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Preparation and Characterization of (1-Me-indenyl)Ni(PR_3)(CC−Ph) (R = Cy, Ph) and Alkyne Polymerization Catalysis

Ruiping Wang, Francine Bélanger-Gariépy, and Davit Zargarian*

Département de Chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

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The complexes (1-Me-Ind)(PR_3)Ni−CC−Ph (R = Ph and Cy) have been prepared and characterized spectroscopically and by means of single-crystal structural analyses. These compounds are inert toward the insertion of alkynes, but when combined with methylaluminoxane (MAO), they form active catalysts for the homogeneous polymerization of phenylacetylene. *cis*-Poly(Ph−CC−H) is thus obtained with M_w values in the range of 10^4 and relatively narrow polydispersities. The combination of the corresponding Ni−Cl complexes with MAO gives similar results with Ph−CC−H and also polymerizes 1-hexyne and 3-hexyne, but the degree of polymerization is much lower. Optimization studies have shown that the polymerization reactions give the best results with THF as solvent and a 1:10 ratio of Ni to MAO. Evidence is presented for the involvement in the catalytic cycle of bimetallic species with a Ni(μ-X)(μ-Me)Al core.

Introduction

The search for effective, transition metal catalyzed systems that can convert alkynes into linear polyalkynes is driven by the significant promise of the latter materials in applications requiring optical nonlinear and magnetic susceptibilities, photoconductivity, and gas permeability.[1] The majority of the catalytic systems reported to date for the preparation of polyalkynes can be divided into two main groups on the basis of the polymerization mechanism, namely, metathesis and insertion polymerizations. Thus, a number of high-valent, early transition metal compounds containing halides, aryl oxides, and alkylidenes (e.g., WCl_6, $MoCl_6$, and $L_n(ArO)_mM{=}CRR'$ where M = Ta, Nb, Mo, W, etc.) are known to catalyze the polymerization of aliphatic alkynes such as *t*-Bu−CC−H to high M_w polyalkynes by a metathetic polymerization.[2] On the other hand, aromatic alkynes undergo insertion polymerizations catalyzed primarily by Rh(I) complexes. For instance, Ph−CC−H can be polymerized to poly(phenylacetylene) (PPA) with M_w in the range of 10^4−10^6 by {(diene)Rh(μ-Cl)}$_2$,[3] $[(COD)Rh]^+[(\eta^6\text{-Ph})BPh_3]^-/HSiEt_3$,[4] and (norbornadiene)(PPh_3)$_{1or2}$Rh−CC−Ph/4-(dimethylamino)pyridine.[5] The latter system is especially attractive because it promotes a living polymerization process that can produce narrow dispersity polymers and copolymers.[5a]

We became interested in the catalytic polymerization of alkynes during the course of our studies on the dehydropolymerization of $PhSiH_3$ catalyzed by the complexes IndNi(PR_3)X.[6] Initial studies on the reactivity of this family of compounds with alkynes showed that although the latter do not undergo unassisted insertion into the Ni−X bond (X = CC−Ph, Me, etc.), linear polyalkynes can be produced in the presence of aluminum alkyls. The present paper reports the results of our studies on the preparation of the complexes (1-Me-Ind)(PR_3)Ni−CC−Ph (R = Ph and Cy) and their activities in alkyne polymerization reactions.

Results and Discussion

The synthesis of (1-Me-Ind)(PPh_3)Ni−CC−Ph, **1**, can be accomplished via a metathetic reaction between the known[7] Ni−Cl precursor and $Ph{-}CC^-Li^+$ in benzene; addition of hexane precipitates the desired product as a yellow-brown solid in ca. 70% yield (eq 1). Complex **2** was prepared by reacting **1** with PCy_3; crystallization from EtOH gave the desired product in ca. 68% yield (eq 2). These new complexes were fully characterized by IR and NMR (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) spectroscopy, elemental analysis, and X-ray diffraction studies (vide infra).

