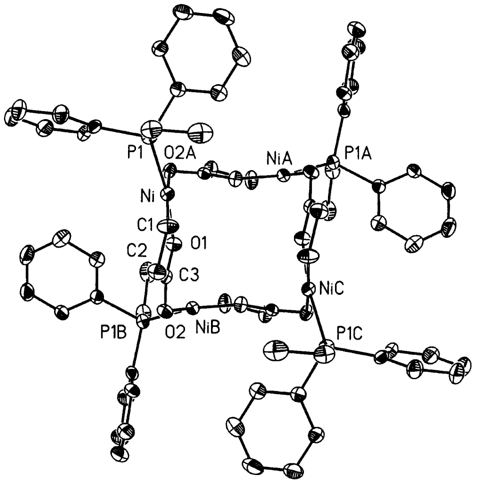


Figure 3. ORTEP drawing of complex **2** (50% probability level, H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg): Ni−O1 1.891(3), Ni−C1 1.912(4), Ni−P1 2.1237(11), Ni−O2A 1.979(3), O1−C3 1.269(4), O2−C3 1.261(4), C1−C2 1.519(5), C2−C3 1.495(5), Ni···NiC 5.488(2), P1···P1A 7.728(2), P1−Ni−O2A 95.66(8), O1−Ni−O2A 85.39(11), P1−Ni−C1 93.59(12), C1−Ni−O1 85.48(15). Symmetry transformations used to generate equivalent atoms: #A y, $-x+1$, $-z$.

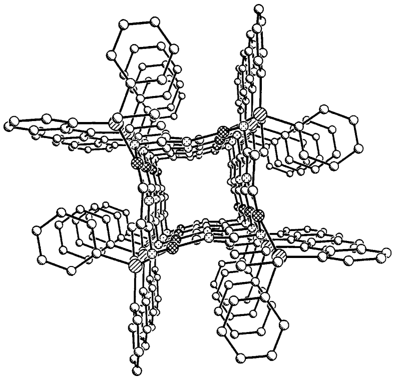


Figure 4. Part of the crystal structure of **2** (view along *c* axis; H atoms are omitted for clarity).

The same type of complex was generated when i-Pr_3P was used as ligand, resulting in complex **5**. Due to the highly disordered isopropyl groups in **5**, only the structure motif (not depicted) was obtained by X-ray crystallography (see Experimental Section). Complex **3** (L = Mes_2PH), which was accessible in pure form only by ligand exchange starting from $[(py)_2Ni(C_2H_4COO)]$ (Scheme 2), stabilizes a cyclic tetramer of the type II as well, according to the X-ray analysis of single crystals (not depicted).

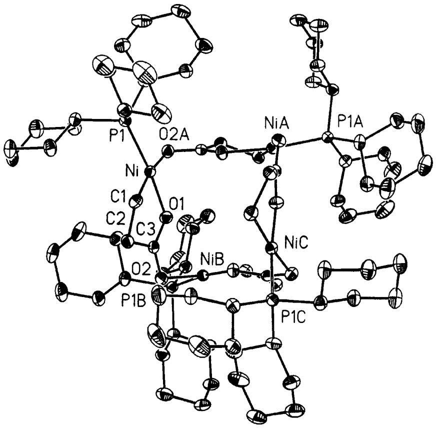


Figure 5. ORTEP drawing of complex **6** (50% probability level, H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg): Ni−O1 1.902(3), Ni−C1 1.933(4), Ni−P1 2.1454(11), Ni−O2A 1.987(3), O1−C3 1.270(5), O2−C3 1.248(5), C1−C2 1.533(6), C2−C3 1.509(5), Ni···NiC 5.416(2), P1···P1A 7.717(2), P1−Ni−O2A 95.59(9), O1−Ni−O2A 85.40(12), P1−Ni−C1 94.50(12), C1−Ni−O1 84.57(15). Symmetry transformations used to generate equivalent atoms: #A y, $-x+1$, $-z$.

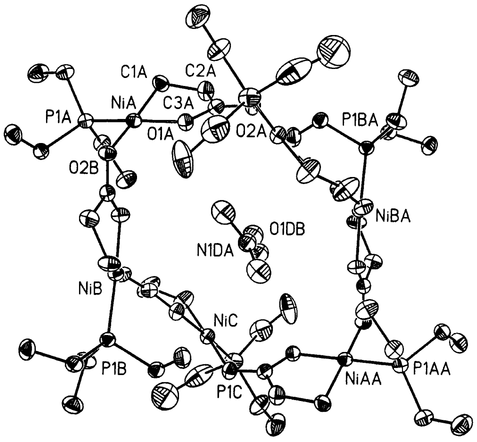


Figure 6. ORTEP drawing of complex **7**·DMF (50% probability level, only one of two independent hexamers shown, H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg): NiA−O1A 1.925(3), NiA−C1A 1.914(5), NiA-P1A 2.1207(15), NiA-O2B 1.943(3), O1A−C3A 1.274(6), O2A−C3A 1.246(6), C1A−C2A 1.522(7), C2A−C3A 1.512(7), NiA···NiAA 10.559(2), NiB···NiBA 8.560(2), NiC···NiCA 8.708(2), P1A···P1B 7.517(2), P1A···P1CA 7.380(2), P1B···P1C 6.914(2), P1A−NiA−O2B 98.57(11), O1A−NiA−O2B 88.48(14), P1A−NiA−C1A 88.09(16), C1A−NiA−O1A 85.87(19).

