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Homogeneous Hydrogenation and Isomerization of 1-Octene Catalyzed by Nickel(II) Complexes with Bidentate Diarylphosphane Ligands

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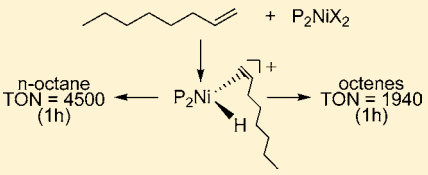
Supporting Information

ABSTRACT: A systematic library of 24 nickel(II) complexes with bidentate diphosphane ligands was synthesized, and the solid-state structures of five of them were determined with X-ray crystallography. The compounds **C1**−**C3** are common $P_2Ni^{II}X_2$-type complexes, while **C4** contains a unique $[P_2Ni^{II}(NH_3)(OAc)]^+$ square-planar structure with a P_2NO donor set and **C5** constitutes a rare $[(P_2Ni^{II})_2(\mu\text{-}OH)_2]^{2+}$ dinuclear compound. The catalytic activity of all complexes was tested in the hydrogenation and/or isomerization of 1-octene in a CH_2Cl_2/CH_3OH reaction medium. Catalyst precursors bearing ligands with *o*-alkoxy aryl rings selectively hydrogentate 1-octene to *n*-octane, while catalytic systems comprising ligands without the *o*-alkoxy functionality selectively isomerize the substrate to a mixture of internal alkenes, mostly *cis*- and *trans*-2-octene. The conversion is enhanced by equipping the ligand aryl rings with electron-donating alkoxy groups, by increasing the steric bulk of the backbone and/or the aryl rings, by employing relatively noncoordinating anions, and by adding a base as the cocatalyst. Using the compound $[Ni(L3X)I_2]$ as the catalyst precursor and upon application of standard hydrogenation conditions, full conversion of the substrate was achieved in 1 h to isomerization products only (TON = 1940). When a catalytic amount of the base is added, a similar result is obtained even in the absence of H_2. A maximum TON of 4500 in 1 h with 96% selectivity for *n*-octane was achieved by employing $[Ni(oMeO\text{-}L3X)(NH_3)(OAc)]PF_6$ as the catalyst precursor.



INTRODUCTION

The hydrogenation and isomerization of alkenes are useful and versatile chemical conversions. Hydrogenation reactions are carried out on a megaton scale in the fine chemical, commodity chemical, pharmaceutical, and food industries; a common process is the hydrogenation of vegetable oils into semisolid fats for the production of margarine.[1,2] Isomerization of terminal alkenes to internal ones can be useful to obtain branched aldehydes via a consecutive isomerization/hydroformylation synthetic pathway.[3,4] Internal alkenes may also be used to obtain branched copolymers of, e.g., 2-butene and ethylene.[5]

Active homogeneous hydrogenation catalysts have been developed that are based on iridium and rhodium [turnover numbers (TON) exceeding 10^4].[6] However, these metals are 2−4 orders of magnitude more expensive than the more abundant nickel.[7] Nature uses nickel in the active site of the enzyme hydrogenase, which can activate molecular hydrogen at ambient temperature and atmospheric pressure.[8] Inspired by these hydrogenases, we initiated the development of nickel(II) compounds supported by bidentate diarylphosphane ligands as catalysts for homogeneous hydrogenation reactions.[9−12] Using 1-octene as the substrate, a cumulative TON of 3000 has been achieved with 88% selective hydrogenation to *n*-octane.[9]

The current study is aimed at expanding the overall mechanistic understanding of the P_2Ni^{II}-catalyzed hydrogenation/isomerization of 1-octene with the hope of finding even more active and/or selective catalytic systems. Thus, a large and systematic library of nickel complexes has been synthesized and characterized. For some complexes, the solid-state structure was elucidated using X-ray diffraction. The catalytic activity of the nickel compounds was tested in the hydrogenation and isomerization of 1-octene.

RESULTS

Complex Synthesis and Characterization. An overview of the ligands used in this study is shown in Table 1. Because we have shown that $[P_2Ni(anion)_2]$ complexes with C_2-bridged phosphane ligands form inactive bischelate $[Ni(P_2)_2]^{2+}$ complexes in solution,[13] a generic C_3-backbone (indicated by "L3") was selected for the present study. Ligands with a butylene-type backbone were not used because these can form

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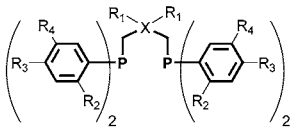
Table 1. Schematic Representation of the Ligands Used in This Study and an Overview of the Nickel Compounds Prepared and Used in Catalysis



Ligand code:	X[a]	R_1[b]	R_2[b]	R_3[b]	R_4[b]	[Ni(L)X_2][c] Cl	Br	I	Other[e]
L3						19	x		
oMe-L3			CH_3			x			
oMeO-L3			OCH_3			20	20		
pMeO-L3				OCH_3		[d]			
oMeOmMe-L3			OCH_3		CH_3	x	x	x	
L3X		CH_3				x	x	x	'OH'
oMeO-L3X		CH_3	OCH_3			x	x	x	'OH' + 'NH_3'
oMeO-L3X^{Si}	Si	CH_3	OCH_3			[d]			
oMeO-L3X*		CH_2CH_3	OCH_3			x	x	x	'OH'
oEtO-L3X*		CH_2CH_3	OCH_2CH_3			[d]		x	

[a]If not specified, X = C. [b]If not specified, R = H. [c]× = prepared in this study. [d]Used as an in situ formed catalyst. [e]'OH' = [{Ni(L)}$_2$(μ-OH)$_2$](PF$_6$)$_2$; 'NH_3' = [Ni(oMeO-L3X)(NH_3)(OAc)]PF_6.

Table 2. Details of the X-ray Crystal Structure Determinations for Complexes C1−C5

	C1	C2	C3	C4	C5
empirical formula	$C_{33}H_{38}Cl_2NiO_4P_2$ + disordered solvent	$C_{35}H_{42}Cl_2NiO_4P_2\cdot 2CH_2Cl_2$	$C_{39}H_{50}I_2NiO_4P_2$	$C_{35}H_{44}F_6NNiO_6P_3$	$C_{66}H_{78}F_{12}Ni_2O_{10}P_6$ + disordered solvent
fw	690.18[a]	956.97	957.24	840.33	1647.45[a]
cryst color	red	red	red	yellow	orange
cryst size [mm^3]	0.36 × 0.09 × 0.06	0.18 × 0.14 × 0.11	0.30 × 0.10 × 0.05	0.39 × 0.36 × 0.12	0.30 × 0.24 × 0.24
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a[A]	14.1806(4)	10.966(2)	20.816(2)	12.8383(3)	11.9615(3)
b[A]	18.1253(7)	19.026(4)	11.3200(10)	13.1291(3)	15.2613(7)
c[A]	34.5607(12)	21.044(4)	17.623(2)	13.6642(3)	22.5847(9)
α [deg]				67.872(1)	97.836(2)
β [deg]	112.3386(14)	98.37(3)	100.130(10)	63.753(1)	101.560(1)
γ [deg]				78.577(1)	96.226(2)
V[Å^3]	8216.4(5)	4343.8(15)	4087.9(7)	1912.17(8)	3962.1(3)
Z	8	4	4	2	2
d_{calc} [g cm^{-3}]	1.116[a]	1.463	1.555	1.456	1.381[a]
μ [mm^{-1}]	0.71[a]	1.05	2.10	0.71	0.74[a]
sin θ/λ [Å^{-1}]	0.59	0.64	0.64	0.65	0.61
reflns (measd/unique)	64249/14457	10004/7905	4682/4140	47353/8767	41917/12857
abs corr	multiscan	multiscan	multiscan	multiscan	multiscan
abs corr range	0.45−0.96	0.83−0.89	0.57−0.90	0.75−0.92	0.69−0.83
no. of param/restraints	769/0	512/57	221/0	488/0	907/0
R1/wR2 [$I > 2\sigma(I)$]	0.0618/01551	0.0397/0.0978	0.0199/0.0469	0.0255/0.0643	0.0569/0.1409
R1/wR2 [all reflns]	0.887/0.1673	0.0582/0.1088	0.0272/0.0512	0.0293/0.0664	0.0920/0.1538
S	0.966	1.083	1.128	1.030	1.056
$\Delta\rho_{min/max}$ [e Å^{-1}]	−0.70/1.63	−0.776/0.659	−1.004/0.340	−0.37/0.32	−0.70/1.41

[a]The derived values do not contain the contribution of the disordered solvent.

inactive trans complexes with the small Ni^{II} ion.[14,15] The length of the backbone was slightly increased in one case by substitution of the central C atom into the backbone by the larger Si atom (indicated by "X^{Si}"). In some instances, the backbone is more rigid by substitution of the H atoms on the central atom by methyl ("X") or ethyl ("X*") groups; such a rigid backbone ensures instantaneous complex formation of in situ formed catalysts[16] and leads to more stable chelates.[17]

The aryl rings of several ligands have been functionalized by methoxy substitution in the ortho position relative to P. To allow discrimination between the electronic and steric effects of this substitution, ligands were equipped with a *p*-methoxy

