Articles

Oxidative Addition of Allylammonium BPh_4^- to Nickel(0): Synthesis, Crystal Structure, Fluxional Behavior, and Catalytic Activity of Chiral [(η^3-allyl)-(NH_3)(PCy_3)Ni]BPh_4

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The synthesis, crystal structure, fluxional behavior, and reactivity of [(η^3-C_3H_5)Ni(PCy_3)-(NH_3)]BPh_4 (**1**) are described. Complex **1** was obtained by oxidative addition of allylammonium tetraphenylborate, (CH_2═$CHCH_2NH_3$)BPh_4, to Ni(0) [(Cy_3P)$_2$Ni(η^2-CO_2) or (Cy_3P)$_2$-NiNNNi(PCy_3)$_2$], under mild conditions, through selective activation of the N−C-allyl bond. Complex **1** is a unique example of an allyl−Ni cationic complex with three different ligands and donor atoms. It has been fully characterized both in the solid state and in solution. The X-ray study shows that the cation [(η^3-C_3H_5)Ni(PCy_3)(NH_3)]$^+$ (**1**$^+$) is chiral as a result of the two possible orientations of the allyl group and the different ancillary ligands bound to the (η^3-C_3H_5)Ni$^+$ moiety. In the solid state, cation **1**$^+$ exists as a racemic mixture of the two enantiomers **1a**$^+$ and **1b**$^+$. In solution, complex **1**$^+$ is involved in a slow fluxional process that causes the left-to-right exchange of *syn* and *anti* protons of the allyl group and leads to the interconversion of the two enantiomeric forms **1a**$^+$ and **1b**$^+$. The thermal stability of **1**, in solution, has also been investigated. At 323 K, in THF, complex **1** is poorly stable and decomposes with formation of organic products, among which are benzene and allylbenzene. The formation of allylbenzene represents the first example of Ni-promoted phenyl transfer from tetraphenylborate to a π-allyl ligand. In the presence of dihydrogen (0.1 MPa) as cocatalyst, **1** promotes the selective head-to-tail oligomerization of methylacrylate (MA) to give dimethyl methyleneglutarate (DMG) and the trimer 2,4,6-tri(carbomethoxy)-1-hexene, through the intermediacy of a Ni−H intermediate. The catalytic activity of the system **1**/H_2 has been compared with that exhibited by [*trans*-(H)Ni(PCy_3)$_2$(η^1(*N*)-$PhCH_2N$═CMe_2)]BPh_4 (**3**), easily obtained by reaction of [($PhCH_2$)HN═CMe_2]BPh_4 with (Cy_3P)$_2$NiNNNi(PCy_3)$_2$, which also promotes the selective head-to-tail oligomerization of MA to afford the same products. The formation of a Ni−H species is demonstrated to be the key step in the di- and trimerization process.

Introduction

In a recent study[1] we have reported on the reactivity of alkylammonium and -iminium BPh_4^- salts, prepared in a rigorously anhydrous form according to a new CO_2-based synthetic procedure,[2,3] toward phosphine complexes of Ni(0). We have described the first examples of oxidative addition of alkylammonium- or -iminium cations to a transition metal center.

The iminium cation of [($PhCH_2$)HN═CMe_2]BPh_4 undergoes a selective N−H activation, and the new

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terminal cationic hydrido complex of Ni produced has been structurally characterized.[1] A different reactivity is shown by $(CH_2{=}CHCH_2NH_3)BPh_4$ and $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$, which oxidatively add to $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$ or $(Cy_3P)_2NiNNNi(PCy_3)_2$ (eqs 1−3), under mild conditions, via a selective activation of the N−C-allyl bond. This uncommon reaction affords $[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]BPh_4$ (**1**) and $[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(\eta^1(N)\text{-}HN{=}CMe_2)]BPh_4$ (**2**) and represents a new, easy-way to synthesize unprecedented asymmetric cationic π-allyl−nickel systems.

$$(Cy_3P)_2Ni(\eta^2\text{-}CO_2) + (CH_2{=}CHCH_2NH_3)BPh_4 \xrightarrow{253\ K,\ THF,\ CO_2\ or\ N_2\ (0.1\ MPa)} [(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]BPh_4 + PCy_3 + CO_2 \quad (1)$$

$$(Cy_3P)_2NiNNNi(PCy_3)_2 + 2(CH_2{=}CHCH_2NH_3)BPh_4 \xrightarrow{293\ K,\ THF,\ N_2} 2[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]BPh_4 + 2PCy_3 + N_2 \quad (2)$$

$$(Cy_3P)_2NiNNNi(PCy_3)_2 + 2[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4 \xrightarrow{293\ K,\ toluene,\ N_2} 2[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(\eta^1(N)\text{-}HN{=}CMe_2)]BPh_4 + 2PCy_3 + N_2 \quad (3)$$

The chiral cationic Ni complexes **1** and **2** have been fully characterized, in solution, by ^1H, ^{13}C, and ^{31}P NMR.[1] We report here the solid state structure of **1** and a VT ^1H NMR study relevant to its solution dynamic behavior.

However, cationic π-allyl−nickel complexes such as $[(\eta^3\text{-}C_3H_5)NiBr]_2/PR_3/AgBF_4$ or $(\eta^3\text{-}C_3H_5)_2Ni/PR_3/HBF_4$ have been proved to be particularly effective, under mild conditions, for the dimerization of methyl acrylate (MA) to afford both dimethyl hex-2-enedioate (DHD) and dimethyl 2-methylpentenedioate (MPD).[4] The formation of these species involves the tail-to-tail and head-to-tail coupling of two monomeric units, respectively. A key role in these reactions seems to be played by cationic nickel hydride species, formed under the working conditions. The new π-allyl−Ni complexes **1** and **2** and the cationic hydride $[trans\text{-}(H)Ni(PCy_3)_2(\eta^1(N)\text{-}PhCH_2N{=}CMe_2)]BPh_4$ (**3**), which bear both P- and N-donor ligands coordinated to the metal, have been compared as catalysts for the oligomerization of methyl acrylate, and the results are described in this paper.

Results and Discussion

Isolation and X-ray Crystal Structure of $[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]BPh_4$ (1). By reacting $(CH_2{=}CHCH_2NH_3)BPh_4$ with $(Cy_3P)_2NiNNNi(PCy_3)_2$ or $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$, **1** is isolated as yellow crystalline air-sensitive needles. **1** has been fully characterized in the solid state by X-ray diffraction.

Figure 1 shows a view of the structure of the $[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]^+$ ($\mathbf{1}^+$) cation of complex **1**, with the atom-numbering scheme. Selected bond distances and angles are given in Table 1.