A nickelalactone with Cy_3P as supporting ligand was already prepared by Yamamoto et al.[15] through an oxidative addition/insertion sequence of acrylic acid on a Cy_3P-stabilized Ni(0) center. Its structure in the solid state was so far not determined. Starting from succinic anhydride and $(cod)_2Ni$, we could obtain single crystals of $[(Cy_3P)Ni(C_2H_4COO)]_4$ (**6**) directly from the reaction mixture. In the infrared spectrum of compound **6** the C=O stretching frequency was observed at 1567 cm^{-1}, comparable with that reported in the literature for $[(Cy_3P)Ni(C_2H_4COO)]_n$ (1570 cm^{-1}), so it seems that those two compounds are actually the same. X-ray crystallography of single crystals (Figure 5) shows that **6** has the same cyclic tetrameric structure as found for **2**, **3**, and **5**.

The third type of nickelamacrocycle was formed when Et_3P was used as supporting ligand (Scheme 3). In the resulting compound **7**, the C=O stretching frequency is also strongly shifted to 1563 cm^{-1}, indicating that the exocyclic oxygen of the carboxylate function should act as donor ligand for an adjacent nickel center, similarly to the tetrameric compounds **2**, **3**, **5**, and **6**. However, the molecular structure determined by X-ray crystallography of single crystals shows a very different architecture (Figure 6). In **7** six monomeric units are connected via a Ni−O−C=O−Ni coordination mode, yielding a cyclic hexameric compound that contains a 24-membered macrocycle of the type [−Ni−O−C−

Table 1. Electronic and Steric Properties of the Phosphines and the Structures of the Metallacycles

ligand	Me$_3$P	Et$_3$P	Mes$_2$PH	EtPh$_2$P	*i*-Pr$_3$P	Cy$_3$P
cone angle θ^{31} [deg]	118	132		140	160	170
cone angle θ (determ) [deg]	123	162[a]	161[b]	173		178
$\Sigma\chi_i{}^{31}$	7.8	5.4	13.7	10.4	3.0	0.3
metallamacrocycle	tetramer **4** type I	hexamer **7** type III	tetramer **3** type II	tetramer **2** type II	tetramer **5** type II	tetramer **6** type II

[a] Average cone angle (6 independent monomeric units). [b] Average cone angle (4 independent monomeric units).

Table 2. C=O Stretching Frequencies in Solid State and Solution

compound	ν(C=O) [cm^{-1}] (Nujol mull)	ν(C=O) [cm^{-1}] (toluene)	ν(C=O) [cm^{-1}] (thf)
[(Me$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (**4**)	1646	1657	1659
[(Et$_3$P)Ni(C$_2$H$_4$COO)]$_6$·ether (**7a**)	1563	1677 + 1572	1679 + 1572
[(*i*-Pr$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (**5**)	1570	1572	1573

O−]$_6$. In the inner part of the nickelamacrocycle one solvent molecule is embedded (dmf or ether depending on the solvents used for the crystallization of single crystals). It seems that those solvent molecules act as templates for the formation of a cyclic hexameric structure.

Influence of the Phosphine on the Molecular Architecture of the Nickelamacrocycles. To obtain further information about the influence of the phosphines on the structures of the cyclic oligomers, we determined whether electronic or steric properties of the ligands decide which types of nickelamacrocycles are built up by self-assembly of the monomeric units.

An easy way to describe these properties of the phosphines is the comparison of their electronic and steric parameters χ_i and θ, introduced by Tolman[31] (Table 1). For the steric parameter θ, however, not only the published values were used but also the cone angle of the phosphines extracted from the X-ray crystal structures of the nickelamacrocycles. Details of the calculation are described in the Experimental Section. The results are summarized in Table 1.

Table 1 clearly shows that the electronic properties of the phosphines have no effect on the type of oligomers formed. Cy$_3$P, the ligand with the lowest value for $\Sigma\chi_i$, and Mes$_2$PH, the phosphine with the highest value for $\Sigma\chi_i$, stabilize the same type of macrocycle. On the other hand, there is a remarkable influence of the steric effect on the molecular architecture. Nickelalactones with small ligands (Me$_3$P) form the smallest metallacycle containing [−Ni−O−Ni−] bridges in the Ni$_4$O$_4$ eight-membered ring of the tetramer (Ni···NiC 3.781(2) Å). The distance between two neighboring phosphorus atoms (P1···P1A) in **3** is approximately 6.2 Å. In contrast, phosphines with large cone angles can stabilize macrocycles only with the larger 16-membered ring containing [−Ni−O−C=O−] bridges (**2**: Ni···NiC 5.488(2) Å; **6**: Ni···NiC 5.416(2) Å). In these complexes of type II the P1···P1A distances are approximately 7.7 Å.

The effect of Et$_3$P on the macrocyclic structure is of particular interest for understanding the aggregation reactions. Since Et$_3$P is larger than Me$_3$P, it is not suitable for stabilizing the type I macrocycle. On the other hand, the steric demand of Et$_3$P is smaller than that of the other phosphines used in this study. Therefore, Et$_3$P is able to generate a third type of nickelamacrocycles, a hexameric derivative in which the average P···P′ distance of about 7.2 Å is longer than in the type I complex but shorter than in the type II complexes. From these results it can be concluded that it is possible to predict the structure of the cyclic oligomers from the minimum cone angle (as defined by Tolman) of the used phosphine, if there are internal degrees of freedom. The cone angles, extracted from the molecular structure of the complexes, are larger but show, in principle, the same order of the ligands. It seems, for highly unsymmetrical ligands such as Mes$_2$PH, that the cone angle is only a coarse tool for describing their steric properties.