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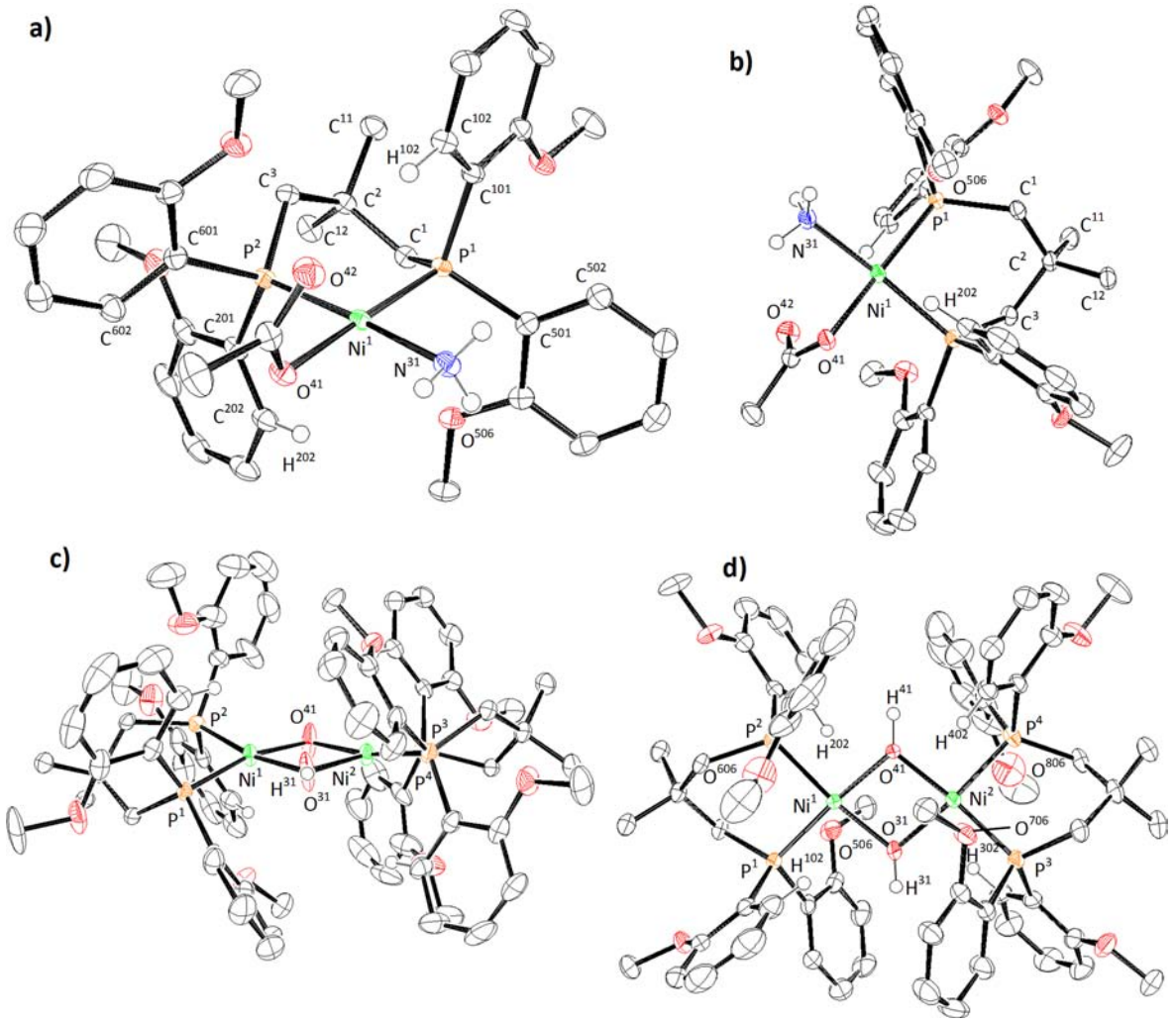

Figure 1. ORTEP projections of **C4**: (a) front view; (b) top view. ORTEP projections of **C5**: (c) side view; (d) top view. Ellipsoids are presented at the 50% probability level. All H atoms (except aryl *o*-H, NH_3, and OH), uncoordinated anions, and solvent molecules are omitted for clarity. Color code: green, Ni; orange, P; red, O; blue, N; black, C; open sphere, H. The variation of the displacement ellipsoids indicates some minor disorder, which has not been resolved (**C5**).

functionality (pMeO-L3), an *o*-methyl group (oMe-L3), or an *o*-ethoxy moiety (oEtO-L3X and oEtO-L3X*). In another ligand, both an *o*-methoxy and a *m*-methyl moiety were introduced (oMeOmMe-L3) because it has been shown that this ligand forms a sterically crowded complex with palladium.[18]

Using the ligands shown in Table 1, a series of nickel(II) halide compounds of the general formula $[Ni(L)X_2]$ (X = Cl, Br, I) has been synthesized using procedures adapted from the literature (see Table 1).[11] In attempts to make mononuclear nickel compounds with noncoordinating PF_6^- counterions similar to the reported compound $[Ni(oMeO\text{-}L3)(H_2O)_2](PF_6)_2$,[20] unexpectedly three new dinuclear hydroxide-bridged complexes with the formula $[\{Ni(L)\}_2(\mu\text{-}OH)_2](PF_6)_2$ were isolated (indicated with 'OH' in Table 1). The compound $[Ni(oMeO\text{-}L3X)(NH_3)(OAc)]PF_6$ ('NH_3') was surprisingly obtained in an attempt to exchange both acetate anions of the in situ formed $[Ni(oMeO\text{-}L3X)(OAc)_2]$ for PF_6^- anions by the addition of NH_4PF_6.[20] All complexes were obtained as microcrystalline or crystalline material in good-to-excellent (nonoptimized) yields. The identity and purity of the isolated complexes were confirmed by (C, H, N, S, and Ni) elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and IR and (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{19}F) NMR spectroscopy.

Characterization by ^{31}P{^{1}H} NMR was not possible for complexes of sterically demanding ligands; such steric crowding causes the ideal square-planar geometry to become distorted to a more tetrahedral-like environment, giving paramagnetic (high-spin) character to Ni^{II}, which quenches the NMR signal of the nearby (i.e., P, C, and H) atoms.[21,22] Because of this paramagnetic behavior, most compounds are ^{31}P NMR silent and the signal of the central CH_2 protons of the propylene bridge of several compounds is rather broad or not observed at all in the ^{1}H NMR spectra.

The axial or equatorial orientation of the ligand aryl rings can be distinguished using ^{1}H{^{31}P} NMR: the anagostic interaction between the Ni and *o*-H atoms of the axial aryl rings causes these *o*-H resonances to shift downfield, whereas an overall upfield shift is observed for the equatorially aligned *o*-H atoms.[13,16,18] At room temperature, dynamic flipping of the backbone causes the aryl rings to alternate between an axial and an equatorial orientation, resulting in a time-average signal. At low temperature, this flipping can be frozen to resolve the resonances of the axial and equatorial rings, as we indeed

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Table 3. Selected Interatomic Distances, Angles, and Torsion Angles for Complexes C1−C5

	C1	C2	C3	C4	C5
X^1	Cl^1	Cl^1	I^1	OAc (O^{41})	OH (O^{31})
X^2	Cl^2	Cl^2		NH_3 (N^{31})	OH (O^{41})
			Distances [Å]		
Ni···Ni					2.8968(7)
Ni−X^1	2.2171(10)	2.2095(5)	2.5382(2)	1.9072(9)	1.887(3)
Ni−X^2	2.2181(11)	2.2109(4)		1.9589(12)	1.889(3)
Ni−P^1	2.1723(12)	2.1725(4)	2.1835(1)	2.1682(3)	2.1440(12)
Ni−P^2	2.1705(11)	2.1760(4)		2.1830(3)	2.1444(12)
Ni−O^{42}				2.8187(11)	
Ni···H^{102}	2.80	2.9792(6)	2.9636(4)	2.75	2.78
Ni···H^{202}	2.90	3.0599(8)		2.87	2.95
Ni···O^{506}	3.405(3)	3.285(5)	3.609(1)	3.4054(11)	3.658(4)
Ni···O^{606}	3.589(3)	2.930(2)		3.6635(11)	3.106(3)
			Angles [deg]		
X^1−Ni−X^2	92.79(4)	92.79(2)	91.97(1)	88.39(5)	79.74(13)
P^1−Ni−X^1	88.76(4)	89.90(2)	90.55(2)	177.86(3)	93.70(9)
P^1−Ni−X^2	169.17(4)	166.36(3)	163.70(2)	91.92(4)	169.23(12)
P^2−Ni−X^1	168.15(4)	164.51(3)		87.95(3)	166.32(13)
P^2−Ni−X^2	88.98(4)	89.82(2)		176.29(4)	95.55(10)
P^1−Ni−P^2	91.70(4)	91.15(2)	91.54(2)	91.715(13)	92.71(4)
Ni···H^{102}−C^{102}	122.46	118.8(1)	119.6(1)	121.40	121.03
Ni···H^{202}−C^{202}	120.56	119.1(1)		119.49	118.56
			Torsion Angles [deg]		
Ni−P^1−C^{101}−C^{102}	1.9(4)	8.80	4.59(18)	0.04(11)	9.6(4)
Ni−P^1−C^{501}−C^{502}	−113.3(3)	−118.77	109.34(15)	−113.39(10)	97.8(4)
Ni−P^2−C^{201}−C^{202}	−2.9(4)	14.17		5.50(12)	−9.4(4)
Ni−P^2−C^{601}−C^{602}	−108.5(3)	−136.01		−106.08(11)	120.8(3)
P^1−C^1−C^2−C^3	−31.7(5)	−38.96	34.45(7)	−32.61(14)	39.5(5)
P^1−C^1−C^2−C^{11}	87.7(4)		−84.96(19)	87.14(12)	−81.7(4)
P^1−C^1−C^2−C^{12}	−154.8(3)		155.19(13)	−156.45(9)	161.9(3)
			Dihedral Angle ω between the NiP_2 and NiX_2 Planes [deg]		
NiP^2−NiX^2	15.76(6)	20.31	22.78	2.23(6)	15.27(16)

typically observed for $[Ni(L)X_2]$-type complexes. This dynamic behavior is absent in the rigid compound $[\{Ni(oMeO\text{-}L3X)\}_2(\mu\text{-}OH)_2](PF_6)_2$, for which a clear diamagnetic NMR spectrum is obtained despite the relatively large distortion from a square-planar geometry (see below), in which the axial and equatorial protons are easily distinguished at room temperature.

To obtain intimate structural knowledge of the complexes and relate this knowledge to their catalytic performances, the X-ray structures of some compounds have been determined.

Complex Structures in the Solid State. Single crystals of the compounds $[Ni(oMeO\text{-}L3X)Cl_2]$ (**C1**), $[Ni(oMeOMe\text{-}L3)Cl_2]$ (**C2**), $[Ni(oEtO\text{-}L3X^*)I_2]$ (**C3**), $[Ni(oMeO\text{-}L3X)(NH_3)(OAc)](PF_6)$ (**C4**), and $[\{Ni(oMeO\text{-}L3X)\}_2(\mu\text{-}OH)_2](PF_6)_2$ (**C5**) were obtained using the solvent-diffusion technique. Their solid-state structures were determined using X-ray diffraction. Crystallographic data and details of the structure refinement are collected in Table 2, and perspective views of **C4** and **C5** are shown in parts a,b and c,d of Figure 1, respectively. Because the structures of complexes **C1**−**C3** are very similar to those of complexes reported with other bidentate phosphane ligands[9,20,23,24] and that of **C4**, their perspective views are given in the Supporting Information (Figure S1). In Table 3 are listed selected structural characteristics such as bond distances, angles, and torsion angles.