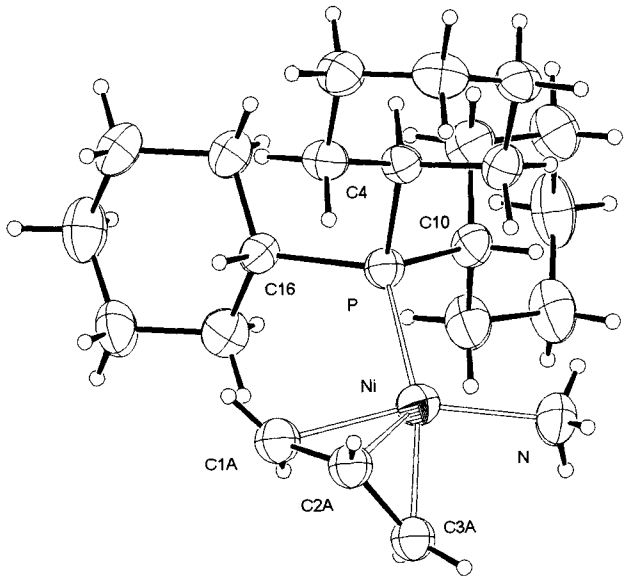

Figure 1. ORTEP view of the structure of the isomer *M* of the cation of the complex **1** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) (with Esd's in Parentheses) for Compound 1

Ni−P	2.222(2)	P−C(4)	1.864(7)
Ni−N	1.962(5)	P−C(10)	1.858(7)
Ni−C(1A)	2.06(2)	P−C(16)	1.849(7)
Ni−C(2A)	2.04(2)	C(1A)−C(2A)	1.57(3)
Ni−C(3A)	2.05(2)	C(2A)−C(3A)	1.50(2)
Ni−C(1B)	2.02(2)	C(1B)−C(2B)	1.43(3)
Ni−C(2B)	2.02(2)	C(2B)−C(3B)	1.36(3)
Ni−C(3B)	2.14(2)		

N−Ni−P	101.4(2)	C(4)−P−Ni	108.6(2)
N−Ni−C(3A)	91.4(6)	C(10)−P−Ni	111.7(3)
N−Ni−C(3B)	90.7(5)	C(16)−P−Ni	116.5(3)
C(1A)−Ni−P	96.5(6)	C(10)−P−C(4)	104.6(3)
C(1B)−Ni−P	96.3(5)	C(16)−P−C(4)	103.8(3)
C(3A)−Ni−C(1A)	69.9(7)	C(16)−P−C(10)	110.6(3)
C(1B)−Ni−C(3B)	70.6(7)		

The coordination around nickel is that expected for a monomeric 16-electron η^3-allyl complex, involving also the P atom from the PCy_3 ligand and N from the ammonia. The bond distances and angles are quite normal. The allyl group is disordered and distributed in two positions with equal occupancy factors. The orientation of the two allyl images is in a such way that the *meso* carbon atoms C2A and C2B are on opposite sides with respect to the PNiN coordination plane. The orientation of these carbon atoms determines chirality in the square-planar complex. The torsion angles that can define the chirality are τ[P−Ni−C1A−C2A] = −143(1)° and τ[P−Ni−C1B−C2B] = 160(1)°. The best terms describing the chirality, in our opinion, are *M* and *P* (related to the signs of the torsion angles).[5] In the [azaphosphole-η^3-allyl-NiCl] complex, the ancillar phosphole ligand is chiral and partially steroselective as the allyl group is disordered and distributed in two positions with approximately 0.80 and 0.20 occupancy factors, with the *M* isomer predominant.[6]

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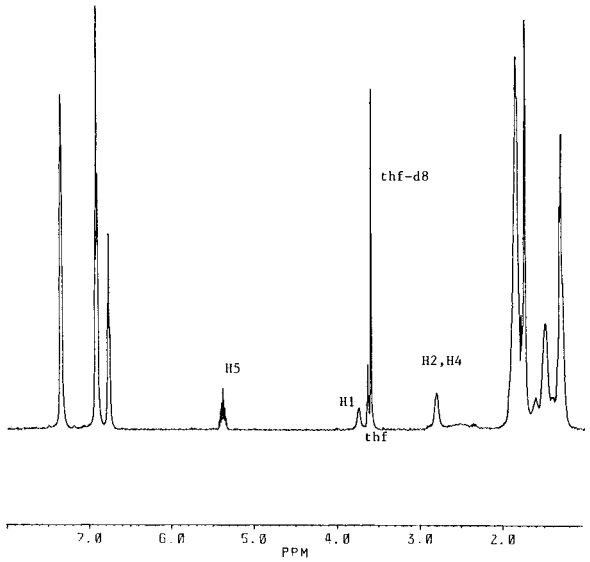
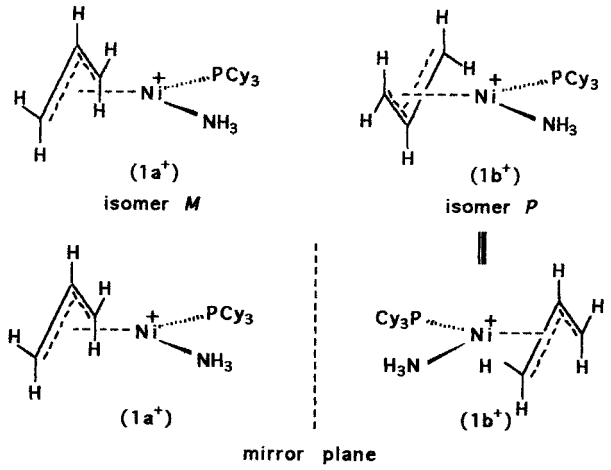


Figure 2. ^{1}H NMR spectrum (THF-d_8, 500 MHz, 293) of complex **1**.

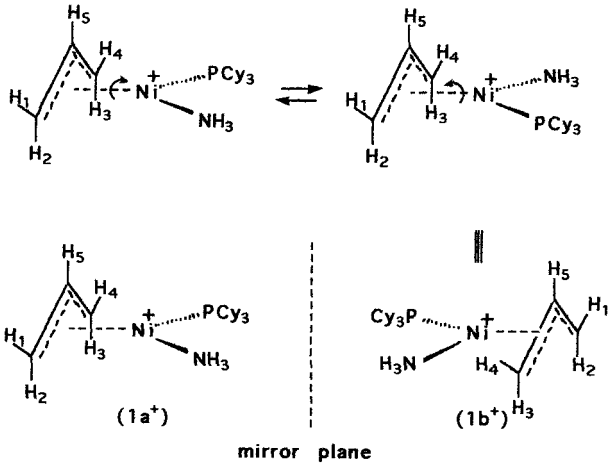
Scheme 1. Schematic Representation of the Two Stereoisomers 1a$^+$ and 1b$^+$ and Their Enantiomeric Relationship



Solution Dynamic Behavior of [(η³-C₃H₅)Ni(PCy₃)(NH₃)]BPh₄ (1). VT ^{1}H NMR of 1. The X-ray study clearly shows that, in the solid state, complex **1**$^+$ exists as a racemic mixture of the two enantiomeric forms **1a**$^+$ and **1b**$^+$ (Scheme 1). This is a consequence of the two possible orientations of the allyl group and of the different ancillary ligands bound to the (η^3-C_3H_5)-Ni^+ moiety.