Behavior of the Macrocyclic Nickelalactones in Solution. Whether the isolated nickelamacrocycles are stable in solution or undergo rearrangement reactions to form other oligomers or solvent-stabilized monomers is an open question. Most of the nickelamacrocycles are soluble in solvents such as thf, dmf, and toluene (except **6**), however only sparingly soluble in *n*-pentane. Therefore, it was possible to crystallize some complexes from different solvents. For example, crystals of compound **5** (L = *i*-Pr$_3$P) were obtained from toluene as well as from thf; however independently from the nature of the solvent the same cyclic tetramer was formed. Similarly, as mentioned above, single crystals of [(Et$_3$P)Ni(C$_2$H$_4$COO)]$_6$·solvent **7** of the same molecular architecture can be prepared with both ether and dmf.

To examine the behavior of the complexes directly in solution, we investigated the C=O stretching frequencies of compounds of each type in two solvents of different polarity (toluene und thf) and compared these values with ν_{CO} of the compounds in the solid state (Table 2).

Table 2 reveals that there is only a little shift of ν_{CO} in **4** when the solid compound is dissolved in thf or toluene, indicating that the connectivity pattern remains stable in solution. As mentioned above, the NMR spectra give evidence for the presence of only one isomer in solution. Therefore, we can conclude that the structure found in the solid state is present in these solutions as well. A representative of the type III compounds [(*i*-Pr$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (**5**) shows the same behavior (Table 1). The C=O valence frequency of solutions lies in the same range as ν_{CO} of the solid state. This suggests that only one isomer is present in both thf and toluene solutions, having the same Ni−OCO−Ni bridges as found in the crystalline compound.

In contrast, the nickelamacrocycle **7** (the compound of type III) behaves differently. When this cyclic hexamer was dissolved in thf or toluene, two C=O frequencies of approximately the same intensity (1677, 1572

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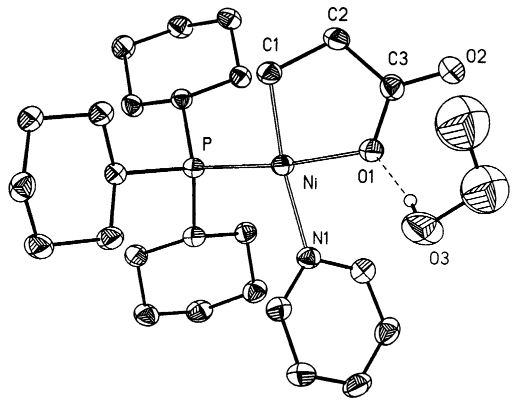

Figure 7. ORTEP drawing of complex **8** (50% probability level, uncoordinated pyridine and H atoms, except the one bond to O3, are omitted for clarity). Selected bond distances (Å) and bond angles (deg): Ni−O1 1.9185(19), Ni−C1 1.927(3), Ni−P 2.1747(7), Ni−N1 1.994(2), O1−C3 1.314(3), O2−C3 1.219(3), C1−C2 1.521(4), C2−C3 1.506(4), O1···O3 2.732(2), P−Ni−N1 100.47(6), O1−Ni−N1 85.27(9), P−Ni−C1 92.05(8), C1−Ni−O1 83.75(10).

cm^{-1} in thf; 1679, 1572 cm^{-1} in toluene) were observed (Table 1). This shows that at least two species with differently coordinated carboxylate groups do exist in solution. This suggestion is underlined by two different ^{31}P signals (26.5 (s) and 27.3 (br) ppm) for this nickelacycle in thf-d_8 in the ^{31}P NMR spectrum. From these data, however, it cannot be concluded which oligomers may be formed in solution. In contrast, only one ^{31}P signal at 28.7 (s) ppm was found, when dmf-d_7 was used as solvent for **7**. It is also noteworthy that attempts to crystallize other than the cyclic hexamer were unsuccessful so far.

In addition, solvents with strong ligand properties such as pyridine are able to split the Ni−O−C=O−Ni bridges, resulting in the formation of monomeric compounds. For example, complex $[(Cy_3P)Ni(C_2H_4COO)]_4$ (**6**), which is insoluble in most organic solvents, readily dissolves in pyridine. From a saturated solution of **6** in pyridine golden single crystals of the monomeric complex $[(Cy_3P)(py)Ni(C_2H_4COO)\cdots EtOH]\cdot 0.5$ py (**8**) can be isolated upon addition of a small amount of EtOH. Figure 7 reveals the molecular structure, which was elucidated by X-ray crystallography, and lists selected bond lengths and angles. The arrangement around the nickel atom is essentially the same as in complex **1**, but the larger cone angle of Cy_3P results in stronger distortion of the square-planar geometry (P−Ni−N = 100.47(6)°). The alcohol forms a hydrogen bond to the endocyclic oxygen of the carboxylate function.

Concluding Remarks

In conclusion, we have shown that a variety of supramolecular nickelamacrocycles are easily accessible either by reaction of succinic anhydride with a 2:1 mixture of a monodentate phosphine and $(cod)_2Ni$ or by displacement of two pyridines in $[(py)_2Ni(C_2H_4COO)]$ by one monodentate phosphine. The metallamacrocycles form three different types of molecular architectures controlled by steric effects of the phosphines. In thf or toluene solution, the cyclic oligomers are stable, except the cyclic hexamer **7**.