The asymmetric unit of **C1** contains two independent molecules of $[Ni(oMeO\text{-}L3X)Cl_2]$; because the differences in the bond distances and angles of the independent molecules are negligible, the data of only one of them are given in Table 3. Within the lattice of **C2** are two CH_2Cl_2 solvent molecules, one of which is disordered. Complex **C3** is located on a 2-fold rotation axis running through the Ni center and the quaternary C atom in the ligand backbone (C^2). The dinuclear compound **C5** cocrystallized with ordered and disordered solvent CH_2Cl_2 molecules. The PF_6^- anions in **C4** and **C5** are found in the second coordination sphere of the complex and are held in place by several weak N−H···F and C−H···F hydrogen-bonding interactions.

All Ni^{II} ions have a *cis*-P_2X_2 (X = anion or NH_3) donor set. The bond distances of the donor atoms to the Ni^{II} ion are about 2.21 Å (Ni−Cl), 2.54 Å (Ni−I), 1.90 Å (Ni−O), and 1.96 Å (Ni−N); the Ni−P distances vary slightly between 2.1388(13) and 2.1835(1) Å. All of these coordination distances, as well as the C−C, C−H, C−O, and C−P distances, can be considered as normal.[25,26] The distance of 2.897 Å between the two Ni ions in **C5** is well below the sum of their van der Waals radii (3.26 Å), which is normal in such $(L_2Ni)_2(\mu\text{-}OH)_2$ clusters.[27]

The coordination geometry in all complexes is essentially square-planar, although the magnitude of the distortion from the ideal square-planar geometry varies considerably: the dihedral angle ω between the P−Ni−P and X−Ni−X planes ranges from 2.23° in **C4** to 22.78° in **C3**. This difference is ascribed to the steric constraints that the phosphane ligand and

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anions (or NH_3 ligand) impose on each other. For example, ω becomes smaller when the ionic radius r of X decreases: I (**C3**; r = 1.98 Å, ω = 22.78°) > Cl (**C2**; r = 1.75 Å, ω = 20.31°) > O (**C5**; r = 1.52 Å, $\omega \approx 16°$) > N (**C4**; r = 1.55 Å, ω = 2.23°).[28] Likewise, the dihedral angle in **C2** (20.31°) is larger than that in **C1** (16°) because of the bulkiness of the introduced *m*-methyl groups.[18] The P−Ni−P coordination angle varies slightly from 91.15(2)° to 91.72(2)° in **C1**−**C4**, whereas this angle is slightly larger in **C5** (92.6°) due to the restricted O−Ni−O angle.

The two aryl rings attached to a P-donor atom can be distinguished as oriented either axially or equatorially with respect to the six-membered NiPCCCP ring. As can be seen in Figure 1, the axial rings have their *o*-H atoms (H^{101} − H^{401}) pointing toward the Ni center. The Ni···$H^{102-402}$−$C^{102-402}$ angles are about 120°, and the Ni···H distances are between 2.75 and 3.06 Å. The Ni···H−C angles in the range of 110−170° and the M···H−C distances of about 2.3−2.9 Å are characteristic for anagostic interactions between the d_{z^2} orbital of a metal ion and the H atom of C−H.[29]

The equatorial rings have their *o*-methoxy groups directed toward the Ni ion, with Ni···O distances in the range of 2.93−4.17 Å. The Ni···$O^{606/806}$ distances in **C2** [2.930(2) Å] and **C5** [3.106(3) and 3.094(3) Å] are shorter than the sum of the van der Waals radii of the Ni and O atoms (3.15 Å), indicating electrostatic interactions between the Ni ion and the O atoms of an alkoxyphenyl ring. Such interactions have never before been reported in a $[P_2Ni^{II}Anion_2]$ or $[(P_2Ni^{II})_2(\mu\text{-Anion})_2]^{2+}$ complex, wherein P_2 is a bidentate phosphane ligand,[30] and are unknown for complexes with other metals and a bidentate *o*-alkoxyaryl-functionalized L3-type ligand.[31] Only for the dicationic compound $[Ni(oMeO\text{-}L3)(H_2O)_2](PF_6)_2$ has a distance of 2.87 Å between one of the methoxy groups and the Ni^{II} ion been reported.[20] The other Ni−O distances in the complexes are well above the sum of the van der Waals radii of the O and Ni atoms [3.285(5)−4.165(5) Å], which can be considered as normal for such complexes.[9,20]

The crystal packing of **C1**−**C3** and **C5** is governed by common weak intermolecular interactions (weak hydrogen bonds and CH···π and π···π stacking forces). **C4** is packed as a dimer because of strong intermolecular hydrogen bonding between the acetate and ammonia ligands (N^{31}−H^{31A}···O^{42} = 2.086 Å), while a weaker intramolecular hydrogen bond is present as well (N^{31}−H^{31C}···O^{41} = 2.389 Å). The non-coordinating O atom of the acetate ion in **C4** shows a weak electrostatic interaction with the Ni ion; the intramolecular Ni···O^{42} distance is 2.819 Å (van der Waals Ni + O = 3.15 Å).

Analogous $P_2Ni^{II}X_2$[9,20,23,24] and $P_2Pd^{II}X_2$[16,18] complexes have been reported to exhibit structural features similar to those described above.

Catalytic Experiments. *General Considerations.* The nickel complexes were tested as homogeneous catalysts for hydrogenation reactions. The catalyst typically was a presynthesized nickel(II) diphosphane complex. Occasionally, the complex was generated in situ by dissolving a nickel(II) salt in combination with 1.5 equiv of the selected diphosphane ligand in the reaction mixture. A 1:1 mixture of CH_2Cl_2/CH_3OH was used in this study because we found that the performance of similar nickel(II) catalysts is best in this solvent mixture.[11] The model substrate chosen for our catalytic experiments is 1-octene, and a typical 1-octene/nickel ratio of 1940 has been used at a 1.0 mM concentration of nickel.

Gas/liquid chromatography (GLC) analysis of reaction mixtures was used to identify and quantify the products after a catalytic experiment. Identification of 1-octene, the hydrogenation product *n*-octane, and the isomerization products *cis*-2-octene and *trans*-2-octene was verified by the injection of authentic samples. The four other internal alkenes were formed typically in trace amounts but were not individually identified and instead were taken together as >2-octenes or taken with *cis*- and *trans*-2-octene as octenes/isomerization products. For quantification of the analytes, it was assumed that the response factor for all analytes is unity and that the mass balance of initially added 1-octene is respected. Indeed, higher-molecular-weight products were never observed with GLC. Furthermore, it has been reported that oligomerization/polymerization of ethylene does not take place with P_2NiX_2-type complexes under similar reaction conditions.[32]

Catalytic Reactions under Standard Conditions Using [Ni(L)X$_2$] Catalysts. The results using catalyst precursors of the type $[Ni(L)X_2]$, wherein L is a ligand with an unsubstituted propylene backbone, are shown in Table 4. Using L3 or oMe-

Table 4. Conversion and Selectivity of $[Ni(L)X_2]$ Complexes with L3-Type Ligands for Hydrogenation and Isomerization Products of 1-Octene[a]

				selectivity (%)	
entry	complex	conversion (%)	TON	*n*-octane	octenes
1	$[Ni(L3)Cl_2]$	0	0	0	0
2	$[Ni(L3)Br_2]$	0	0	0	0
3	$[Ni(oMe\text{-}L3)Cl_2]$	0	0	0	0
4	$[Ni(pMeO\text{-}L3)Cl_2]$[b]	21	410	0	100
5	$[Ni(oMeO\text{-}L3)Cl_2]$	21	410	100	0
6	$[Ni(oMeO\text{-}L3)Br_2]$	49	950	99	1
7	**C2**	35	680	100	0
8	$[Ni(oMeOmMe\text{-}L3)Br_2]$	66	1280	99	1
9	$[Ni(oMeOmMe\text{-}L3)I_2]$	100	1940	98	2

[a]Reaction conditions: A total of 27.9 μmol of complex (or 27.9 μmol of $NiCl_2$ and 41.9 μmol of ligand) dissolved in 28.5 mL of a 1.90 M 1-octene solution in CH_3OH/CH_2Cl_2 (1:1) was heated at 50 °C under 50 bar of H_2 for 1 h. [Ni] = 1 mM; 1-octene/Ni = 1940. The TON (mol of substrate converted/mol of Ni) is also given. [b]Catalyst formed in situ.

L3 as the supporting ligand did not give any conversion of 1-octene (entries 1−3). The inactivity of $[Ni(oMe\text{-}L3)Cl_2]$ can be ascribed to the poor stability of the complex; the ligand readily dissociates in a methanolic solution, as was confirmed with NMR experiments. A conversion of 21% is reached when the ligand aryl rings are functionalized with electron-donating methoxy substituents in the para (pMeO-L3, entry 4) or ortho (oMeO-L3, entry 5) positions. The effect of this substitution on the selectivity of the catalytic system is drastically different however; pMeO functionalization results in the formation of only isomerization products, whereas oMeO substitution results in the formation of *n*-octane, as has been reported earlier.[9,10] About 50% conversion to *n*-octane is reached when $[Ni(oMeO\text{-}L3)Br_2]$ (entry 6) is used compared to 21% for the chloride analogue (entry 5). When the ligand anisyl rings in the catalyst $[Ni(oMeO\text{-}L3)X_2]$ are additionally functionalized with *m*-methyl moieties (i.e., oMeOmMe-L3, entries 7−9), the conversion increases roughly by a factor of 1.5; $[Ni(oMeOmMe\text{-}L3)I_2]$ even gives full conversion of the substrate in 1 h (TON = 1940).