Figure 2 shows the ^{1}H NMR spectrum of **1** in THF-d_8, at 500 MHz and 293 K. An ABCDX spin pattern can be observed for the allyl ligand,[7] apparently consistent with a static structure. However, in solution, at 293 K, cation **1**$^+$ is involved in a slow (with respect to the chemical shift time scale) dynamic process that brings about the left-to-right exchange of *syn* and *anti* protons of the allyl group[8,9] and causes the interconversion of the enantiomeric forms **1a**$^+$ and **1b**$^+$ (Scheme 2).

Scheme 2. Fluxional Behavior of Cation 1$^+$; Interconversion of the Two Enantioconformers 1a$^+$ and 1b$^+$



In fact, irradiation of the accidentally isochronous resonances at 2.78 ppm (H2 and H4, 2H) causes the almost complete disappearance of the signal at 3.72 ppm (H1), while the multiplet at 5.37 ppm (H5) collapses into a broad singlet, suggesting the existence of an exchange process through which spin saturation[9b,d,10] is transferred from H2 and H4 to the other end protons of the allyl group. Accordingly, but more informatively for the clarification of the nature of the exchange process, irradiation of the signal at 3.72 ppm (H1) also causes saturation of one of the two accidentally isochronous resonances at 2.78 ppm (as clearly indicated by the intensity of this signal that, under the above conditions, practically integrates for 1H), while the multiplet at 5.37 ppm (H5, 1H) converts into a triplet ($J \cong 13.5$ Hz), showing that, under the working conditions, H5 can couple only to the *anti* protons (H2 and H3). This feature clearly reveals that, upon irradiation of H1, spin saturation is transferred through the exchange process from H1 to H4 and not to H2, establishing in an unambiguous way that the related dynamic process involves the "left to right" exchange of *syn* and *anti* protons of the allyl group.[11]

Accordingly, the NMR spectrum of **1** is temperature dependent. At temperatures below 293 K the rate of the exchange process is slowed. Figure 3 shows the ^{1}H spectrum (THF-d_8, 500 MHz) of **1** at 233 K in the range 5.6−2.6 ppm.

H2 and H4, accidentally isochronous at 293 K, show resonances at 2.89 and 2.81 ppm, respectively. The signal due to H4 is broad, without any fine structure, whereas the H2 signal is roughly a doublet of doublets

(7) The signal due to H3 cannot be located, as it is masked by the resonances due to the PCy_3 protons. H2 and H4 are accidentally isochronous in the solvent used (THF-d_8). However, in CD_2Cl_2, at 293 K, at either 500 or 200 MHz, H2 and H4 give two distinct, albeit broad and partially overlapped, signals at 2.57 and 2.60 ppm.[1]

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(11) Most likely, the interconversion takes place intramolecularly through rotation of the η^3-allyl group around the allyl baricenter−Ni vector.[1]

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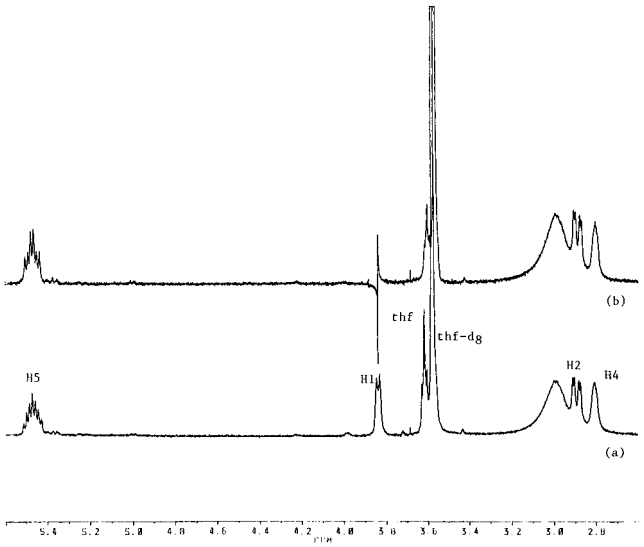
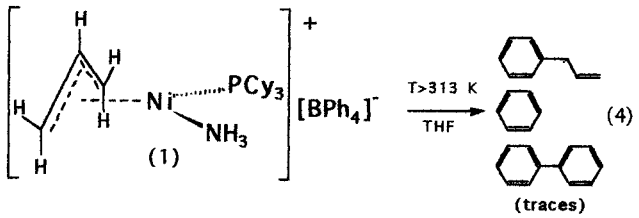


Figure 3. (a) ^{1}H NMR (THF-d_8, 500 MHz, 233 K) spectrum of complex **1** in the range 5.6−2.6 ppm. (b) Proton spectrum (THF-d_8, 500 MHz, 233 K, 5.6−2.6 ppm) obtained upon irradiation on the H1 resonance.

(J = 14.5 Hz, 4.7 Hz).[12] Interestingly, at 233 K, irradiation of the doublet at 3.83 ppm (J = 7.6 Hz, H1) does not produce any significant change for the signals due to H2 and H4, but converts the septet at 5.46 ppm ($J \cong 7$ Hz, H5) into a triplet of doublets (J = 7 Hz, 13.7 Hz), as expected, for a static allyl ligand, because of coupling of H5 with H2, H3, and H4. These results clearly indicate that, at 233 K, the mechanism able to transfer spin saturation effectively between H1 and H4 is no longer operating and the dynamic process that is responsible for their exchange at room temperature is practically blocked.

The poor thermal stability of **1** (see below) makes difficult a correct interpretation of the dynamic behavior of **1** above 293 K. At 313 K (200 MHz, THF-d_8) the H1 and H4 resonances coalesce into a broad signal (2H) approximately centered at 3.25 ppm. However, the corresponding signal resulting from the coalescence of the signals of the *anti* protons H2 and H3 is masked by the phosphine protons. From T_c = 313 K, the energy barrier, ΔG^* (313 K), for the exchange process (under the new working conditions) can be estimated (61 kJ/mol).[13] Unfortunately, the reactivity exhibited by **1** above 293 K prevented any further investigation.