$$\text{(1-Me-Ind)Ni(PPh}_3\text{)Cl} \xrightarrow[-\,Li^+Cl^-]{+\,Ph\text{-}CC^-Li^+} \underset{\mathbf{1}}{\text{(1-Me-Ind)Ni(PPh}_3\text{)(CC-Ph)}} \qquad (1)$$

$$\mathbf{1} \xrightarrow[-\,PPh_3]{+\,PCy_3} \underset{\mathbf{2}}{\text{(1-Me-Ind)Ni(PCy}_3\text{)(CC-Ph)}} \qquad (2)$$

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Table 1. Results of Alkyne Polymerization Reactions Catalyzed by (1-Me-Ind)Ni(PR_3)X + MAO

run	catalyst	substrate	solvent	cat.:MAO:substrate	M_w ($\times 10^{-3}$)	M_w/M_n
1	**1**	Ph−CC−H	benzene	1:10:100^a	28.1	1.72
2	**2**	Ph−CC−H	benzene	1:10:100^a	31.8	1.55
3	**1**	Ph−CC−H	benzene	1:20:100^a	10.9	1.73
4	**1**	Ph−CC−H	THF	1:10:100^b	47.4	1.27
5	**1**	Ph−CC−H	THF	1:10:60^b	58.7	1.32
6	**5**	Ph−CC−H	benzene	1:10:100^a	15.2	2.13
7	**6**	Ph−CC−H	benzene	1:10:60^a	18.1	1.66
8	**5**	Ph−CC−H	toluene	1:10:100^c	30.7	1.16
9	**6**	Ph−CC−H	toluene	1:10:100^c	20.5	1.09
10	**6**	Ph−CC−H	Et_2O	1:10:200^b	35.2	2.69
11	**5**	1-hexyne	toluene	1:10:100^d	2.4	1.37
12	**5**	3-hexyne	toluene	1:10:100^d	1.3	1.01

^{a} Workup with AcOH + Et_2O. ^{b} Workup with AcOH + MeOH. ^{c} Workup with acetone. ^{d} Workup with MeOH.

Polymerization Activities. Our previous studies had indicated that combining the precursor Ni−Cl compounds with MAO (methylaluminoxane), $AgBF_4$, or $LiAlH_4$ forms catalytically active species for the polymerization of $PhSiH_3$.[6] In the case of Ph−CC−H as substrate, $AgBF_4$ and $LiAlH_4$ proved ineffective as initiators, but the combination of MAO and complexes **1** or **2** did form an active catalyst for the preparation of PPA. $AlMe_3$ can replace MAO, but the yield of the PPA and its M_w decrease. The PPA obtained from the MAO reactions is a yellow powder whose ^{1}H NMR spectrum ($CDCl_3$) contained a sharp singlet at 5.85 ppm for the vinylic proton in addition to a doublet at 6.64 ppm ($^3J_{H-H}$ = 6.6 Hz, *o*-H) and a multiplet at 6.94 ppm (*m*- and *p*-H) for the protons of the Ph rings; this pattern is characteristic of the head-to-tail cis−transoidal PPA frequently obtained by a cis insertion mechanism.[3,5a]

Table 1 summarizes the results of the alkyne polymerization reactions we have studied to date. When the polymerization of Ph−CC−H was carried out in benzene with 1% of **1** or **2**, we obtained PPA samples with similar M_w and polydispersities (runs 1 and 2). Approximately 10 equiv of MAO with respect to Ni seems to be optimal; less MAO significantly reduces the yield of PPA, whereas more MAO leads to smaller M_w polymers (run 3). The use of THF as solvent for the polymerization reaction led to significantly longer chains and more narrow polydispersity (run 4); reducing the Ni-to-Ph−CC−H ratio also resulted in longer chain lengths (run 5).

The Ni−Cl analogues of **1** and **2** also catalyze the polymerization of Ph−CC−H in the presence of MAO. Thus, when combined with MAO, (1-Me-Ind)(PPh_3)Ni−Cl, **5**, and (1-Me-Ind)(PCy_3)Ni−Cl, **6**, give PPA, albeit with somewhat lower M_w than that produced by their alkynyl counterparts **1** and **2** (compare runs 6 and 7 to runs 1 and 2). With toluene as reaction solvent, however, **5** and **6** give PPA with comparable M_w and narrower polydispersities (runs 8 and 9), while in Et_2O we obtain relatively high M_w PPA but at the cost of polydispersity (run 10). Finally, 1-hexyne and 3-hexyne give low M_w oligomers (runs 11 and 12).