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Next, the series of catalyst precursors with substituents on the propylene backbone was tested, and the results are shown in Table 5. Surprisingly, when L3X with unsubstituted aryl rings

Table 5. Conversion and Selectivity of $[Ni(L)X_2]$ Complexes with Substituted L3-Type Ligands for Hydrogenation and Isomerization Products of 1-Octene[a]

		conversion		selectivity (%)	
entry	complex	%	TON	*n*-octane	octenes
1	$[Ni(L3X)Cl_2]$	6	120	0	100
2	$[Ni(L3X)Br_2]$	75	1460	0	100
3	$[Ni(L3X)I_2]$	99	1920	0	100
4a	**C1**	26	500	98	2
4b	**C1**[b]	35	680	96	4
5	$[Ni(oMeO\text{-}L3X)Br_2]$	57	1110	91	9
6	$[Ni(oMeO\text{-}L3X)I_2]$	95	1840	93	7
7	$[Ni(oMeO\text{-}L3X^{Si})Cl_2]$[b]	60	1160	96	4
8	$[Ni(oMeO\text{-}L3X^*)Cl_2]$	28	540	93	7
9	$[Ni(oMeO\text{-}L3X^*)Br_2]$	41	800	94	6
10	$[Ni(oMeO\text{-}L3X^*)I_2]$	60	1160	90	10
11	$[Ni(oEtO\text{-}L3X^*)Cl_2]$[b]	68	1320	96	4
12	**C3**	100	1940	94	6
13	**C3**[c]	18	3550	100	0

[a]Reaction conditions: A total of 27.9 μmol of complex (or 27.9 μmol of $NiCl_2$ and 41.9 μmol of ligand) dissolved in 28.5 mL of a 1.90 M 1-octene solution in CH_3OH/CH_2Cl_2 (1:1) was heated at 50 °C under 50 bar of H_2 for 1 h. [Ni] = 1 mM; 1-octene/Ni = 1940. The TON (mol of substrate converted/mol of Ni) is also given. [b]Catalyst formed in situ. [c]10 times less catalyst was used.

is employed as the ligand, active catalytic systems are obtained; its $NiCl_2$ and $NiBr_2$ complexes give 6% and 75% conversion of the substrate, yielding only isomerization products (entries 1 and 2). Nearly full conversion of 1-octene to isomerization products is achieved when employing $[Ni(L3X)I_2]$, which thus almost reached the maximum TON of 1940 within 1 h of reaction time (entry 3). Catalysts formed with the ligand oMeO-L3X (entries 4–6) show conversion and selectivity similar to those of their simpler oMeO-L3 analogues (see Table 4). Interestingly, when the backbone in the ligand is made slightly longer by substitution of the central (quaternary) C atom in the ligand backbone with Si, the hydrogenation activity is roughly doubled from ∼30% for **C1** to 60% for $[Ni(oMeO\text{-}L3X^{Si})Cl_2]$ (entries 4 and 7). When the size of the substituents on the ligand backbone is increased by replacing the methyl groups in oMeO-L3X with ethyl groups (entries 8–10), the conversion drops from 95% for $[Ni(oMeO\text{-}L3X)I_2]$ (entry 6) to 60% for $[Ni(oMeO\text{-}L3X^*)I_2]$ (entry 10), also giving lower selectivity for *n*-octane. On the other hand, when the steric bulk of the substituent on the phenyl ring is enlarged from a methoxy group (oMeO-L3X*) to an ethoxy group (oEtO-L3X*), the conversion is roughly doubled from 30 to 70% for the chloride complexes (entry 8 vs 11) and from 60 to 100% for the iodide-containing compounds (entry 10 vs 12). Actually, the pressure drop observed for the reaction employing **C3** as the catalyst precursor indicated that full conversion is already reached after about 30 min. When this reaction is repeated using 10 times less catalyst (entry 13), 18% conversion is reached in 1 h, corresponding to a TON of 3550.

Catalytic Reactions Using Cationic Nickel Catalysts. Because the mononuclear nickel compound $[Ni(oMeO\text{-}L3)(H_2O)_2](PF_6)_2$, with noncoordinating counterions, has been reported to have the highest activity of a series of nickel compounds with this ligand,[20] attempts were undertaken to synthesize similar complexes with the ligands oMeO-L3X, oMeO-L3X*, and L3X. Despite the fact that different types of compounds were formed with these ligands, their catalytic activity in the hydrogenation of 1-octene has been investigated; the results are given in Table 6. Because of the anticipated

Table 6. Conversion and Selectivity for Hydrogenation and Isomerization Products of 1-Octene Using Cationic Nickel Complexes[a]

		conversion		selectivity (%)	
entry	complex	%	TON	*n*-octane	octenes
1	$[Ni(oMeO\text{-}L3X)I_2]$	37	3580	93	7
2	**C4**	46	4450	96	4
3	$[\{Ni(oMeO\text{-}L3X)\}_2(\mu\text{-}OH)_2](PF_6)_2$	17	820	99	1
4	$[\{Ni(oMeO\text{-}L3X^*)\}_2(\mu\text{-}OH)_2](PF_6)_2$	11	530	100	0
5	$[\{Ni(L3X)\}_2(\mu\text{-}OH)_2](PF_6)_2$	0	0	0	0

[a]Reaction conditions: A total of 5.6 μmol of complex is dissolved in 28.5 mL of a 1.90 M 1-octene solution in CH_3OH/CH_2Cl_2 (1:1) and heated at 50 °C under 50 bar of H_2 for 1 h. [complex] = 0.2 mM; 1-octene/Ni = 9670 (entries 1 and 2) and 4830 (entries 3–5). The TON (mol of substrate converted/mol of Ni) is also given.

activity, the catalyst loading was 5 times lower [maximum TON 9670 for the mononuclear complex and 4830 for the dinuclear complexes (based on Ni)]. For comparison, the catalytic activity of $[Ni(oMeO\text{-}L3X)I_2]$ was also measured under these conditions (entry 1). With **C4** as the catalyst precursor (entry 2), 46% conversion is reached, corresponding to a TON of 4450, the highest of all complexes tested. The two dinuclear, dicationic, hydroxide-bridged complexes comprising a ligand with the oMeO functionality (entries 3 and 4) are about equally reactive to their $[Ni(L)Cl_2]$ analogues. The use of the complex with L3X (entry 5) does not result in any conversion at all.

Effect of Acid or Base on the Isomerization Activity. Surprised by our finding that $[Ni(L3X)I_2]$ is an efficient isomerization catalyst (Table 5), it was decided to study this catalyst in more detail; the results are collected in Table 7. The isomerization products formed in a standard experiment (entry 1) were identified as *cis*-2-octene (24%), *trans*-2-octene (28%), and other internal alkenes (48%, >2-octenes). In another reaction, 2 equiv (relative to Ni) of *p*-toluenesulfonic acid (HOTs) was added (entry 2). Although the conversion again is essentially quantitative, the product distribution reveals a higher selectivity for *cis*-2-octene (60%). Conversely, the addition of 2 equiv (on Ni) of the base 1,8-bis(dimethylamino)naphthalene (DMAN, entry 3) results in more *trans*-2-octene and >2-octenes, also with full conversion of 1-octene. These three experiments were repeated in the absence of H_2 gas (entries 4–6). Under a nitrogen atmosphere, approximately 14% 1-octene is converted to mainly *cis*-2-octene when no acid or base is added (entry 1); the addition of HOTs results in complete suppression of the reactivity (entry 5). Interestingly, full conversion is reached when DMAN is added (entry 6), yielding *cis*-2-octene as the major product.

DISCUSSION

Complex Synthesis and Structures. The synthetic procedures to obtain nickel complexes are straightforward,

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Table 7. Activity of $[Ni(L3X)I_2]$ in the Isomerization of 1-Octene under a Hydrogen or Nitrogen Atmosphere and with and without Added Acid (HOTs) or Base (DMAN)[a]

			conversion		selectivity (%)			
entry	atmosphere	additive	%	TON	*n*-octane	*cis*-2-octene	*trans*-2-octene	>2-octenes
1	50 bar of H_2		99	1920	0	24	28	48
2	50 bar of H_2	2 equiv of HOTs	100	1940	0	60	11	29
3	50 bar of H_2	2 equiv of DMAN	100	1940	0	13	33	54
4	1 bar of N_2		14	270	0	75	8	17
5	1 bar of N_2	2 equiv of HOTs	0	0	0	0	0	0
6	1 bar of N_2	2 equiv of DMAN	100	1940	0	61	11	28

[a]Reaction conditions: A total of 27.9 μmol of $[Ni(L3X)I_2]$ (and 55.8 μmol of HOTs or DMAN) dissolved in 28.5 mL of a 1.90 M 1-octene solution in CH_3OH/CH_2Cl_2 (1:1) was heated at 50 °C for 1 h under the indicated atmosphere. [Ni] = 1 mM; 1-octene/Ni = 1940.

and the complexes could be isolated in reasonable-to-good (nonoptimized) yields and high purity. P_2Ni complexes very similar to **C1**−**C3** have previously been reported.[9,20,23,24] Compound **C4** was formed in an attempt to exchange both acetate anions for PF_6^- using NH_4PF_6, following a procedure that has been reported to yield $[Ni(oMeOL3)(H_2O)_2](PF_6)_2$.[20] Similarly, three bis(hydroxide)-bridged compounds were obtained in attempts to make the corresponding bis(aqua) complexes starting from nickel chloride solutions, using $AgPF_6$ to avoid the formation of the ammonia adduct. At this moment, we do not know what factors govern the formation of either $[P_2Ni(NH_3)(OAc)](PF_6)$ or $[\{P_2Ni(OH)\}_2](PF_6)_2$ types of complexes instead of $[P_2Ni(H_2O)_2](PF_6)_2$ when this synthetic procedure is applied. Compound **C4** is truly unique; compounds with a $P_2Ni^{II}(NH_3)(OAc)$ or $P_2Ni^{II}(NH_3)$ coordination sphere thus far have not been reported.[33] To the best of our knowledge, only one example[34] of a *cis*-P_2NiNO donor set has been reported, although in this compound both the N- and O-donor atoms are anionic and all donor atoms belong to the same ligand.[35] An $(L_2Ni)_2(\mu\text{-}OH)_2$ cluster such as that found in **C5** is also rather rare (only 11 examples are known),[27] and merely two structures are known wherein L_2 is a diphosphane ligand.[36,37]

From the solid-state structures studied, it is clear that the *o*-alkoxy-functionalized diphosphane ligands shield the axial positions of the nickel(II) complex. This is a well-documented phenomenon for both nickel(II)[11,13,20] and palladium(II)[16,18] complexes and is known to pertain in solution.[13,16,18] Complexes without this *o*-alkoxy functionality, such as $[Ni(L3)Cl_2]$,[23] are known to be relatively unhindered in the axial positions of nickel(II).