Experimental Section

General Considerations. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AC 200 or AC 400 MHz spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard. IR measurements were carried out on a Perkin-Elmer System 2000 FT-IR.

All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofuran, toluene, and diethyl ether were dried over potassium hydroxide and distilled over Na/benzophenone. Dmf and pyridine were distilled over CaH_2. $[(py)_2Ni(C_2H_4COO)]$ and $(cod)_2Ni$ were prepared according to literature procedures.[28,32]

Synthesis of $[(o\text{-MeOPhPh}_2P)(py)Ni(C_2H_4COO)]\cdot thf$ (1). A mixture of $[(py)_2Ni(C_2H_4COO)]$ (0.75 g, 2.60 mmol) and $EtPh_2P$ (0.76 g, 2.60 mmol) in dmf (15 mL) was stirred for 1 h at rt. The solution was filtered to remove impurities, and the solvent was slowly distilled of at rt under reduced pressure. The resulting sticky oil was dissolved in thf (15 mL) and kept at −20 °C for 2 days. The formed, yellow product was collected by filtration and dried in a vacuum. Yield: 0.91 g (61%). $C_{31}H_{34}PNNiO_4$ (574.28) calcd: C 64.84, H 5.97, N 2.44. Found: C 64.80, H 5.96, N 2.31. IR (Nujol, cm^{-1}): ν(C=O) 1628 (s). ^1H NMR (200 MHz, dmso-d_6, 25 °C): δ −0.07 (m, 2H, Ni-CH_2), 1.70−1.80 (m, 2H + 4H, CH_2COO + CH_2 thf), 3.59 (t, 4H, CH_2 thf), 3.87 (s, 3H, CH_3), 6.85−7.75 (m, 15H, CH Phenyl + py), 8.46 (br, 2H, CH py) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, dmso-d_6, 25 °C): δ 5.0 (Ni-CH_2), 25.0 (2 × CH_2 thf), 38.3 (CH_2COO), 55.9 (CH_3), 66.9 (2 × CH_2 thf), 111.8 (CH), 118.0 (d, $^1J_{C,P}$ = 44.9 Hz, *i*-C), 120.6 (d, $^2J_{C,P}$ = 7.3 Hz, CH), 123.9 (2 × *m*-CH py), 128.2 (d, $^3J_{C,P}$ = 9.2 Hz, 4 × m-CH phenyl), 129.9 (2 × CH), 130.6 (d, $^1J_{C,P}$ = 44.6 Hz, 2 × *i*-C phenyl), 132.6 (2 × CH), 133.6 (d, $^2J_{C,P}$ = 11.1 Hz, 4 × *o*-CH phenyl), 136.8 (*p*-CH py), 149.9 (2 × *o*-CH py), 160.0 (*i*-C), 185.1 (COO) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, thf-d_8, 25 °C): δ 32.2 (s) ppm. Crystals, suitable for X-ray diffraction, were obtained from a solution of thf.

Synthesis of $[(EtPh_2P)Ni(C_2H_4COO)]_4$ (2). Method 1. $EtPh_2P$ (0.32 g, 1.49 mmol) was added to a stirred solution of $[(py)_2Ni(C_2H_4COO)]$ (0.43 g, 1.49 mmol) in dmf (10 mL). After stirring the resulting yellow brown solution for 30 min at rt, the solvent was slowly distilled off at reduced pressure. The sticky brown residue was treated with ether (10 mL) with rapid stirring. The formed yellow solid was collected by filtration and dried in a vacuum. Yield: 0.39 g (76%).

Method 2. To a stirred mixture of $(cod)_2Ni$ (1.30 g, 4.72 mmol) and $EtPh_2P$ (1.95 g, 9.10 mmol) in thf (20 mL) was added succinic anhydride at 0 °C. The solution was allowed to warm to rt and was stirred for 1 h. Then the solution was heated to 40 °C for an additional 30 min. The solvent was removed in a vacuum, ether (20 mL) was added, and formed solids were removed by filtration. From the clear solution, brown crystals were obtained at 5 °C after a few days together with some yellow precipitate. The solution with the yellow solid was decanted, and the separated crystals were dried in a vacuum. Yield: 0.55 g (53%). $C_{68}H_{76}P_4Ni_4O_8$ (1380.02) calcd: C 59.18, H 5.55. Found: C 58.87, H 5.49. IR (Nujol, cm^{-1}): ν(C=O) 1558 (s). ^1H NMR (400 MHz, thf-d_8, 25 °C): δ −0.24 (m, 2H, Ni-CH_2), 1.27 (dt, $^3J_{H,H}$ = 7.2 Hz, $^3J_{P,H}$ = 16.4 Hz, 3H, CH_3), 1.46 (m, 1H, C*H*H′-COO), 1.88 (m, 1H, CH*H′*-COO), 2.18 (m, 2H, CH_2), 7.38 (m, 6H, CH phenyl), 7.97 (m, 4H, CH phenyl) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, thf-d_8, 25 °C): δ 0.2 (d, $^2J_{C,P}$ = 33.8 Hz, Ni-CH_2), 9.5 (s, CH_3), 20.0 (d, $^1J_{C,P}$ = 26.6 Hz, CH_2), 38.9 (s, CH_2), 128.6 (d, $^3J_{C,P}$ = 7.0 Hz, 2 × *m*-CH), 128.7 (d, $^3J_{C,P}$ = 7.0 Hz, 2 × *m*-CH), 129.8 (s, *p*-CH), 130.0 (s, *p*-CH), 133.5 (d, $^1J_{C,P}$ = 42.3 Hz, *i*-C), 134.0 (d, $^1J_{C,P}$ = 42.3 Hz, *i*-C), 134.0 (d, $^2J_{C,P}$ = 10.1 Hz, 2 × *o*-CH), 134.4 (d, $^2J_{C,P}$ =

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10.1 Hz, 2 × *o*-CH), 188.9 (s, COO) ppm. ^{31}P{^{1}H} NMR (81 MHz, thf-d_8, 25 °C): δ 32.6 (s) ppm.