The results of our preliminary studies aimed at identifying the catalytically active species in this system allow us to make the following comments about the alkyne polymerization process. The aluminum alkyls (e.g., MAO) are indispensable for the process, as no alkyne polymerization takes place in their absence. Indeed, the alkynyl moiety in compounds **1** and **2** is fairly inert and does not undergo insertion with alkynes, alkenes, ketones, aldehydes, or nitriles. Protonation of the alkynyl moiety in **1** with strong acids such as aqueous HBF_4 gives the known[8] cation [(1-Me-Ind)Ni(PPh_3)$_2$]$^+$, presumably by the intermediary of [(1-Me-Ind)Ni(PPh_3)(η^2-H−CC−Ph)]$^+$;[9] these cations do not catalyze the polymerization of alkynes.

Monitoring the reaction of **1** and **2** with MAO in C_6D_6 revealed that these complexes are converted to species displaying the characteristic ^{31}P{^{1}H} and ^{1}H NMR signals of the corresponding Ni−Me analogues;[7] addition of Ph−CC−H to this mixture led to the formation of PPA. On the other hand, similar experiments revealed that the isolated samples of the Ni−Me species *cannot* catalyze the formation of PPA in the absence of MAO. We believe, therefore, that the initial interaction of MAO with **1** and **2** forms a bimetallic species with a Ni(μ-CC−Ph)(μ-Me)AlX_2 core; the μ-alkynyl ligand in this compound may eventually be replaced by a second μ-Me from excess MAO. Similarly, combining the Ni−Cl precursors **5** and **6** with MAO leads to the species Ni(μ-Me)$_2$$AlX_2$, which initiate the polymerization (Scheme 1). The Ni−C bonds in these intermediates undergo alkyne insertion more readily because they are weaker than the corresponding Ni−C bonds in the monometallic Ni−CC−Ph and Ni−Me compounds.

Characterization of Complexes 1 and 2. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the new complexes display the characteristic signals observed for the analogous compounds (1-Me-Ind)Ni(PR_3)X (X = Cl, Me, etc.).[7] For instance, the ^{31}P{^{1}H} signal for **1** is a singlet resonating at ca. 40 ppm, intermediate between the corresponding signals for the Ni−Cl (31 ppm) and Ni−Me (48 ppm) analogues. Similarly, the ^{1}H NMR signal for the H3 proton in **1** (ca. 3.9 ppm) is intermediate between the analogous signals for the Ni−Cl (ca. 3.3 ppm) and Ni−Me (ca. 4.2 ppm) species.[7] Interestingly, the corresponding ^{31}P{^{1}H} and ^{1}H resonances for **2** are quite similar to those of the Ni−Me analogue of **2**, indicating that the hapticity of the 1-Me-Ind ligand in these compounds is similar (vide infra). The IR spectra of both complexes contained the characteristic absorption for the ν(CC) at ca. 2090 cm^{-1}.

The solid-state structures of **1** and **2** are depicted in Figure 1; the crystallographic data and some selected bond lengths and angles for these compounds are listed in Tables 2 and 3, respectively. Some of the structural features for **1** and **2** are very similar to those found in