It is also clear that *o*-alkoxy substituents make the resulting nickel(II) complex more sterically crowded in the equatorial positions of the Ni^{II} ion, as reflected by distortion of the P_2Ni/NiX_2 dihedral angle from the ideal 0°. For example, in $[Ni(L)(Halogen)_2]$-type complexes, this dihedral angle is about 6° when L = L3 or L3X, but it is 18° when L = oMeO-L3.[38] This distortion becomes even larger when the steric bulk on the ligand aryl rings is further enlarged, as exemplified by the $P_2Ni/Ni(anion)_2$ dihedral angles of 20.31° and 22.78° observed in respectively **C2** and **C3** (compare with 17.45° reported for $[Ni(oMeO\text{-}L3)Cl_2]$).[20]

Catalysis. *General Structure–Activity Relationships.* We have earlier reported that the activity of the nickel diphosphane catalysts for hydrogenation depends crucially on the ligand structure. Also, under the reaction conditions used in our studies the nickel catalysts are known to be truly homogeneous;[12] the different activities and selectivities observed for the catalysts with various ligands as described in this work are in further support of the homogeneity of the system. The use of the unsubstituted ligand L3 in combination with nickel salts does not give any conversion of 1-octene. Functionalization of the phenyl rings with *o*-methoxy groups leads to nickel compounds that are active homogeneous hydrogenation catalysts, which also produce small amounts of isomerization products.[12] The proposed mechanism for the hydrogenation and isomerization activity of the nickel diphosphane complexes is based on monohydridonickel(II) intermediate species and activation of H_2 via heterolytic cleavage, thus avoiding the intermediacy of highly unstable nickel(0) or nickel(IV) compounds.[10]

In this study, the selection of diphosphane ligands has been extended to include ligands that are substituted at the central C atom of the propylene linker and/or with additional functionalization of the ligand aryl rings. Substitution of the H atoms on the central atom by methyl (L3X) or ethyl (L3X*) groups results in a more rigid structure; such a rigid backbone ensures instantaneous complex formation of in situ formed catalysts[16] and leads to more stable complexes.[17]

In the reaction conditions used in this study, catalysts comprising the ligand L3 do not show any hydrogenation or isomerization activity; however, at higher temperatures and with less-coordinating acetate anions, low conversion to mainly isomerization products is observed.[12] The use of the functionalized analogues L3X and pMeO-L3 yielded active isomerization catalysts, with *cis*-2-octene and *trans*-2-octene being the main kinetic and thermodynamic isomerization products, respectively.[39] This change in activity is most likely due to the more electron-donating nature of the ligands, facilitating dissociation of the anions of the precatalyst to allow substrate coordination. When the axial positions of the Ni ion are sterically shielded by *o*-alkoxy groups on the ligand aryl rings (i.e., oMeO-L3 and oMeO-L3X), the catalysts are almost exclusively involved in hydrogenation. This dramatic difference in selectivity can easily be understood because isomerization requires the formation of a secondary nickel alkyl complex that is sterically more crowded than the primary nickel alkyl species; formation of the latter species will lead to rapid hydrogenation.

When the aryl rings in oMeO-L3 are further functionalized (i.e., oMeOmMe-L3 vs oMeO-L3) or when the central C atom in the backbone is replaced by Si (i.e., oMeO-L3X^{Si} vs oMeO-L3X), more active hydrogenation catalysts are obtained. As expected, the catalytic activity (either hydrogenation or isomerization) of the catalytic systems is enhanced by employing less-coordinating anions, an effect that was reported earlier.[10,11] For each ligand series, the reactivity increases in the order Cl < Br < I, which may be explained by the more ready dissociation of the larger halide ions: the I^- anion (r_{vdW} = 1.98

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Å) has a lower charge density than the Cl^- anion (r_{vdW} = 1.75 Å) and generally is less coordinating in nature.

Catalyst Activation. Our observations employing [Ni(L3X)-I_2] (Table 7), in which added acid can suppress and added base can promote the isomerization reaction (in the absence or presence of a hydrogen atmosphere), have important mechanistic implications. The activation of the catalyst precursor [P_2NiX_2] is commonly assumed to proceed via heterolytic cleavage of H_2 by [P_2NiX_2], leading to [P_2NiHX] and 1 equiv of acid.[11] However, as implicated by our results in the absence of H_2, another activation process must also be possible in our reaction medium [1:1 (v/v) CH_2Cl_2/CH_3OH]. We therefore propose that methanol can be used to form the first metal hydride [P_2NiHX] with the coproduction of HX. In this reaction, the equilibrium [P_2NiX_2] + CH_3OH ⇆ [$P_2NiX(OCH_3)$] + HX is followed by a β-hydrogen abstraction of coordinated methoxide to form [$P_2NiH(O{=}CH_2)$]X, which may give [P_2NiHX] by displacement of formaldehyde by the anion. Such a process is similar to that proposed for the [P_2PdX_2]-catalyzed oxidation of methanol in a CO-reducing atmosphere when nitrobenzene is used as the oxidant.[40−42] Both activation pathways imply that the addition of acid will hamper the formation of the active species [P_2NiHX] by protonation of the hydride, whereas the addition of base will facilitate [P_2NiHX] formation, in agreement with our observations.

CONCLUSIONS

A collection of nickel(II) complexes supported by bidentate diarylphosphane ligands was synthesized, and of five of them, the solid-state structure was investigated using X-ray diffraction. The reactivity of these complexes was investigated for the hydrogenation and/or isomerization of 1-octene.

It was found that catalysts comprising ligands with *o*-alkoxy aryl rings can suppress the otherwise observed isomerization in favor of hydrogenation, which is most likely due to the steric constraint that these alkoxy moieties impose on the axial positions of the P_2Ni^{II} center. The conversion was found to increase when the ligand aryl rings are equipped with electron-donating alkoxy groups, when the steric bulk of the backbone [CH_2 < $C(CH_3)_2$ ≈ $C(CH_2CH_3)_2$ < $Si(CH_3)_2$] and/or the aryl rings (*o*H < *p*MeO ≈ *o*MeO < *o*MeO*m*Me < *o*EtO) is enlarged, when the anions are noncoordinative in nature, and when a catalytic amount of base is added.

The most active isomerization catalyst precursor tested is [Ni(L3X)I_2], with which un unprecedented 100% of the substrate is converted (TON = 1940) solely to isomerization products within only 1 h of reaction time. Notably, a similar activity could be achieved under a nitrogen atmosphere at ambient pressure when a base is added as the cocatalyst. The novel compound [Ni(oMeO-L3X)(NH_3)(OAc)]PF_6 is the most active hydrogenation catalyst precursor tested with an observed TON of 4500 and 96% selectivity to *n*-octane within 1 h of reaction time, which is a record for nickel diphosphane based catalysts.

It is our hope that the information collected in this study opens a venue for the development of even more active catalytic systems for the hydrogenation and isomerization of alkenes or for the development of nickel-based catalysts for, e.g., hydroformylation or hydrocarboxylation. Studies on the development of catalysts based on the abundant first-row transition metals are important for the desired replacement of the scarce and expensive catalysts that are currently used for many reactions.

EXPERIMENTAL SECTION

Materials. All chemicals were used as received unless stated otherwise. Solvents were all of analytical reagent purity and were obtained from Biosolve. 1-Octene and 1,3-bis(diphenylphosphanyl)-propane (L3) were purchased from Acros Organics. All other ligands were generously provided by Shell Global Solutions Amsterdam BV, where they were synthesized according to literature procedures.[43−51] Prior to use, all liquids were distilled under an argon atmosphere over the appropriate drying agent [sodium metal (1-octene), calcium hydride (dichloromethane and tetrahydrofuran), potassium carbonate (acetone), or magnesium metal (methanol)].[52] Complex syntheses were performed under an inert atmosphere of dry argon. The compounds [Ni(L3)Cl_2],[23] [Ni(oMeO-L3)Cl_2],[20] and [Ni(oMeO-L3)Br_2][20] were prepared following literature procedures; their purity was checked with elemental analysis and NMR spectroscopy.

Analytical Methods. Elemental analyses were performed using a Perkin-Elmer 2400 series II CHNS/O analyzer. The metal content was determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX CCD simultaneous ICP-OES spectrometer. Samples were measured as <5% (m/m) metal dilutions in 3% nitric acid. A Finnigan Aqua mass spectrometer with ESI was used to record mass spectra. Sample introduction was achieved through a Dionex ASI-100 automated sample injector with an eluent flow rate of 0.2 mL min^{-1}. The voltages of the capillary and aquamax were set at 3 kV and 20 V, respectively. $^1H\{^{31}P\}$, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX300 (300 MHz) or a Bruker DMX400 (400 MHz) machine. Chemical shifts are recorded in δ (parts per million) relative to the solvent peak (^1H and ^{13}C NMR) or relative to phosphoric acid (^{31}P NMR). IR spectra were recorded with 4 cm^{-1} resolution on a Perkin-Elmer Paragon 1000 Fourier transform infrared fitted with a Golden Gate Diamond ATR.

Samples from the catalytic experiments were analyzed with a Hewlett-Packard 6890 series gas chromatograph equipped with an autosampler. An AT-1 column (length, 30 m; diameter, 0.25 mm; film thickness, 1.00 μm) was used as the stationary phase with helium as the mobile phase. The column was maintained at a temperature of 50 °C, the injection port at 120 °C, and the detector at 250 °C throughout the whole 40 min run time. An injection volume of 1 μL was taken with a split ratio of 60:1.

Structure Determinations. The crystal structures of complexes **C1**−**C5** were determined using X-ray crystallography. A single crystal was mounted to a glass fiber using the oil drop method. Reflections were measured on a Nonius Kappa CCD diffractometer with a rotating anode and a graphite monochromator (λ = 0.71073 Å). Software packages used for the intensity integration were *Eval15*[53] (**C1** and **C4**) and *Eval14*[54] (**C5**). Absorption correction was performed with *SADABS*.[55] The structures were solved with *SHELXS-97*[56] (**C1**−**C3** and **C5**) or *SIR-97*[57] (**C4**) and refined with *SHELXL-97*[56] against F^2 of all reflections. Non-H atoms were refined freely with anisotropic displacement parameters. H atoms were included in calculated positions (**C1** and **C5**) or located in difference Fourier maps (**C4**). H atoms of N−H in **C4** were refined freely with isotropic displacement parameters, and all other H atoms were refined with a riding model. The crystal of **C5** was cracked into two fragments, and only nonoverlapping reflections were used in the refinement (completeness 87%).