Synthesis of [(Mes$_2$PH)Ni(C$_2$H$_4$COO)]$_4$ (3). [(py)$_2$Ni(C$_2$H$_4$COO)] (0.36 g, 1.25 mmol) was dissolved in dmf (10 mL). After Mes$_2$PH (0.34 g, 1.26 mmol) was added, the resulting solution was stirred for 30 min at rt. After that, the solvent was slowly removed in a vacuum, yielding a brown sticky residue. To this oil was added ether (10 mL) with rapid stirring. The yellow solid formed was separated by filtration and dried in a vacuum. Yield: 0.45 g of crude product (contains dmf and [(py)$_2$Ni(C$_2$H$_4$COO)]). For analytical characterization, the crude product was recrystallized from thf, resulting in [(Mes$_2$PH)Ni(C$_2$H$_4$COO)]$_4$·THF·DMF. $C_{91}H_{123}P_4NNi_4O_{10}$ (1748.66) calcd: C 62.46, H 7.09, N 0.80. Found: C 62.31, H 7.07, N 0.63. IR (Nujol, cm^{-1}): ν(C=O) 1566 (s). ^{1}H NMR (400 MHz, dmf-d_7, 25 °C): δ 0.30 (m, 8H, Ni-CH$_2$), 1.78 (m, 4H, CH$_2$ thf), 1.89 (m, 8H, CH$_2$-COO), 2.26 (s, 24H, *p*-CH$_3$), 2.74 (s, 48H, *o*-CH$_3$, signal overlaps with one signal of the solvent), 2.78 (s, 3H, CH$_3$ dmf), 2.95 (s, 3H, CH$_3$ dmf), 3.63 (m, 4H, O-CH$_2$ thf), 5.86 (d, $^{1}J_{\mathrm{P,H}}$ = 371.0 Hz, 4H, PH), 6.98 (s, 16H, CH), 8.02 (s, HCO dmf) ppm. ^{13}C{^{1}H} NMR (100 MHz, dmf-d_7, 25 °C): δ 0.8 (d,$^{2}J_{\mathrm{P,C}}$ = 25.9 Hz, Ni-CH$_2$), 20.9 (s, *p*-CH$_3$), 23.0 (d, $^{3}J_{\mathrm{P,C}}$ = 8.3 Hz, *o*-CH$_3$), 26.0 (s, CH$_2$ thf), 39.7 (s, *CH$_2$*-COO), 67.9 (s, O-CH$_2$ thf), 123.2 (d, $^{1}J_{\mathrm{P,C}}$ = 38.2 Hz, P-*i*-C), 130.4 (d, $^{3}J_{\mathrm{P,C}}$ = 6.9 Hz, CH), 140.7 (s, *i*-C), 142.5 (d, $^{2}J_{\mathrm{P,C}}$ = 8.3 Hz, *i*-C), 184.7 (s, COO) ppm. ^{31}P NMR (81 MHz, dmso-d_6, 25 °C): δ −29.1 (d, $^{1}J_{\mathrm{P,H}}$ = 372 Hz) ppm. Single crystals suitable for X-ray diffraction were obtained from a thf/ether mixture.

Synthesis of [(Me$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (4). thf (10 mL) was added to (Me$_3$P)$_2$Ni(cod) (1.5 g, 4.7 mmol). The resulting solution was cooled to −10 °C, and succinic anhydride (0.31 g, 3.13 mmol) was added. Then the solution was slowly heated to 35 °C and stirred for 45 min at this temperature. The resulting, yellow solid was collected by filtration at rt and dried under reduced pressure. Yield: 0.55 g (62%), $C_{24}H_{52}P_4Ni_4O_8$ (827.34). The elemental data for C showed in each of three measurements of different crystalline samples too high values with the same deviation from calculated value. Possibly, a pyrolysis product interfered with CO$_2$ detection. IR (Nujol, cm^{-1}): ν(C=O) 1646 (s). ^{1}H NMR (400 MHz, toluene-d_8, 25 °C): δ 0.09 (m, 2H, Ni-CH$_2$), 1.10 (d, $^{2}J_{\mathrm{P,H}}$ = 10.2 Hz, 9H, CH$_3$), 1.92 (m, 1H, C*H*H′-COO), 2.47 (dddd, J = 3.2 Hz, J = 8.2 Hz, J = 8.2 Hz, $^{2}J_{\mathrm{H,H}}$ = 17.3 Hz, 1H, CH*H′*-COO) ppm. ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ −3.0 (d, $^{2}J_{\mathrm{P,C}}$ = 36.3 Hz, Ni-CH$_2$), 12.7 (d, $^{1}J_{\mathrm{P,C}}$ = 28.7 Hz, CH$_3$), 37.3 (*CH$_2$*-COO), 185.4 (COO) ppm. ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 25 °C): δ −3.5 ppm. Single crystals suitable for the X-ray diffraction were obtained from a solution of toluene.