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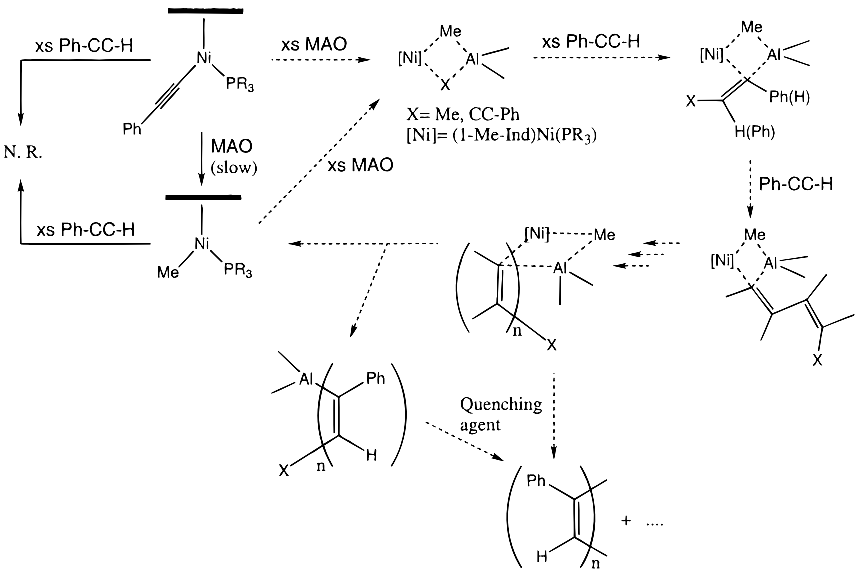
(9) Interestingly, reactions with HBF_4 etherate led to the protonation of PPh_3 and decomposition of the remainder of the compound.

Scheme 1



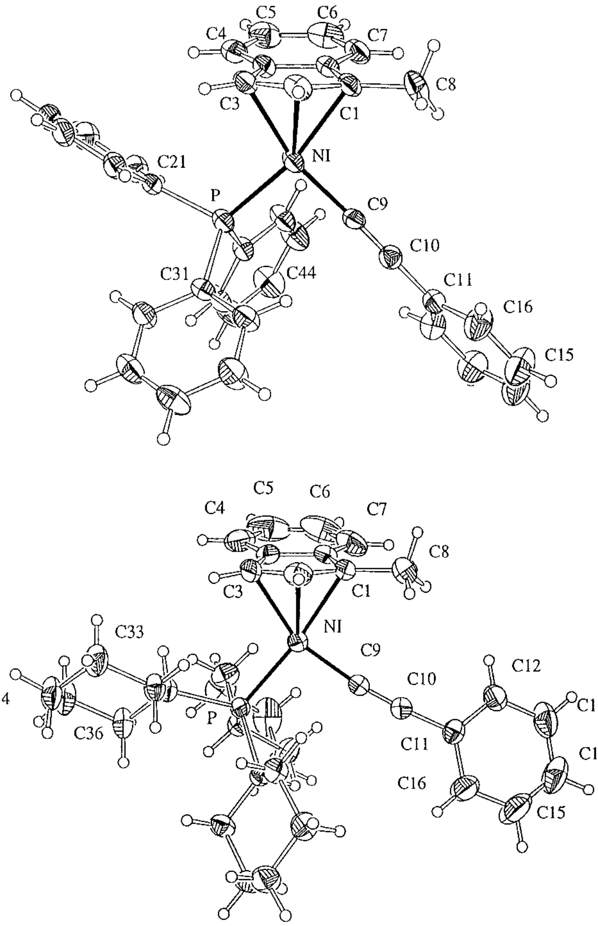


Figure 1. ORTEP plots of complexes **1** and **2** with atom-numbering scheme.

the Ni−Cl,[7] Ni−Me,[7] and Ni−phthalimidato[10] analogues. For example, the atoms P, C1, C2, C3, and C9 are within expected bonding distance from the nickel center, while the atoms C3a and C7a are considerably farther. The geometry around Ni may be described as distorted square planar with the C1=C2 occupying a single coordination site. The Ni−P bond lengths are similar in complexes **1** (ca. 2.168 Å) and **2** (ca. 2.161 Å), falling between the corresponding bonds in the Ni−Me derivative (2.121 Å) on one hand and the Ni−phthalimidato and the Ni−Cl analogues on the other (2.181 and 2.178 Å, respectively). The alkynyl moiety is essentially linear (Ni−C9−C10 ≈ 176° and C9−C10−C11 ≈ 178°), and the C9−C10 bond length of ca. 1.200 Å is in the expected range for a triple bond.[11] The sp character of C9 results in a significantly shorter Ni−C9 bond in **1** and **2** than the corresponding distance in the Ni−Me analogue: ca. 1.86 Å versus ca. 1.99 Å, $\Delta > 30\sigma$.