Thermal Behavior of 1 in Solution. Both the ^{1}H and ^{13}C NMR spectra of a THF-d_8 solution of **1** clearly demonstrate that, above 313 K, complex **1** is poorly stable and decomposes with formation of organic products (eq 4). A new resonance at 7.29 ppm (singlet) in the ^{1}H spectrum (500 MHz, 323 K) reveals the formation of benzene, further confirmed by GC−MS. New signals are also evident at 3.36 (d, $^3J_{H-H}$ = 6.6 Hz), 5.04 (dm, $^3J_{HC=CH,trans}$ = 17.0 Hz), 5.01 (dm, $^3J_{HC=CH,cis}$ = 10.2 Hz),



and 5.95 ppm (m). The integration of these signals and the determination of the coupling constants show that these resonances are intercorrelated and can be reasonably assigned to the protons of the allyl group of allylbenzene. The GC−MS analysis of the solution confirms the presence of this species, together with the formation of minor amounts of isomeric products and biphenyl.

The formation of allylbenzene represents the first example of Ni-promoted phenyl transfer from tetraphenylborate to a π-allyl ligand. It recalls the phenylation of cationic allyl−palladium(II) complexes by a tetraphenylborate anion.[14] Such phenyl transfer[15] has been reported for transition metal coordinated isocyanides,[16] mono-[17a,c] and diolefins,[18] and aldehydes.[17b]

It is worth noting that, in our case, allylbenzene is formed in slightly higher amount than benzene. In fact, after 1 h at 323 K, the PhC_3H_5/PhH molar ratio is equal to 1.7 (as determined by NMR).

Most likely (Scheme 3), the formation of allylbenzene involves in a first step the migration of phenyl from boron to nickel[19] with formation of an allyl−phenyl nickel complex, from which allylbenzene can be obtained by reductive elimination. The implication of BPh_3 seems to be less probable.[20]

Phenyl transfer from BPh_4^- to a transition metal center[15] is a well-known reaction, which we have deeply investigated using Rh-based systems.[17] We have shown that this reaction is promoted by the π-coordination of the anion to Rh and is a key step in several processes of functionalization of unsaturated organic substrates, such as olefins[17c] or aldehydes.[17b]

The formation of benzene and biphenyl is a typical feature of the reactivity of tetraphenylborate anion in the presence of Rh systems.[17] In the present case, we

(12) Other minor couplings are also evident in the spectrum, but they are not well resolved. This feature makes difficult the exact evaluation of the coupling constants from the signal. Nevertheless, the line separation of 14.5 and 4.7 Hz reflects the fact that H2 is coupled to H5 and the P atom of the PCy_3 ligand, respectively.[8]

(13) The temperature range investigated was 295−328 K. It is worth noting that, upon cooling the NMR sample from 328 back to 295 K, the spectrum of the allyl group protons was different from the starting one, most probably because the reaction occurred and species were present in solution.

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(20) The BPh_3 mechanism is reminiscent, in some aspects, of that proposed by Venanzi[21] for the reaction of BAr_4^- with cationic disolvento complexes *cis*-$[Pt(ROH)_2L_2]^{2+}$ (R = H or Me), which affords platinum−aryl derivatives *trans*-$[PtAr(ROH)L_2]^+$. In this case, BAr_3, formed by rapid proton transfer from the coordinated protic solvent, ROH, to BAr_4^-, has been demonstrated to be the phenylating species, most likely through the intermediate formation of an alkoxo-bridged Pt−OR−BAr_3 species. If, in our case, an analogous mechanism were operating (with coordinated ammonia playing a role similar to that of bound-ROH), benzene should form faster than allylbenzene, or, if the phenylation step were more rapid than the proton transfer, the PhC_3H_5/PhH molar ratio should remain close to 1 throughout the reaction.

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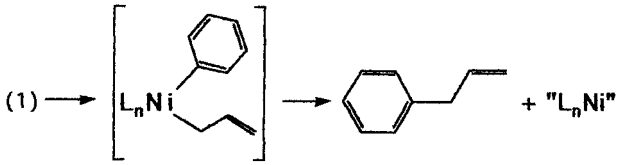
Scheme 3. Phenyl Transfer from Tetraphenylborate Boron Atom to Coordinated π-Allyl in Complex 1

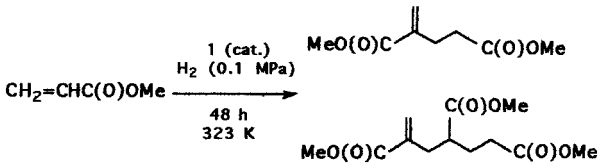


can rule out that the hydrogen source for the formation of benzene is the solvent (THF-d_8). As a matter of fact, Ph-D is detected in solution (by GC−MS) in traces or not at all. It is worth noting that the GC−MS analysis of the reaction solution does not show any signal that can be attributed to free BPh_3. It is plausible that BPh_3 generated upon phenyl transfer from the boron atom of BPh_4^- ion to nickel might be further involved in the formation of benzene. However, we do not exclude that a very minor part of benzene formed might arise from the direct protolysis of one of the B−C bonds of BPh_4^- by coordinated ammonia. This reaction is reminiscent of the solution behavior of alkylammonium tetraphenylborate salts (RR′R″NH)BPh_4 (R = R′ = R″ = H, alkyl), which can decompose intramolecularly to give benzene and an RR′R″NBPh_3 adduct.[2] For (RR′R″NH)-BPh_4 salts, in THF solution at room temperature, as a result of cation−solvent H-bonding interactions, such a process usually takes place slowly depending on the nature of the alkylammonium ion, but can be accelerated by increasing the temperature.

Catalytic Activity of Complexes 1 and 3: Selective Head-to-Tail Oligomerization of Methyl Acrylate. Catalytic oligomerization of methyl acrylate has received growing attention in the past few years. Interest for this topic mainly comes from the fact that catalytic tail-to-tail dimerization of acrylates represents an attractive alternate route to adipic acid, used for Nylon-66 production. Also head-to-tail dimerization of acrylic esters has synthetic relevance, as it affords dicarbonyl compounds successfully used as monomers in copolymerization reactions.[22,23] H−T oligomerization of acrylic compounds and, more generally, of α,β-unsaturated esters, amides, and nitriles is known to be promoted by phosphines, aminophoshines, and related compounds.[24] In general, the synthetic utility of H−T dimerization has been limited by the modest yield and selectivities toward the H−T dimeric products, but it would be greatly enhanced if new selective catalytic systems could be found.