Synthesis of [(*i*-Pr$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (5). Isopropyl$_3$P (1.82 mL, 9.3 mmol) was added to a suspension of (cod)$_2$Ni (1.28 g, 4.65 mmol) in thf (20 mL). To the resulting solution was added succinic anhydride (0.31 g, 3.1 mmol), and the mixture was stirred for 30 min at rt and for an additional 30 min at 40 °C. A yellow precipitate formed and was collected by filtration, washed with ether, and dried in a vacuum. Yield: 0.76 g (84%). $C_{48}H_{100}P_4Ni_4O_8$ (1163.99) calcd: C 49.53, H 8.66. Found: C 49.41, H 8.38. IR (Nujol, cm^{-1}): ν(C=O) 1570 (s). ^{1}H NMR (400 MHz, thf-d_8, 25 °C): δ −0.13 (br, 1H, Ni-C*H*H′), 0.26 (br, 1H, Ni-CH*H′*), 1.30−1.45 (m, 18H, CH$_3$), 1.78 (br, 1H, C*H*H′-COO), 1.86 (m, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 3H, CH), 2.07 (br, 1H, CH*H′*-COO) ppm. ^{13}C{^{1}H} NMR (50 MHz, thf-d_8, 25 °C): δ −5.2 (d, $^{2}J_{\mathrm{C,P}}$ = 32.7 Hz, Ni-CH$_2$), 19.9 (s, CH$_3$), 23.7 (d, $^{1}J_{\mathrm{C,P}}$ = 20.1 Hz, CH), 40.4 (d, $^{3}J_{\mathrm{C,P}}$ = 2.8 Hz, CH$_2$), 190.7 (m, $^{3}J_{\mathrm{C,P}}$ = 1.7 Hz, COO) ppm. ^{31}P{^{1}H} NMR (162 MHz, thf-d_8, 25 °C): δ 47.3 (s) ppm. Single crystals suitable for X-ray diffraction were obtained from a solution of toluene or thf.

Synthesis of [(Cy$_3$P)Ni(C$_2$H$_4$COO)]$_4$ (6). A clear solution of (cod)$_2$Ni (0.52 g, 1.89 mmol) and Cy$_3$P (1.06 g, 3.78 mmol) in thf (20 mL) was prepared. Succinic anhydride (0.13 g, 1.30 mmol) was added at 5 °C with rapid stirring. After the anhydride was completely dissolved, the stirring bar was removed. Suitable crystals of **6** for X-ray diffraction were obtained from this reaction mixture at rt besides side products. IR measurements suggest **6** to be essentially the same product as [(Cy$_3$P)Ni(C$_2$H$_4$COO)]$_n$ described by Yamamoto previously. IR (Nujol, cm^{-1}): ν(C=O) 1567 (s) (1570 lit.[15]).

Synthesis of [(Et$_3$P)Ni(C$_2$H$_4$COO)]$_6$·Solvent (7). A suspension of (cod)$_2$Ni (1.47 g, 5.34 mmol) in thf (10 mL) was mixed with Et$_3$P (1.56 mL, 10.68 mmol). After the yellow (cod)$_2$Ni was completely dissolved, succinic anhydride was added. The reaction mixture was stirred 30 min at rt and additionally for 30 min at 40 °C. After cooling to rt the solvent was removed in a vacuum. The red, sticky residue was dissolved in ether (10 mL) and filtered through Celite. From this clear, reddish solution yellow-brown crystals of [(Et$_3$P)Ni(C$_2$H$_4$COO)]$_6$·Et$_2$O (**7a**) could be obtained at 5 °C overnight besides some yellow amorphous precipitate. These crystals were suitable for X-ray diffraction. Analogously, [(Et$_3$P)Ni(C$_2$H$_4$COO)]$_6$·DMF (**7b**) was formed if dmf (5 mL) was used instead of Et$_2$O. $C_{57}H_{121}P_6NNi_6O_{13}$ (**7b**) (1566.59) calcd: C 43.70, H 7.79, N 0.89. Found: C 43.73, H 7.87, N 0.81. IR (Nujol, cm^{-1}): ν(C=O) 1563 (s). ^{1}H NMR (200 MHz, dmf-d_7, 25 °C): δ 0.13 (br, 2H, Ni-CH$_2$), 1.00−1.80 (m, 15H, CH$_3$ + CH$_2$), 1.83 (br, 2H, CH$_2$-COO) ppm. ^{13}C{^{1}H} NMR (50 MHz, dmf-d_7, 25 °C): δ −3.8 (d, $^{2}J_{\mathrm{C,P}}$ = 30.6 Hz, Ni-CH$_2$), 8.4 (s, 3 × CH$_3$), 14.6 (d, $^{1}J_{\mathrm{C,P}}$ = 20.6 Hz, 3 × CH$_2$), 39.1 (s, CH$_2$), 185.1 (s, COO) ppm. ^{31}P{^{1}H} NMR (81 MHz, dmf-d_7, 25 °C): δ 28.7 ppm.