The tendency of Ni(II) to form 16-electron complexes results in some degree of allyl-ene distortion in the Ind ligand, which is reflected in the different C−C bond lengths inside the five-membered-ring moiety and the Ni−C bond distances: C1−C7a and C3−C3a > C1−C2 and C2−C3; Ni−C(3a, 7a) > Ni−C (1−3).[12] Interestingly, although the allyl moiety of the Ind ligand is essentially delocalized in both **1** and **2** (i.e., C1−C2 ≈ C2−C3; $\Delta < 4\sigma$), the local symmetry in the coordination of the allyl moiety is quite different in the two complexes. Thus, Ni−C1 ≈ Ni−C3 ($\Delta < 4\sigma$) in complex **2**, whereas Ni−C1 > Ni−C3 ($\Delta > 19\sigma$) in complex **1**. Similar patterns of Ind coordination are also present in the solid-state structures of the analogous complexes (Ind)(PPh_3)Ni−X, leading us to propose[7] that the coordination of the Ind in each case is determined by the relative trans influences of PPh_3 and X. Thus, the coordination of Ind is unsymmetrical when X is a ligand such as Cl or phthalimidato with a relatively weak trans influence compared to PPh_3, whereas a symmetrical coordination is observed with strong trans influence ligands such as Me. On the basis of the structural

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[10] Dubuc, I.; Dubois, M.-A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1999**, *18*, 30.

[11] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1995; Vol. C.

[12] (a) This type of "slip-fold" distortions may be measured in terms of such parameters as the slip value, defined as $\Delta M{-}C = [1/2(M{-}C3a + M{-}C7a) - 1/2(M{-}C1 + M{-}C3)$, and the hinge and fold angles (HA and FA), representing the bending of the Ind ligand at C1/C3 and C3a/C7a, respectively (refs 12b and 12c); the values of these parameters for **1** and **2** are listed in Table 3. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (c) Westcott, s. A.; Kakkar, A.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

Table 2. X-ray Crystallographic Data for 1 and 2

	1	2
formula and mol wt	$C_{36}H_{29}NiP$, 551.272	$C_{36}H_{47}NiP$, 569.416
crystal color, habit	dark red, parallelepiped	dark red, parallelepiped
crystal dimens, mm	0.13 × 0.13 × 0.07	0.20 × 0.14 × 0.08
cell setting, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	10.686(3)	9.916(3)
b, Å	11.493(5)	11.034(4)
c, Å	12.797(3)	15.906(4)
α, deg	92.70(2)	102.63(2)
β, deg	95.52(2)	94.97(2)
γ, deg	115.73(3)	110.24(2)
V, Å^3	1402.3(8)	1568.1(8)
Z	2	2
D (calc), g cm^{-1}	1.3056	1.2059
λ (Cu Kα), cm^{-1}	1.54056	1.54056
temp, K	293(2)	293(2)
diffractometer	Nonius CAD-4	Nonius CAD-4
$2\theta_{max}$, deg	140.0	140.0
data coll method	$\omega/2\theta$ scan	$\omega/2\theta$ scan
refl used ($I > 2\sigma(I)$)	5370	5940
R, R_w	0.0361, 0.0534	0.0377, 0.0605
max residual, e Å^{-3}	0.170	0.383

Table 3. Selected Bond Distances (Å), Angles (deg), and Other Structural Parameters for 1 and 2