The crystal structures of **C1** and **C5** contain large voids (2391 $Å^3$/unit cell in **C1** and 499 $Å^3$/unit cell in **C5**) filled with disordered solvent molecules. Their contribution to the structure factors was taken into account using the *SQUEEZE* routine of *PLATON* software,[58] resulting in 824 electrons/unit cell in **C1** and 104 electrons/unit cell in **C5**. One of the chloroform solvent molecules in **C3** is disordered in two positions and was thus refined with population parameters 0.75 and 0.25. Geometry calculations and checking for higher symmetry were performed with the *PLATON* program.[58] Further details are given in Table 2.

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Catalytic Experiments. Stainless steel autoclaves (100 mL) heated by a HEL polyBLOCK electrical heating system were used to perform catalytic experiments. The autoclaves were equipped with glass liners and magnetic stirbars that were both freshly washed with a 1:3 (v/v) HNO_3/HCl mixture. The temperature and pressure were measured with probes connected to a computer interface, making it possible to record these parameters throughout the course of the reaction. An amount of complex (typically 27.9 μmol), and when appropriate an additive, was weighed into the glass liners. In the case of in situ experiments, metal salt and ligand were weighed in a 1:1.5 (M/L) ratio. The autoclaves were tightly closed after insertion of the liners and subsequently filled with argon through a Schlenk system. Following this, 28.5 mL of a 1.90 M 1-octene stock solution in dichloromethane/methanol (1:1, v/v) was added to the autoclaves through one of the valves, resulting typically in a 1 mM nickel solution with a 1-octene/Ni ratio of 1940. The autoclaves were inserted into the heating block and put under 50 bar of H_2 gas. After heating of the autoclaves at 50 °C for 60 min (including the heating up of the system), the autoclaves were cooled. After 30 min of cooling, room temperature was reached, the remaining hydrogen pressure was released, and the autoclave was opened to take a sample. Throughout the reaction and the cooling process, a constant stirring speed of 500 rpm was maintained. Gas chromatography was used to analyze the contents of the solution (vide supra).

Complex Synthesis. Unless stated otherwise, complexes were prepared and isolated using the following general procedures:

[Ni(ligand)Cl_2] Complexes. $NiCl_2{\cdot}6H_2O$ (240 mg, 1.00 mmol) was dissolved in 6 mL of ethanol and then added dropwise to an equimolar amount of the ligand dissolved in 6 mL of acetone or chloroform. The solution changed color immediately, and after a few seconds, a precipitate was formed. The solution was concentrated (if necessary), after which the solid was collected by filtration. The product was washed with diethyl ether and petroleum ether. Crystalline complexes could be obtained by layering a solution of the complex in dichloromethane with diethyl ether.

Procedure A for [Ni(ligand)Br_2] Complexes. $NiBr_2$ (218.94 mg, 1.00 mmol) was dissolved in 0.4 mL of water, after which 10 mL of ethanol was added. The resulting green solution was degassed and added to the ligand (1.01 mmol) dissolved in 10 mL of dry and degassed acetone or chloroform. Over time, a precipitate was obtained from the resulting dark-red solution. The solid compounds were collected by filtration and dried in vacuo.

Procedure B for [Ni(ligand)Br_2] Complexes. A solution of the ligand (1.00 mmol) in 10 mL of acetone or chloroform was added to a suspension of $NiBr_2$ (327 mg, 1.50 mmol) in 10 mL of ethanol. The mixture was refluxed for 3−4 h and then slowly cooled to room temperature. After cooling, the crystalline precipitate was collected by filtration.

[Ni(ligand)I_2] Complexes. $Ni(OAc)_2{\cdot}4H_2O$ (249 mg, 1.00 mmol) was dissolved in 10 mL of ethanol and mixed with an equimolar amount of ligand (1.00 mmol) in 10 mL of acetone or chloroform. To this solution was added 0.25 mL of concentrated hydrogen iodide (55−58% in water, 1.80 mmol), and a dark-purple solution was obtained. If necessary, the solution was refluxed for 3.5 h, after which the solution was slowly cooled. The crystalline precipitate was isolated by filtration.

[(Ni(ligand))$_2$(μ-OH)$_2$](PF_6)$_2$-Type Complexes. $NiCl_2{\cdot}6H_2O$ (178 mg, 0.75 mmol) was dissolved in 5 mL of ethanol and then added dropwise to an equimolar amount of ligand dissolved in 5 mL of chloroform. The solution changed color immediately, and after a few seconds, a precipitate had formed. The precipitate was filtered and then dissolved in 100 mL of dichloromethane. To this solution was added a solution of $AgPF_6$ (475 mg, 1.75 mmol) in 10 mL of water. The two-layer system was stirred for 2 days. Most of the water was taken from the mixture by using a pipet, and dichloromethane was dried over magnesium sulfate. Dichloromethane was slowly put under diethyl ether using a pipet, resulting in a two-layer system. After a few days, a crystalline compound formed and was isolated by filtration.

[Ni(oMe-L3)Cl_2]. $Ni(OAc)_2{\cdot}4H_2O$ (51 mg, 0.20 mmol) was mixed with an equimolar amount of oMe-L3 (94 mg) in 20 mL of ethanol. The mixture was refluxed overnight. After partial cooling, 0.5 mL of hydrochloric acid (1 M in diethyl ether, 0.5 mmol) was added. The solution turned darker red, but also some white precipitate appeared. Therefore, more $Ni(OAc)_2{\cdot}4H_2O$ (12 mg, 0.05 mmol) and 0.12 mL of hydrochloric acid (1 M in diethyl ether, 0.12 mmol) were added. After refluxing for 3 h more, the solution was allowed to cool to room temperature. Red crystals were formed and isolated by filtration and washed with methanol and ethanol (58 mg, 0.097 mmol, 48%). Elem anal. Found (calcd) for $C_{31}H_{34}Cl_2NiP_2$: Ni, 9.83 (9.81); C, 62.43 (62.25); H, 6.09 (5.73). ESI-MS. Found (calcd) for $[M + H]^+$: m/z 596.09 (598.15). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.37 (s, 12H, $-CH_3$) 7.12 (m, 12H, Ph−H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

*[Ni(oMeOmMe-L3)Cl_2] (**C2**).* From $NiCl_2{\cdot}6H_2O$ (174.45 mg, 0.734 mmol) and oMeOmMe-L3 (402.18 mg, 0.683 mmol), dark-purple crystals were obtained (410 mg, 64%). Elem anal. Found (calcd) for $C_{35}H_{42}Cl_2NiO_4P_2{\cdot}1.5CHCl_3{\cdot}2H_2O$: C, 47.10 (46.97); H, 5.12 (5.13); Ni, 6.34 (6.29). ESI-MS. Found (calcd) for $[M - Cl]^+$: m/z 681.17 (681.16). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.65 (br, 2H, PCH_2CH_2), 3.06 (vbr, 4H, PCH_2CH_2), 2.32 (s, 12H, $-CH_3$), 3.86 (s, 12H, OCH_3), 7.02 (d, 4H, *m*-H), 7.25 (d, 4H, *p*-H), 8.00 (br, 4H, *o*-H). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ 19.49 (s, PCH_2CH_2), 20.67 (s, $-CH_3$), 56.07 (s, $-OCH_3$), 111.56 (s, PCC(OMe)CH), 129.91 (s, PCCHCMe), 133.78 (s, PCCH), 140.89 (s, *p*-C), 161.09 (s, PCC(OMe)CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ 1.41 (vbr). IR (neat, cm^{-1}): 2961 (w, CH), 1572 (w, Ph), 1486 (vs, Ph−Me), 1471 (m, Ph), 1251 (st, C═CO), 1019 (st, CO), 757 (vs, PPh).

[Ni(L3X)Cl_2]. Starting from 237 mg (1.00 mmol) of $NiCl_2{\cdot}6H_2O$ and 436 mg (1.00 mmol) of L3X, 352 mg (0.62 mmol, 62%) of orange crystals was isolated. Elem anal. Found (calcd) for $C_{29}H_{30}Cl_2NiP_2$: C, 60.14 (61.10); H, 5.52 (5.30). ESI-MS. Found (calcd) for $[M - Cl]^+$: m/z 534.61 (534.64). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ 1.00 (s, 6H, $CH_2C(CH_3)_2CH_2$), 2.31 (d, 4H, J = 3.2 Hz, $CH_2C(CH_3)_2CH_2$), 7.28 (m, 12H, *o*-Ph−H and *p*-Ph−H), 7.38 (m, 8H, *m*-Ph−H). $^{31}P\{^1H\}$ NMR (121 MHz, MeOD, 25 °C): no peaks.