Synthesis of [(Cy$_3$P)(py)Ni(C$_2$H$_4$COO)···EtOH]·0.5 py (8). Yellow **6** was dissolved in pyridine, and a saturated, greenish yellow solution was obtained. After addition of a small amount of EtOH and standing at 5 °C for a few days golden crystals were formed. These crystals were collected by filtration and dried in a vacuum. $C_{30.5}H_{50.5}PN_{1.5}Ni_4O_8$ (575.91) calcd: C 63.61, H 8.84, N 3.65. Found: C 63.78, H 9.06, N 3.42. IR (Nujol, cm^{-1}): ν(O−H) 3336 (s) ν(C=O) 1650 (s). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5, 25 °C): δ 1.2 (d, $^{2}J_{\mathrm{C,P}}$ = 29.8 Hz, Ni-CH$_2$), 19.1 (s, CH$_3$ EtOH), 27.9 (s, 6 × CH$_2$), 30.0 (s, 3 × CH$_2$), 31.4 (d, $^{2}J_{\mathrm{C,P}}$ = 12.4 Hz, 6 × CH$_2$), 33.8 (d, $^{1}J_{\mathrm{C,P}}$ = 20.5 Hz, 3 × CH), 39.7 (d, $^{3}J_{\mathrm{C,P}}$ = 2.1 Hz, *CH$_2$*-COO), 57.2 (s, CH$_2$ EtOH), 187.4 (s, br) ppm. ^{31}P{^{1}H} NMR (81 MHz, pyridine-d_5, 25 °C): δ 37.6 ppm. Besides the signals of **8** also a set of signals for free phosphine and for the bis(pyridine-d_5) complex in equilibrium with **8** was observed.

Crystal Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[33,34]

The structures were solved by direct methods (SHELXS[35]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[36]). The hydrogen atom of the hydroxyl group of the ethanol molecules of **8** was located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[36] Compound **3** contains disordered thf molecules resulting in the insufficient quality of the data (R_1 = 11.6%). In the case of complex **5** the errors of the cell parameters are very small; however, the isopropyl groups cause a disorder that could not be solved. Therefore, we will publish the conformation of the molecules and the crystallographic data of only **3** and **5**. We will not deposit the data in the Cambridge

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Crystallographic Data Centre. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Determination of the cone angles from solid-state structure was performed as follows. Each phosphine was treated as unsymmetrical ligand, using $\theta = (2/3)\sum^{3}_{i=1}(\theta_i/2)$ to minimize the sum of half-angles. The angles $\theta_i/2$ for each substituent can be obtained from the angle P−Ni−H(X) by mathematical addition of the van der Waals radii to the hydrogen atoms. The hydrogen atom resulting in the highest corrected value $\theta_i/2$ is chosen.

Crystal Data for 1:[37] $C_{31}H_{34}NNiO_4P$, M_r = 574.27 g mol^{-1}, green-yellow prism, size 0.03 × 0.03 × 0.02 mm^3, triclinic, space group $P\bar{1}$, a = 9.9387(3) Å, b = 11.9818(3) Å, c = 14.1601(5) Å, α = 113.074(1)°, β = 90.262(1)°, γ = 112.983(1)°, V = 1403.25(7) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.359 g cm^{-3}, μ(Mo Kα) = 7.85 cm^{-1}, F(000) = 604, 10 199 reflections in h(−12/12), k(−15/15), l(−17/18), measured in the range 1.98° ≤ θ ≤ 27.42°, completeness θ_{max} = 99.2%, 6344 independent reflections, R_{int} = 0.042, 4769 reflections with $F_o > 4\sigma(F_o)$, 343 parameters, 0 restraints, R_{1obs} = 0.075, wR_{2obs} = 0.1714, R_{1all} = 0.104, wR_{2all} = 0.184, GOOF = 1.094, largest difference peak and hole 1.365/−0.714 e Å^{-3}.

Crystal Data for 2:[37] $C_{68}H_{76}Ni_4O_8P_4$, M_r = 1380.01 g mol^{-1}, yellow-orange prism, size 0.03 × 0.03 × 0.02 mm^3, tetragonalic, space group $I\bar{4}$, a = b = 17.3790(12) Å, c = 10.6941(6) Å, V = 3229.9(4) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.419 g cm^{-3}, μ(Mo Kα) = 13.01 cm^{-1}, F(000) = 1440, 6056 reflections in h(−17/22), k(−21/17), l(−13/13), measured in the range 2.24° ≤ θ ≤ 27.47°, completeness θ_{max} = 99.8%, 3507 independent reflections, R_{int} = 0.046, 2782 reflections with $F_o > 4\sigma(F_o)$, 190 parameters, 0 restraints, R_{1obs} = 0.043, wR_{2obs} = 0.077, R_{1all} = 0.068, wR_{2all} = 0.085, GOOF = 1.015, Flack parameter −0.025(17), largest difference peak and hole 0.277/−0.287 e Å^{-3}.

Crystal Data for 3: $C_{84}H_{108}Ni_4O_8P_4\cdot C_4H_8O\cdot 0.5$“$CH_4O$”, M_r = 1692.55 g mol^{-1}, yellow prism, size 0.02 × 0.02 × 0.01 mm^3, triclinic, space group $P\bar{1}$, a = 13.7113(7) Å, b = 17.3512(6) Å, c = 22.2884(11) Å, α = 67.570(3)°, β = 72.655(2)°, γ = 84.481(3)°, V = 4677.6(4) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.202 g cm^{-3}, μ(Mo Kα) = 9.12 cm^{-1}, F(000) = 1794, 31 763 reflections in h(−17/16), k(−20/22), l(−28/27), measured in the range 2.54° ≤ θ ≤ 27.49°, completeness θ_{max} = 96.9%, 20 812 independent reflections.