Unlike Pd-,[25] Ru-,[26] and Rh-[27]based systems, widely investigated as catalysts, Ni-based complexes have been sparingly used as promoters in the oligomerization of methyl acrylate, the only precedents being limited to the cationic π-allyl systems mentioned in the Introduction.[4,28]

Scheme 4. Head-to Tail Oligomerization of Methyl Acrylate Promoted by Complex 1



We have found that in the temperature range 293−323 K, complex **1**, as well **2**, is totally inactive, as no significant amounts of oligomerization products could be detected in the reaction medium even after 24 h. This finding says that complex **1** and **2** are stable in solution without phosphine release. Phosphorus ligands are known to promote the H−T oligomerization of MA,[24] affording dimers, trimers, and tetramers among other oligomers. PCy_3 is able to start such an oligomerization process. However, a drastic change of reactivity has been observed working under a H_2 atmosphere (0.1 MPa). In the presence of dihydrogen (0.1 MPa), **1** promotes the highly selective (100%) head-to-tail oligomerization of MA with formation of dimethyl methyleneglutarate (DMG). Trimer 2,4,6-tri(carbomethoxy)-1-hexene (Scheme 4) was also formed in very minor amounts without any time dependence. No other oligomerization products could be detected in the reaction mixture. As an example, in THF (7 mL; MA/**1** = 160 mol/mol), at 323 K, the observed TON (mole of converted monomer per mole of Ni) for DMG was close to 30. Both pure DMG and the trimer could be easily isolated by column chromatography. Dioxygen must be excluded in order to prevent radical polymerization.

The drastic change of reactivity upon addition of dihydrogen can be ascribed to a modification of the catalyst. It has been proposed[4] that a nickel−hydride species most probably acts as effective catalyst of the oligomerization process. Support for this hypothesis comes from studying the reactivity of **1** toward H_2 by ^{1}H NMR spectroscopy. At room temperature (293 K), **1** is to be quite unreactive toward dihydrogen; however, it easily reacts with H_2 at 313 K. The ^{1}H spectrum (500 MHz) of a THF-d_8 solution of **1**, heated at 313 K for about 2 h under H_2, shows the appearance of new signals assigned to benzene, allylbenzene, and 1-phenylpropane and a triplet (1:2:1) at −24.40 ppm

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Table 2. Catalytic Head-to-Tail Oligomerization of MA in the Presence of 3

run	MA/**3** (mol/mol)	solvent	*T* (K)	time (h)	DMG yield (%)	trimer yield (%)	TON[a]
1[b]	287	CH_2Cl_2	293	27	10[c]	≅1[c]	≅30[d]
2[e]	364	none	293	48	38[c]	7[c]	≅140[d]
3[f]	3388	THF	343	24	13[g]	*h*	440
4[i]	3112	none	343	24	33[g]	2[g]	1030

[a] Moles of MA converted into DMG per mole of Ni. [b] CH_2Cl_2 5 mL; MA 0.9 mL (10.0 mmol); **3** 0.038 g (0.035 mmol). [c] Isolated (by column chromatography) yield. [d] Calculated on the basis of isolated DMG. [e] MA 1.5 mL (16.7 mmol); **3** 0.050 g (0.046 mmol). The system was not homogeneous throughout the run. [f] THF 3 mL; MA 5 mL; (55.6 mmol); **3** 0.018 g (0.0164 mmol); eicosane (internal standard) 0.167 g; 0.59 mmol. [g] GC yield. [h] Not determined. [i] MA 7 mL; (77.8 mmol); **3** 0.025 g (0.023 mmol); eicosane (internal standard) 0.231 g; 0.82 mmol.

(J_{H-P} = 72.1 Hz). The formation of benzene and allylbenzene does not require any further comment, as they are the typical products of thermal decomposition of **1**, as discussed above. 1-Phenylpropane formation can be easily rationalized in terms of hydrogenation of allylbenzene under the working conditions (see also Experimental Part). The presence of the triplet at high field clearly demonstrates the formation of a Ni−hydride species (**4**) in the reaction solution. The definition of the exact nature of **4** is still in progress, as, to date, it has not been yet isolated in a pure form. Nevertheless, it is worth pointing out that its spectroscopic features (location of hydride resonance, its multiplicity, and the value of the J_{H-P} coupling constant) are very close to those exhibited by $\mathbf{3}^{+}$ [1] or a few other cationic complexes of formula *trans*-$[HNi(PCy_3)_2X]BPh_4$, where X is an N-donor ligand.[29]

The new hydride species is responsible for the observed catalytic activity. Interestingly, addition of an excess of MA (MA/Ni = 1000 mol/mol) to the above solution causes the fast disappearance in the proton spectrum of the hydride signal due to **4** and the GC−MS analysis of the reaction solution, left overnight at 293 K under H_2, clearly shows the formation of DMG.

Further evidence in support of the intermediacy of a Ni−H species comes from the fact that also complex **3** catalytically promotes the selective head-to-tail oligomerization of MA to give, as the unique products, DMG and, in very minor yield, the trimer 2,4,6-tri(carbomethoxy)-1-hexene. The data in Table 2 clearly demonstrate that **3** is a more active catalyst than **1**. The oligomerization process (Table 2) smoothly proceeds under N_2, even at room temperature, without requiring the addition of any cocatalyst. Increasing temperature over the ambient value greatly enhances the catalytic activity of **3**, as emphasized by the very interesting TONs observed at the temperature of 343 K (Table 2, runs 3 and 4).

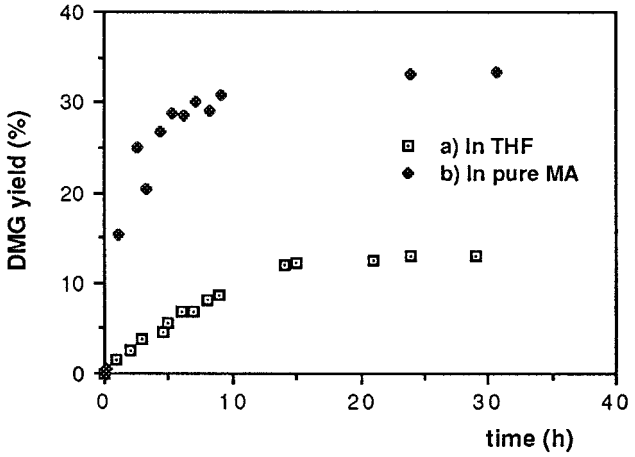
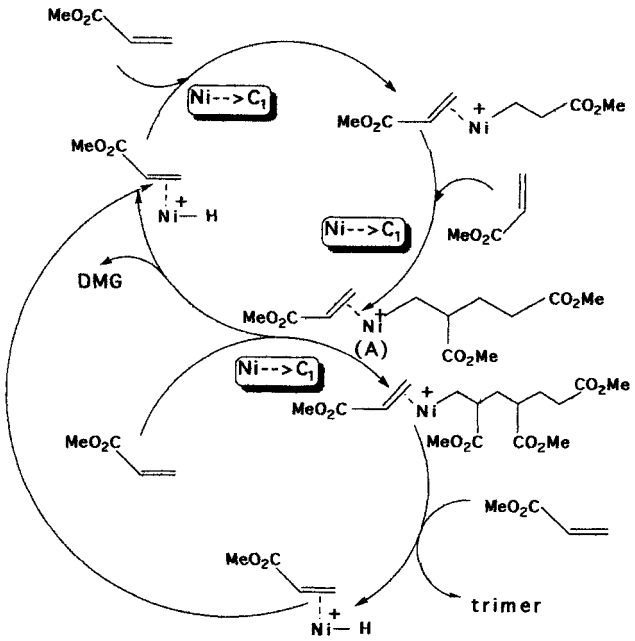