*[Ni(oMeO-L3X)Cl_2] (**C1**).* Starting from 237 mg (1.00 mmol) of $NiCl_2{\cdot}6H_2O$ and 563 mg (1.00 mmol) of oMeO-L3X, 619 mg (0.90 mmol, 90%) of red crystals was isolated. Elem anal. Found (calcd) for $C_{33}H_{38}Cl_2NiO_4P_2$: C, 57.04 (57.43); H, 5.80 (5.55). ESI-MS. Found (calcd) for $[M - Cl]^+$: m/z 654.73 (654.75). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.58 (s, 6H, $CH_2C(CH_3)_2CH_2$), 2.7 (br, 4H, $CH_2C(CH_3)_2CH_2$), 3.98 (s, 12H, $-OCH_3$), 7.02 (d, 4H, J = 7.8 Hz, $-C(OMe)CH-$), 7.10 (t, 4H, J = 6.9 Hz, $-PCCHCH-$), 7.48 (t, 4H, J = 7.5 Hz, *p*-Ph−H), 8.38 (br, 4H, *o*-Ph−H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oMeO-L3X)Cl_2].* Starting from 237 mg (1.00 mmol) of $NiCl_2{\cdot}6H_2O$ and 590 mg (1.00 mmol) of oMeO-L3X*, 369 mg (0.51 mmol, 51%) of red crystals was isolated. Elem anal. Found (calcd) for $C_{35}H_{42}Cl_2NiO_4P_2$: C, 58.42 (58.53); H, 5.91 (5.89). ESI-MS. Found (calcd) for $[M + H]^+$: m/z 682.75 (682.80). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.47 (t, 6H, J = 7.5 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 0.83 (q, 4H, J = 7.5 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 2.5 (vbr, $CH_2C(CH_2CH_3)_2CH_2$), 3.95 (s, 12H, $-OCH_3$), 7.08 (br, 8H, 2 × *m*-Ph−H), 7.47 (t, 4H, J = 7.8 Hz, *p*-Ph−H), 8.41 (br, 4H, *o*-Ph−H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(L3)Br_2]. Following procedure A, 475 mg (75%) of a brick-red solid was obtained from $NiBr_2$ (218.94 mg, 1.00 mmol) and L3 (416.2 mg, 1.01 mmol). Elem anal. Found (calcd) for $C_{27}H_{26}Br_2NiP_2$: C, 51.51 (51.40); H, 4.04 (4.15); Ni, 10.26 (9.30). ESI-MS. Found (calcd) for $[M - 2Br + OH]^+$: m/z 488.50 (487.09). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ −2.95 (br, 2H, PCH_2CH_2), 2.03 (br, 4H, PCH_2CH_2), 2.03 (m, 4H, *p*-H), 4.18 (m, 4H, *m*-H), 13.69 (m, 4H, *o*-H). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): no signal. IR (neat, cm^{-1}): 3048 (w, CH), 1433 (s, CH), 1098 (s, PPh), 687 (vs, PPh).

[Ni(oMeOmMe-L3)Br_2]. Following procedure A and starting from $NiBr_2$ (226.65 mg, 1.04 mmol) and oMeOmMe-L3 (591.5 mg, 1.00 mmol), 495 mg (61%) of a purple solid was isolated. Elem anal. Found (calcd) for $C_{35}H_{42}Br_2NiO_4P_2$: C, 52.43 (52.08); H, 5.90 (5.24); Ni, 7.53 (7.27). ESI-MS. Found (calcd) for $[M - Br]^+$: m/z 726.89

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(727.11). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.43 (br, 2H, PCH_2CH_2), 2.21 (s, 12H, $-CH_3$), 3.92 (s, 12H, OCH_3), 7.09 (m, 8H, *m*-*H* + *p*-*H*), 7.87 (br, 4H, *o*-*H*). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ 21.55 (s, $-CH_3$), 57.37 (s, $-OCH_3$), 112.70 (s, PCC(OMe)CH), 130.71 (s, PCCHCMe), 135.21 (s, PCC). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no signal. IR (neat, cm^{-1}): 2922 (w, CH), 1575 (w, Ph), 1486 (vs, Ph-Me), 1247 (vs, C═CO), 1014 (s, CO), 755 (m, PPh).

[Ni(L3X)Br$_2$]. Starting from 327 mg (1.50 mmol) of $NiBr_2$ and 441 mg (1.00 mmol) of L3X and employing procedure B, 639 mg (0.97 mmol, 97%) of brown-reddish crystals was isolated. Elem anal. Found (calcd) for $C_{29}H_{30}Br_2NiP_2$: C, 53.30 (52.85); H, 4.98 (4.59). ESI-MS. Found (calcd) for $[M + H]^+$: *m*/*z* 659.84 (659.00). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 25 °C): δ 0.93 (s, 6H, $CH_2C(CH_3)_2CH_2$), 2.27 (d, 4H, *J* = 2.9 Hz, $CH_2C(CH_3)_2CH_2$), 7.26 (m, 12H, *o*-Ph−H and *p*-Ph−H), 7.34 (m, 8H, *m*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, DMSO-*d*$_6$, 25 °C): no peaks.

[Ni(oMeO-L3X)Br$_2$]. Employing procedure B while starting from 327 mg (1.50 mmol) of $NiBr_2$ and 559 mg (1.00 mmol) of oMeO-L3X, 316 mg (0.41 mmol, 41%) of dark-pink crystals was isolated. Elem anal. Found (calcd) for $C_{33}H_{38}Br_2NiO_4P_2$: C, 50.01 (50.87); H, 5.06 (4.92). ESI-MS. Found (calcd) for $[M - Br]^+$: *m*/*z* 698.65 (699.20) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.55 (s, 6H, $CH_2C(CH_3)_2CH_2$), 3.00 (vbr, 4H, $CH_2C(CH_3)_2CH_2$), 3.99 (s, 12H, $-OCH_3$), 7.09 (m, 8H, 2 × *m*-Ph−H), 7.45 (t, 4H, *J* = 7.8 Hz, *p*-Ph−H), 8.37 (br, 4H, *o*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oMeO-L3X)Br$_2$]*. Using procedure B and starting from 327 mg (1.50 mmol) of $NiBr_2$ and 588 mg (1.00 mmol) of oMeO-L3X*, 513 mg (0.64 mmol, 42%) of pink crystals was isolated after recrystallization from a dichloromethane/diethyl ether mixture. Elem anal. Found (calcd) for $C_{35}H_{42}Br_2NiO_4P_2$: C, 53.36 (52.08); H, 5.31 (5.24). ESI-MS. Found (calcd) for $[M - Br]^+$: *m*/*z* 726.82 (727.25). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.47 (t, 6H, *J* = 7.0 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 0.82 (q, 4H, *J* = 7.2 MHz, $CH_2C(CH_2CH_3)_2CH_2$), 2.5 (vbr, $CH_2C(CH_2CH_3)_2CH_2$), 3.97 (s, 12H, $-OCH_3$), 7.14 (br, 8H, 2 × *m*-Ph−H), 7.44 (t, 4H, *J* = 7.4 Hz, *p*-Ph−H), 8.40 (br, 4H, *o*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oMeOmMe-L3)I$_2$]. $Ni(OAc)_2{\cdot}4H_2O$ (248.2 mg, 1.00 mmol) and oMeOmMe-L3 (597.9 mg, 1.00 mmol) were dissolved in 5 mL of acetone, resulting in a dark-red-brown solution. The subsequent addition of 3 mL of hydroiodic acid (57 wt %) gives a black solution. Layered recrystallization of the obtained precipitate in dichloromethane/heptane resulted in the formation of deep-purple crystals. Filtration and drying in vacuo yielded purple crystals (165 mg, 18%). Elem anal. Found (calcd) for $C_{35}H_{42}I_2NiO_4P_2$: C, 47.00 (46.65); H, 4.54 (4.70); Ni, 7.41 (6.51). ESI-MS. Found (calcd) for $[M - I]^+$: *m*/*z* 773.3 (773.1). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.56 (br, 2H, PCH_2CH_2), 2.30 (s, 12H, $-CH_3$), 4.03 (s, 12H, $-OCH_3$), 7.16 (br, 4H, *m*-*H*), 7.16 (br, 4H, *p*-*H*), 7.96 (br, 4H, *o*-*H*). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ 16.19 (s, PCH_2CH_2), 19.79 (s, PCH_2CH_2), 21.00 (s, $-CH_3$), 57.13 (s, OCH_3), 112.22 (s, PCC(OMe)CH), 129.93 (s, PCCHCMe), 134.60 (s, PCCH), 142.01 (s, PCCH), 163.68 (PCC(OMe)CH). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no signal. IR (neat, cm^{-1}): 2980 (w, CH), 1600 (w, Ph), 1495 (vs, Ph−Me), 1249 (m, Ph), 1249 (vs, C═CO), 1010 (s, CO), 750 (s, PPh).

[Ni(L3X)I$_2$]. Starting from 249 mg (1.00 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ and 440 mg (1.00 mmol) of L3X, 727 mg (0.97 mmol, 97%) of dark-purple crystals was isolated. Elem anal. Found (calcd) for $C_{29}H_{30}I_2NiP_2$: C, 46.05 (46.26); H, 4.11 (4.02). ESI-MS. Found (calcd) for $[M + H]^+$: *m*/*z* 751.08 (753.00). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.52 (s, 6H, $CH_2C(CH_3)_2CH_2$), 1.24 (d, 4H, *J* = 5.8 Hz, $CH_2C(CH_3)_2CH_2$), 6.72 (t, 4H, *J* = 7.4 Hz, *p*-Ph−H), 7.62 (d, 8H, *J* = 7.6 Hz, *o*-Ph−H), 8.54 (t, 8H, *J* = 7.3 Hz, *m*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oMeO-L3X)I$_2$]. Starting from 249 mg (1.00 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ and 561 mg (1.00 mmol) of oMeO-L3X, 765 mg (0.88 mmol, 88%) of dark-purple crystals was isolated. Elem anal. Found (calcd) for $C_{33}H_{38}I_2NiO_4P_2$: C, 45.55 (45.40); H, 4.59 (4.39). ESI-MS. Found (calcd) for $[M - I]^+$: *m*/*z* 746.61 (746.20). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.51 (s, 6H, $CH_2C(CH_3)_2CH_2$), 2.80 (br, 4H, $CH_2C(CH_3)_2CH_2$), 3.97 (s, 12H, $-OCH_3$), 7.02 (d, 4H, *J* = 8.3 Hz, −C(OMe)C*H*−), 7.10 (t, 4H, *J* = 7.4 Hz, −PCCHC*H*-), 7.46 (t, 4H, *J* = 7.4 Hz, *p*-Ph-H), 8.38 (br, 4H, *o*-Ph-H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oMeO-L3X)I$_2$]*. Starting from 249 mg (1.00 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ and 590 mg (1.00 mmol) of oMeO-L3X*, 615 mg (0.68 mmol, 68%) of dark-purple crystals was isolated. Elem anal. Found (calcd) for $C_{35}H_{42}I_2NiO_4P_2$: C, 47.48 (46.65); H, 4.73 (4.70). ESI-MS. Found (calcd) for $[M - I]^+$: *m*/*z* 772.75 (774.25). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.46 (t, 6H, *J* = 7.1 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 0.77 (q, 4H, *J* = 6.9 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 2.5 (vbr, 4H, $CH_2C(CH_2CH_3)_2CH_2$), 3.95 (s, 12H, $-OCH_3$), 7.11 (br, 8H, 2 × *m*-Ph−H), 7.45 (br, 4H, *p*-Ph−H), 8.39 (br, 4H, *o*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no peaks.