Crystal Data for 4:[37] $C_{24}H_{52}Ni_4O_8P_4$, M_r = 827.38 g mol^{-1}, yellow prism, size 0.04 × 0.04 × 0.03 mm^3, cubic, space group $P\bar{4}3n$, a = 18.9491(5) Å, V = 6804.0(3) Å^3, T = −90 °C, Z = 6, ρ_{calcd} = 1.212 g cm^{-3}, μ(Mo Kα) = 18.07 cm^{-1}, F(000) = 2592, 4772 reflections in h(−24/24), k(−17/17), l(−16/16), measured in the range 3.88° ≤ θ ≤ 27.47°, completeness θ_{max} = 99.2%, 2572 independent reflections, R_{int} = 0.036, 2196 reflections with $F_o > 4\sigma(F_o)$, 104 parameters, 0 restraints, R_{1obs} = 0.041, wR_{2obs} = 0.098, R_{1all} = 0.054, wR_{2all} = 0.104, GOOF = 1.106, Flack parameter 0.01(2), largest difference peak and hole 0.556/−0.411 e Å^{-3}.

Crystal Data for 5: $C_{48}H_{98}Ni_4O_8P_4$, M_r = 1161.98 g mol^{-1}, yellow prism, size 0.03 × 0.03 × 0.02 mm^3, tetragonalic, space group $P\bar{4}$, a = b = 23.2593(5) Å, c = 10.9689(2) Å, V = 5934.1(2) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.301 g cm^{-3}, μ(Mo Kα) = 14.02 cm^{-1}, F(000) = 2488, 23 828 reflections in h(−26/24), k(−30/28), l(−14/12), measured in the range 1.96° ≤ θ ≤ 27.46°, completeness θ_{max} = 99.5%, 12 566 independent reflections.

Crystal Data for 6:[37] $C_{84}H_{148}Ni_4O_8P_4$, M_r = 1644.74 g mol^{-1}, yellow prism, size 0.03 × 0.03 × 0.02 mm^3, tetragonalic, space group $I\bar{4}$, a = b = 18.7303(4) Å, c = 12.5854(2) Å, V = 4415.26(15) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.237 g cm^{-3}, μ(Mo K$_\alpha$) = 9.62 cm^{-1}, F(000) = 1776, 15 825 reflections in h(−23/24), k(−23/24), l(−15/16), measured in the range 2.92° ≤ θ ≤ 27.48°, completeness θ_{max} = 99.8%, 5043 independent reflections, R_{int} = 0.044, 4408 reflections with $F_o > 4\sigma(F_o)$, 227 parameters, 0 restraints, R_{1obs} = 0.048, wR_{2obs} = 0.135, R_{1all} = 0.059, wR_{2all} = 0.144, GOOF = 1.052, Flack parameter 0.486(19) (twin refined, meoedric twin), largest difference peak and hole 1.772/−0.348 e Å^{-3}.

Crystal Data for 7:[37] $C_{54}H_{114}Ni_6O_{12}P_6\cdot C_3H_7NO$, M_r = 1566.63 g mol^{-1}, green prism, size 0.03 × 0.03 × 0.03 mm^3, triclinic, space group $P\bar{1}$, a = 15.0676(5) Å, b = 16.0297(5) Å, c = 16.1476(6) Å, α = 98.279(2)°, β = 104.586(2)°, γ = 93.720(2)°, V = 3714.2(2) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.401 g cm^{-3}, μ(Mo Kα) = 16.72 cm^{-1}, F(000) = 1664, 25 864 reflections in h(−18/19), k(−20/19), l(−19/20), measured in the range 2.64° ≤ θ ≤ 27.46°, completeness θ_{max} = 97.3%, 16 553 independent reflections, R_{int} = 0.052, 10 794 reflections with $F_o > 4\sigma(F_o)$, 761 parameters, 0 restraints, R_{1obs} = 0.062, wR_{2obs} = 0.137, R_{1all} = 0.112, wR_{2all} = 0.165, GOOF = 1.037, largest difference peak and hole 1.341/−0.677 e Å^{-3}.

Crystal Data for 8:[37] $C_{28}H_{48}NNiO_3P\cdot 1/2\ C_5H_5N$, M_r = 575.90 g mol^{-1}, yellow prism, size 0.12 × 0.12 × 0.10 mm^3, triclinic, space group $P\bar{1}$, a = 9.3259(4) Å, b = 12.5108(7) Å, c = 13.5807(8) Å, α = 88.669(3)°, β = 87.244(3)°, γ = 70.259(3)°, V = 1489.6(1) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.284 g cm^{-3}, μ(Mo Kα) = 7.37 cm^{-1}, F(000) = 622, 10 440 reflections in h(−10/12), k(−15/16), l(−17/16), measured in the range 1.73° ≤ θ ≤ 27.54°, completeness θ_{max} = 97.4%, 6694 independent reflections, R_{int} = 0.068, 5330 reflections with $F_o > 4\sigma(F_o)$, 328 parameters, 0 restraints, R_{1obs} = 0.053, wR_{2obs} = 0.147, R_{1all} = 0.065, wR_{2all} = 0.153, GOOF = 1.079, largest difference peak and hole 1.286/−0.797 e Å^{-3}.

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Supporting Information Available: X-ray structural information of complexes **1**, **2**, **4**, **6**, **7**, and **8**. This material is available free for charge via the Internet at http://pubs.acs.org.

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(37) CCDC-246705 (**1**), CCDC-246706 (**2**), CCDC-246707 (**4**), CCDC-246708 (**6**), CCDC-246709 (**7**), and CCDC-246710 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).