Figure 4. Kinetics of formation of DMG, at 343 K, in the presence of **3** as the catalyst. (a) Solvent: THF. (b) Solvent: MA.

Scheme 5. Methyl Acrylate Oligomerization: Proposed Mechanism



The catalytic activity of **3** markedly increases when MA itself is used as reaction medium for the oligomerization process. This is clearly evident also in Figure 4, which compares the kinetics of formation of DMG (in the presence of **3** as the catalyst) at 343 K, in THF (curve a) and pure MA (curve b). The presence of the solvent markedly slows down the dimerization reaction, but has little influence on the deactivation of the catalyst. Further kinetic experiments unambiguously demonstrate that the trimer formation is not a step following the formation of DMG, unlike the process proposed for phosphine-promoted H−T oligomerization of acrylic compounds.[24] The trimerization reaction does not exhibit any induction time, but immediately starts, albeit at much lower rate than the dimerization rate.

Scheme 5 summarizes a plausible mechanism for the formation of DMG and the trimer. According to the above results, the catalytically active species is proposed to be a Ni−H species that upon double insertion of the monomer converts into **A**. From this intermediate, DMG can be easily formed by β-hydrogen transfer. Alterna-

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tively, **A** can insert a third MA molecule and afford the trimer. It is evident that the β-H elimination is faster (about 17 times, at 343 K) than the MA insertion.

The above mechanism invokes the intermediacy of a Ni−H species, but differs, in a few respects, from that proposed by Wilke for Ni−PMe_3 systems, as a different regioselectivity is observed for the insertion steps controlling the nature of the products obtained. According to the Wilke mechanism, the main T−T cycle, leading to the predominant formation of DHD, involves an initial Ni → C1 addition, which is followed by a Ni → C2 attack, whereas in the slower H−T cycle, through which minor amounts of MPD are formed, both insertion steps involve Ni → C2 addition.

In the present work, the nature of the observed products requires that each insertion step involves a Ni → C1 addition, namely, the attack of the metal must take place at the less substituted olefin carbon to give a primary alkyl group. As a matter of fact, in our case, the first insertion step takes place with a high regioselectivity (100%, Ni → C1 attack). A steric control by the bulky PCy_3 ligands cannot be excluded in this step. Moreover, the combined effects of the steric hindrance of the growing organic moiety and of the bulkiness of the PCy_3 ligands force the second (and third) monomer molecule to be incorporated in the observed way. Tetramers and other oligomers were never detected.

Experimental Section

General Comments. Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere (as specified in the text), by using vacuum line techniques. All solvents were dried as described in the literature[30] and stored under N_2. MA was purchased from Fluka and stored under N_2. $(CH_2{=}CHCH_2NH_3)BPh_4$,[1,2] $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$,[1,2] $[(PhCH_2)HN{=}CMe_2]BPh_4$,[1,2] $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$,[31] and $(Cy_3P)_2NiNNNi(PCy_3)_2$[32] have been prepared as previously reported.

Complexes **2** and **3** have been synthesized according to the procedures described in ref 1. Both complexes have been spectroscopically characterized by IR (Nujol), ^1H (CD_2Cl_2, 200 MHz, 293 K), $^{13}C\{^1H\}$ (CD_2Cl_2, 125.76 MHz, 293 K), and ^{31}P NMR (CH_2Cl_2, 81 MHz, 293 K) spectroscopy.[1]

IR spectra were obtained with a Perkin-Elmer 883 spectrophotometer. NMR spectra were run on a Varian XL-200 or a Bruker AM 500 instrument. ^1H and ^{13}C chemical shifts are in ppm vs TMS and referenced to the solvent peak. GC−MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GCMS-QP5050 selective mass detector (capillary column: 60 m × 0.25 mm Supelco MDN-5S, 0.25 μm film thikness) or with a HP 5890 gas chromatograph connected with a HP 5970 MS (capillary column: 30 m SE-30, 0.25 μm film thickness). GC analyses were performed using a HP 5800 Series II GC (capillary column: AT 1000 Heliflex, 30 m × 0.25 mm, 0.25 μm film thickness).

Synthesis of $[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)]BPh_4$ 1 from $(Cy_3P)_2NiNNNi(PCy_3)_2$. To a solution of $(Cy_3P)_2NiNNNi(PCy_3)_2$ (0.294 g, 0.232 mmol) in THF (5 mL), prepared under dinitrogen at 243 K, was added $(CH_2{=}CHCH_2NH_3)BPh_4$ (0.178 g, 0.471 mmol) dissolved in THF (5 mL) and the resulting mixture stirred at room temperature (293 K) until its color turned to orange. The reaction mixture was filtered, concentrated in vacuo, and, after addition of pentane (10 mL), cooled to 253 K. The yellow crystals precipitated were isolated by filtration, washed with pentane (2 × 10 mL), and dried in vacuo (0.246 g, 75%). Anal. Calcd for $C_{45}H_{61}NBPNi$: C, 75.43; H, 8.58; N, 1.95; Ni, 8.19; P, 4.32. Found: C, 75.10; H, 8.53; N, 1.92; Ni, 8.14; P, 4.40.

Complex **1** could be synthesized, in less satisfactory yield, also by adding the tetraphenylborate salt to a toluene solution of the Ni(0) complex, prepared under dinitrogen at 243 K. Upon warming the reaction mixture to room temperature, a yellow precipitate was obtained. The suspension was stirred at 293 K for about 3 h and, then, filtered out. The yellow solid was washed with toluene and pentane and dried in vacuo. Upon recrystallization from THF/pentane or CH_2Cl_2/pentane, pure **1** was obtained.

1 can be obtained in a similar manner by reacting $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$ with the allylammonium BPh_4 salt.