[Ni(oEtO-L3X)I$_2$] (**C3**)*. $Ni(OAc)_2{\cdot}4H_2O$ (47.9 mg, 0.19 mmol) was dissolved in 5 mL of ethanol. The resulting green solution was degassed and added to oEtO-L3X* (112.3 mg, 0.19 mmol) dissolved in 5 mL of acetone. This resulted in a brown solution. The subsequent addition of 2 mL of hydroiodic acid (57 wt %) gave a precipitate. Filtration and drying in vacuo yielded a dark-purple powder (86.00 mg, 50%). Elem anal. Found (calcd) for $C_{39}H_{50}I_2NiO_4P_2$: C, 48.47 (48.93); H, 5.51 (5.26); Ni, 6.57 (6.13). ESI-MS. Found (calcd) for $[M - 2I + OH]^+$: *m*/*z* 720.33 (719.26). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 0.47 (t, 6H, $PCH_2C(CH_2CH_3)_2$), 0.78 (q, 4H, $PCH_2C(CH_2CH_3)_2$), 1.13 (br, 12H, OCH_2CH_3), 1.49 (br, 4H, $PCH_2C(CH_2CH_3)_2$), 4.31 (br, 8H, OCH_2CH_3), 7.20 (br, 8H, *m*-*H*), 7.39 (br, 4H, *p*-*H*), 8.16 (br, 4H, *o*-*H*). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): 6.94 (s, $PCH_2C(CH_2CH_3)_2$), 14.44 (s, OCH_2CH_3), 30.83 (s, $PCH_2C(CH_2CH_3)_2$), 64.29 (s, OCH_2CH_3), 104.69 (s, PCCHCH), 167.41 (s, PCC(OMe)CH). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): no signal. IR (neat, cm^{-1}): 2978 (w, CH), 1573 (m, Ph), 1480 (m, Ph), 1436 (s, ROR), 1259 (m, C═CO), 1031 (s, CO), 750 (vs, PPh).

[(Ni(L3X))$_2$(μ-OH)$_2$](PF$_6$)$_2$. Starting from 178 mg (0.75 mmol) of $NiCl_2{\cdot}6H_2O$ and 330 mg (0.75 mmol) of L3X, 37 mg (0.03 mmol, 8%) of orange crystals was isolated. Elem anal. Found (calcd) for $C_{58}H_{62}F_{12}Ni_2O_2P_6$: C, 53.12 (52.68); H, 5.19 (4.73). ESI-MS. Found (calcd) for $[M]^{2+}$: *m*/*z* 516.30 [516.20]. ^{1}H NMR (300 MHz, MeOD, 25 °C): δ 0.60 (s, 12H, $CH_2C(CH_3)_2CH_2$), 1.1 (d, 8H, $CH_2C(CH_3)_2CH_2$), 7.39 (br, 24H, *o*-Ph−H and *p*-Ph−H), 7.63 (br, 16H, *m*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, MeOD, 25 °C): δ 17.3. IR (neat, cm^{-1}): 731.6 (Ar−H), 830.0 (P−F), 2951.7 (CH_2 alkane), 3607.0 (μ-OH).

*[(Ni(oMeO-L3X))$_2$(μ-OH)$_2$](PF$_6$)$_2$ (**C5**)*. From 178 mg (0.75 mmol) of $NiCl_2{\cdot}6H_2O$ and 420 mg (0.75 mmol) of oMeO-L3X, 266 mg (0.17 mmol, 45%) of red needlelike crystals was isolated. Elem anal. Found (calcd) for $C_{66}H_{78}F_{12}Ni_2O_{10}P_6$: C, 49.51 (50.73); H, 5.28 (5.03). ESI-MS. Found (calcd) for $[M]^{2+}$: *m*/*z* 637.33 (636.30). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ 0.59 (s, 12H, $CH_2C(CH_3)_2CH_2$), 2.20 (t, 8H, *J* = 5.7 Hz, $CH_2C(CH_3)_2CH_2$), 3.91 (s, 24H, $-OCH_3$), 7.09 (m, 16H, 2 × *m*-Ph−H), 7.59 (m, 8H, *p*-Ph−H), 7.61 (br, 8H, *o*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, MeOD, 25 °C): δ 15.7 (s), −143.6 (pentet, *J* = 708 Hz, PF_6). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ 3.46 (s, PF_6), 5.36 (s, PF_6) ppm. IR (neat, cm^{-1}): 764.3 (Ar−H), 836.3 (P−F), 1245.9 (Ar−O−CH_3), 2946.1 (CH_2 alkane), 3613.2 (μ-OH).

[(Ni(oMeO-L3X))$_2$(μ-OH)$_2$](PF$_6$)$_2$*. Starting from 178 mg (0.75 mmol) of $NiCl_2{\cdot}6H_2O$ and 442 mg (0.75 mmol) of oMeO-L3X*, 174 mg (0.11 mmol, 29%) of red crystals was isolated. Elem anal. Found (calcd) for $C_{70}H_{86}F_{12}Ni_2O_{10}P_6$: C, 51.86 (51.94); H, 5.77 (5.36). ESI-MS. Found (calcd) for $[M]^{2+}$: *m*/*z* 664.25 (664.35). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ 0.38 (t, 12H, *J* = 7.2 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 0.81 (q, 8H, *J* = 7.5 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 2.08 (t, 8H, *J* = 6.0 Hz, $CH_2C(CH_2CH_3)_2CH_2$), 3.80 (s, 24H, $-OCH_3$), 6.98 (t, 16H, *J* = 8.0 Hz, 2 × *m*-Ph−H), 7.55 (t, 8H, *J* = 8.0 Hz, *p*-Ph−H), 7.80 (br, 8H, *o*-Ph−H). ^{31}P{^{1}H} NMR (121 MHz, MeOD, 25 °C): δ 14.3 (s), −143.4 (pentet, *J* = 711 Hz,

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PF_6). IR (neat, cm^{-1}): ν 755.3 (Ar−H), 835.2 (P−F), 1242.8 (Ar−O−CH_3), 2962.8 (CH_2 alkane), 3609.2 (μ-OH).

*[Ni(oMeO-L3X)(NH_3)(OAc)](PF_6) (**C4**).* $Ni(OAc)_2{\cdot}4H_2O$ (124 mg, 0.50 mmol) was dissolved in 15 mL of ethanol and mixed with an equimolar amount of oMeO-L3X (280 mg) in 12.5 mL of chloroform. After the solutions were mixed, a clear red solution was obtained. Then, NH_4PF_6 (245 mg, 1.50 mmol) in 5 mL of ethanol was added, and a clear orange solution was obtained. The solution was slowly pipetted under a layer of diethyl ether. After a few days, a yellow/golden crystalline compound was formed and collected by filtration (354 mg, 0.42 mmol, 83%). Elem anal. Found (calcd) for $C_{35}H_{44}F_6NNiO_6P_3$: C, 50.06 (50.02); H, 5.36 (5.28); N, 1.73 (1.67). ESI-MS. Found (calcd) for $[M - NH_3]^+$ and $[M - OAc]^+$, respectively: m/z 678.88 (678.34), 635.83 (635.32). ^1H NMR (300 MHz, MeOD, 25 °C): δ 0.71 (s, 6H, $CH_2C(CH_3)_2CH_2$), 1.06 (s, 3H, OAc), 2.39 (br, 4H, $CH_2C(CH_3)_2CH_2$), 3.88 (s, 6H, $-OCH_3$), 3.97 (s, 6H, $-OCH_3$), 7.13 (br, 8H, 2 × *m*-Ph−H), 7.65 (br, 4H, *p*-Ph−H), 8.11 (br, 4H, *o*-Ph−H). $^{31}P\{^1H\}$ NMR (121 MHz, MeOD, 25 °C): δ 13.8 (s, P trans to NH_3), 13.1 (s, P trans to OAc), −143.4 (pentet, J = 705 Hz, PF_6). IR (neat, cm^{-1}): 755.3 (Ar−H), 834.2 (P−F), 1246.7 (Ar−O−CH_3), 2967.0 (CH_2 alkane).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, perspective views of **C1**−**C3** (Figure S1), and activities and selectivities of catalytic experiments (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(30) A total of 19 CIFs were found in the Cambridge Structure Database (version 5.33, Nov 2011, including four updates) that contained a P_2Ni unit, wherein at least one of the P-donor ligands had an *o*-alkoxy substituent. The oxidation state of Ni was 2+ for all structures except POHMEE (Ni^{3+}) and XOBJOO (Ni^0). No short Ni···O(alkoxyaryl) distances are present in OKUFUV, QOFCAP, QOFCET, QOSTEX, QOSTIB, XABPIA, and XOBJII (all containing a bidentate PP ligand) or in XAWVIB, ZAXPEV, ZAXPIZ, ZAXPOF, and ZAXPUL (all containing a bidentate PO ligand). Short Ni···O(alkoxyaryl) distances were found in MUPFOT (2.621 and 2.604 Å), MUPFUZ (2.948 Å), and MUPGAG (2.861 Å), which all contain the (for MUPFUZ and MUPGAG demethylated) tetradentate P-ligand 1,2,3,4-tetrakis[bis(2-methoxyphenyl)phosphino]cyclobutane. The two short Ni···O(alkoxyaryl) distances (both 2.785 Å) in POHMAA (containing two bidentate PO ligands) might well be due to the two very bulky 2,4,6-trimethoxyphenyl substituents on each P-donor atom. Finally, a short Ni···O(alkoxyaryl) distance (2.866 Å) is present in QOSTAT, which has a $[P_2Ni(H_2O)_2]^{2+}$ coordination sphere.

(31) A total of 12 CIFs were found in the Cambridge Structure Database (version 5.33, Nov 2011, including four updates) containing a $MP(o\text{-alkoxyaryl})_2CCCP(o\text{-alkoxyaryl})_2$ ring (M = any metal except Ni). Neither BUGVOP, BUGVUV, BUGWAC, JOCJAN, MEKTAY, MEKTEC, and PEYXEX ($[P_2Pd^{2+}Anion_2]$ type), nor BUGWEG, EKUQOR, and EKUQUX ($[(P_2)_2Pd^{2+}]^{2+}$ type), nor TUCSUG ($[P_2Ru^{2+}CpCl]$ type) exhibit a M···O(alkoxyaryl) interaction. Short Pd···O(alkoxyaryl) distances (2.811 and 2.825 Å) were found in

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