^1H NMR (THF-d_8, 500 MHz, 293 K): δ 1.2−2.0 (Cy protons and H3), 2.5 (v br, NH_3), 2.80 (br s, H2 and H4), 3.73 (br s, H1), 5.38 (septet, H5, $J \cong 7$ Hz), 6.74 (t, H_{para,BPh_4}, $J = 7.17$ Hz), 6.89 (t, H_{meta,BPh_4}, $J = 7.40$ Hz), 7.32 (m, H_{ortho,BPh_4}). ^1H NMR (THF-d_8, 500 MHz, 233 K): δ 1.2−2.2 (Cy protons and H3), 2.81 (br, H4), 2.89 (slightly br, dd, H2, $J = 14.5$ and 4.7 Hz), 2.98 (br, NH_3), 3.83 (br d, H1, $J = 7.6$ Hz), 5.46 (sept, H5, $J \cong 7$ Hz), 6.73 (br, H_{para,BPh_4}), 6.87 (br, H_{meta,BPh_4}), 7.25 (br, H_{ortho,BPh_4}). $^{13}C\{^1H\}$ NMR (THF-d_8, 125.76 MHz, 293 K): δ 25.78 (s, C_{δ,PCy_3}), 26.96 (d, diastereotopic C_{γ,PCy_3} and C_{γ',PCy_3}, $^3J_{CP} = 10.44$ Hz), 29.58 (s, diastereotopic C_{β,PCy_3} and C_{β',PCy_3}), 33.34 (d, C_{α,PCy_3}, $^1J_{CP} = 19.24$ Hz), 47.6 (s, br, allylic C_{cis}), 73.5 (br, allylic C_{trans}), 114.11 (s, allylic C_{meso}), 120.65 (s, C_{para,BPh_4}), 124.57 (s, C_{meta,BPh_4}), 135.82 (s, C_{ortho,BPh_4}), 163.88 (q, C_{ipso,BPh_4}, $^1J_{CB} = 49.4$ Hz).

X-ray Data Collection, Structure Determination, and Refinement of Complex 1. Suitable crystals were sealed in a Lindemann capillary under dry nitrogen and used for data collection. The crystallographic data are summarized in Table 3.

Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 24 randomly

Table 3. Summary of Crystal Data for Compound 1

formula	$C_{45}H_{61}BNNiP$
fw	716.44
cryst syst	monoclinic
space group	$P2_1/n$
diffractometer	Enraf-Nonius CAD4
radiation	Cu Kα, $\lambda = 1.54184$ Å
monochromator	graphite
temp, K	293(2)
a, Å	14.913(4)
b, Å	17.559(6)
c, Å	16.333(5)
β, deg	110.59(2)
V, Å^3	4004(2)
Z	4
D_{calcd}, g cm^{-3}	1.189
$F(000)$	1544
cryst dimens, mm	0.20 × 0.25 × 0.30
μ(Cu Kα), cm^{-1}	12.93
2θ range, deg	6−120
no. of reflns measd, range h, k, l	−16/15, 0/19, 0/18
total no. of unique data	5928 ($F_o^2\epsilon - 3\sigma(F_o^2)$)
no. of unique obsd data	1463 ($F_o \epsilon 4\sigma(F_o)$)
no. of data/restraints/params	5928/0/269
goodness of fit[a]	0.748
R1[b]	0.0546
wR2[c]	0.0948
weighting scheme, a, b[d]	0.0346, 0.0000

[a] GOOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

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distributed and carefully centered reflections with θ in the range 18−31°. The data collections were performed by the $\theta/2\theta$ scan mode, at 293 K. One standard reflection was monitored every 100 measurements, and no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects and reduced to F_o^2. The structure was solved by direct methods (SIR92[33]) andrefined by full-matrix least-squares on F^2 using SHELXL-97,[34] first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms except the phenyl carbon atoms of the BPh_4 anion and the coordinated allyl carbon atoms, which were found disordered and distributed in two positions with equal occupancy factors. All the hydrogen atoms were placed at their geometrically default-distances calculated positions and refined "riding" on their parent atoms. All calculations were carried out on the DIGITAL AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. The details of the crystal structure investigations are deposited at the Cambridge Crystallographic Data Center as supplementary publications no. CCDC 132375. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)-336-033, e-mail: deposit@ccdc.cam.ac.uk].

Thermal Behavior of 1 in Solution. A THF-d_8 (0.75 mL) solution of **1** (0.030 g, 0.042 mmol), prepared under N_2, was introduced into a NMR tube, avoiding contact with air. The tube was sealed and the solution monitored by ^{1}H NMR (500 MHz) at the following temperatures: 293, 303, 313, and 323 K. No significant changes with respect to the room-temperature spectrum were evident until 313 K. At this temperature, under the working conditions (500 MHz), both H1 and H2/H4 (still isochronous, as at 293 K) gave distinct, but slightly broader than at 293 K, resonances at 3.72 (1 H) and 2.79 ppm (2 H), respectively. However, new, low-intensity signals, due to incipient decomposition of **1**, began to be evident in the spectrum. The intensity of these new resonances, assigned to the formation of benzene (s, 7.29 ppm) and allylbenzene [3.36 (d, $^3J_{H-H}$ = 6.6 Hz), 5.04 (dm, $^3J_{HC=CH,trans}$ = 17.0 Hz), 5.01 (dm, $^3J_{HC=CH,cis}$ = 10.2 Hz) and 5.95 ppm (m)], markedly grew when the system was heated to 323 K. After 1 h at 323 K, the PhC_3H_5/PhH molar ratio was equal to 1.7 (as determined by integration).

The formation of benzene and allylbenzene (together with a trace amount of byphenyl) was further confirmed by analyzing the reaction mixture (previously cooled to room temperature (293 K) and, then, transferred into a vial out of contact with air) by GC and GC−MS.

An analogous experiment was repeated at 200 MHz, measuring the spectrum of the reaction solution at intervals of 5 K, between 293 and 328 K. The use of a weaker magnetic field allowed us to observe the coalescence of the signals due to H1 and H4 at T_c = 313 K (see also Results and Discussion).[13]

Reaction of 1 with Dihydrogen. A THF-d_8 (0.75 mL) solution of **1** (0.020 g, 0.028 mmol), saturated with H_2 (0.1 MPa) at 293 K, was introduced into a NMR tube, under a dihydrogen stream. The solution was monitored by ^{1}H NMR (500 MHz). The ^{1}H spectrum of the solution, after 1 h at room temperature, did not show any other signal besides the resonance of H_2 (4.55 ppm) and the typical signals of **1** in the solvent used.[35] Heating the system for 45 min at 313 K caused the color of solution to turn from yellow to dark red and the appearance of new signals in the spectrum. In addition to the resonances of benzene and allylbenzene (see above) a triplet was clearly evident at −24.40 ppm (J_{H-P} = 72.1 Hz). This signal was still present in the spectrum even after protracting heating (at 313 K) for a further hour. However, the new spectrum showed the almost complete disappearance of the signals due to **1** and those assigned to allybenzene, while new resonances attributed to propylbenzene were found at 2.60 (t, $PhCH_2$, 7 Hz) and 0.90 ppm (quar, CH_3, 7 Hz).[36]

The solution, cooled to room temperature (293 K), was treated with an excess of MA (MA/Ni = 1000 mol/mol) and left at 293 K overnight. The GC−MS analysis of the reaction mixture after this time showed the presence of DMG, benzene, propylbenzene, phenylpropanoic acid methyl ester (m/z = 164 (M^+), 104, 91, 77, 65, 51, 39), and some residual allylbenzene.

Methyl Acrylate Oligomerization: Experimental Procedure. In all runs, the reaction vessel was a 50 mL tube sealed with a two-way valve that allowed the solution to be withdrawn without contact with air using a GC syringe.

(A) MA Oligomerization Promoted by 1 in the Presence of Dihydrogen. In a typical experiment, the reaction mixture, containing **1** (0.070 mg, 0.1 mmol), MA (1.5 mL, 16.7 mmol), and the solvent (THF, 7 mL), was prepared under N_2, then saturated with H_2 (0.1 MPa) at 293 K, and heated to the working temperature.

After cooling the reaction mixture to 293 K, the oligomerization products were isolated in pure form by column chromatography on silica gel using hexane/diethyl ether (2:1 v/v) as eluent.

(B) MA Oligomerization Promoted by 3. The reaction mixture (see also Table 2) containing the catalyst **3**, the substrate (MA), the solvent (if used), and eventually the internal standard (eicosane) was prepared under N_2 at 293 K and then heated to the working temperature.

The reaction was easily monitored by GC or GC−MS. The isolation of the oligomerization products in pure form was achieved by column chromatography on silica gel using hexane/diethyl ether (2:1 v/v) as eluent.

(C) MA Oligomerization in the Presence of PCy_3. A blank test was carried out using the free phosphine. The same reaction conditions as for **A** and **B** runs (see above) were used. Quite different results were obtained with respect to the Ni-catalyzed reaction. In fact, the nature of the products (higher oligomers are formed) and their distribution (loss of selectivity) are not comparable with those of the Ni-catalized process. Moreover, the kinetics were also different.

Spectroscopic Characterization of DMG. IR (neat, KBr disks, cm^{-1}): 1735 and 1715 (s), 1627 (m), 1435 (m−s), 1360 (m), 1260 (m−s), 1195 (m−s), 1165 (m−s), 1135 (m−s), 945 (m), 830 (m), 815 (m). ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ 2.47 (m, 2H, =C−CH_2), 2.58 (t, 2H, −CH_2C(O)OMe, $^3J_{H-H}$ = 7.4 Hz), 3.61 (s, 3H, O*Me*), 3.70 (s, 3H, O*Me*), 5.54 (quartet, 1H, *H*HC=, $^2J_{h-H}$ = $^4J_{H-H}$ = 1.28 Hz), 6.13 (s, 1H, H*H*C=). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.76 MHz, 293 K): δ 172.92 (−CH_2*C*(O)OMe), 166.91 (MeO(O)*C*−C=), 138.64 (H_2C=*C*), 125.76 (H_2*C*=C), 51.70 (O*Me*), 51.40 (O*Me*), 32.73 (−CH_2C(O)-OMe), 27.17 (*C*H_2−CH_2C(O)OMe). The above assignments are supported by a DEPT experiment. GC−MS: m/z 172 (M^+), 140, 112, 97, 81, 59, 53, 39.

Spectroscopic Characterization of the Trimer 2,4,6-Tri(carbomethoxy)-1-hexene. IR (neat, KBr disks, cm^{-1}): 1725 (vs), 1627 (m), 1435 (s), 1375 (m), 1330 (m−s), 1305 (m−s), 1255 (m−s), 1195 (s), 1165 (s), 1140 (m−s), 1045 (m), 990 (m), 955 (m), 830 (m), 815 (m). ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ 1.80−1.93 (m, 2H, −CH_2−CH_2−), 2.37−2.26 (m,

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(35) No reaction was observed at 293 K, even after longer reaction times. A bright yellow THF (4 mL) solution of **1** (0.218 g, 0.30 mmol) was stirred under H_2 (0.1 MPa) for 7 h at 293 K, then treated with pentane (20 mL), and cooled to 253 K. Upon filtration, pure **1** was recovered in practically quantitative yield.

(36) The resonances of the aromatic protons and the β-methylene protons of propylbenzene could not be easily identified, as they were overlapped with or masked by other signals. However, the formation of propylbenzene was unambiguosly confirmed by the GC−MS analysis of the reaction solution (see text).

2H, $-CH_2-CH_2-$), 2.48 (dd, 1H, $-C(H)H-C(=CH_2)CO_2Me$, $^2J_{H-H} = 14.0$ Hz, $^3J_{H-H} = 5.85$ Hz), 2.58 (dd, 1H, $-C(H)H-C(=CH_2)CO_2Me$, $^2J_{H-H} = 14.0$ Hz, $^3J_{H-H} = 8.77$ Hz), 2.68 (m, 1H, C*H*), 3.62 (s, 3H, O*Me*), 3.64 (s, 3H, O*Me*), 3.70 (s, 3H, O*Me*), 5.57 (s, 1H, *H*HC=), 6.17 (s, 1H, H*H*C=). The methylene protons are diastereotopic. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.76 MHz, 293 K): δ 175.03 (*C*(O)OMe), 173.18 (*C*(O)OMe), 166.97 (MeO(O)*C*−C=), 137.39 ($H_2C=C$), 127.21 ($H_2C=C$), 51.91 (O*Me*), 51.60 (O*Me*), 51.53 (O*Me*), 43.72 (*C*H), 34.68 (CH_2), 31.57 (CH_2), 26.93 (CH_2). The above assignments are supported by a DEPT experiment. GC−MS: *m*/*z* 227 ($M^+ - OMe$), 198, 194, 167, 134, 125, 106, 79, 59, 41.

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Supporting Information Available: Table of the final atomic coordinates for the non-hydrogen atoms (Table SI) and for the hydrogen atoms (Table SII), anisotropic thermal parameters (Table SIII), complete list of bond distances and angles (Table SIV), and complete crystallographic data (Table SV). This material is available free of charge via the Internet at http://pubs.acs.org.

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