	1	2
Ni−C1	2.112(3)	2.092(3)
Ni−C2	2.088(3)	2.067(3)
Ni−C3	2.053(3)	2.079(3)
Ni−C3a	2.276(4)	2.310(3)
Ni−C7a	2.313(3)	2.293(3)
Ni−P	2.1685(12)	2.1614(10)
Ni−C9	1.861(4)	1.855(3)
C1−C2	1.415(4)	1.398(3)
C2−C3	1.407(4)	1.405(3)
C3−C3a	1.435(4)	1.442(4)
C3a−C7a	1.413(4)	1.410(3)
C7a−C1	1.456(4)	1.434(4)
C9−C10	1.200(4)	1.200(3)
C10−C11	1.428(4)	1.440(3)
P−Ni−C9	93.30(10)	94.66(8)
P−Ni−C1	167.31(11)	171.85(8)
P−Ni−C3	103.14(11)	106.14(8)
C9−Ni−C1	97.80(14)	92.95(11)
C9−Ni−C3	163.30(14)	158.95(11)
C1−Ni−C2	39.36(12)	39.30(9)
C1−Ni−C3	66.21(14)	66.11(10)
C2−Ni−C3	39.73(12)	39.62(10)
Ni−C9−C10	176.7(3)	172.7(2)
HA (deg)[a]	10.24	9.4
FA (deg)[b]	12.01	8.7
ΔM−C (Å)[c]	0.21	0.21

[a] Hinge angle, between the planes defined by C1, C2, C3 and C1, C3, C3a, C7a. [b] Fold angle, between the planes defined by C1, C2, C3 and C3a, C4, C5, C6, C7, C7a. [c] "Slippage": {Ni−C3a + Ni−C7a}/2 − {Ni−C1 + Ni−C3}/2.

results for complexes **1** and **2** and the Ni−X analogues reported earlier,[7,10] we propose that the trans influences of the various ligands in this family of compounds vary in the order PPh$_3$ ≈ Me > PCy$_3$ ≈ CC−Ph > phthalimidate ≈ Cl.

Conclusion. The combination of MAO with the nickel alkynyl complexes **1** or **2**, or with the analogous Ni−Cl complexes **5** or **6**, forms effective catalysts for the polymerization of Ph−CC−H to all-cis-PPA. In terms of M_w and polydispersity, the PPA obtained from our Ni-based system is comparable to those obtained from most of the reported Rh-based systems[3,4] with the exception of Noyori's system,[5] which gives the highest M_w PPA. Moreover, the present system represents a rare example of a group 10 metal-based system for the polymerization of phenylacetylene. To our knowledge, the only other group 10 compounds reported to catalyze the polymerization of alkynes are the following: (a) Cp$_2$Ni is reported to react with Ph−CC−H at 115 °C to give cyclic trimers and PPA with M_w of 460−1600;[13] (b) Pd(OAc)$_2$ and (PPh$_3$)$_2$PdCl$_2$ are reported to give PPA with M_w of 600−2400;[14] (c) (PPh$_3$)$_2$Pt(CC−Ph)$_2$ has been reported to give PPA with M_w in the range of 1000−2000.[15]

On the basis of our preliminary results we propose that the polymerization in the present system proceeds by the insertion of an alkyne into the Ni−R or Ni−Me bond in the neutral, bimetallic intermediates of the type (Ind)(PPh$_3$)Ni(μ-R)(μ-Me)AlX$_2$. Studies aimed at elucidating the operating mechanism of these reactions and the optimization of the polymerization conditions are in progress.

Experimental Section

General Comments. All manipulations and experiments were performed under an inert atmosphere of nitrogen using standard Schlenk techniques and/or in an argon-filled glovebox. Dry, oxygen-free solvents were employed throughout. The elemental analyses were performed by Laboratoire d'Analyse Élémentaire (Université de Montréal). The ^{1}H (400 MHz), ^{13}C{^{1}H} (100.56 MHz), and ^{31}P{^{1}H} (161.92 MHz) NMR spectra were recorded at ambient temperature; the IR spectra were recorded as KBr pellets. The GPC measurements were done using a R410 Waters instrument equipped with a differential refractometer and ultra styragel columns.

(1-Me-Ind)Ni(PPh$_3$)(CC−Ph) (1). A stirring benzene (20 mL) solution of (1-Me-Ind)(PPh$_3$)Ni−Cl (361 mg, 0.74 mmol) was added dropwise to the stirring benzene (10 mL) suspension of Ph−CC$^-$Li$^+$ (104 mg, 0.96 mmol). The resultant dark yellow mixture was stirred for 30 min at room temperature and filtered, and the filtrate evaporated to dryness. The residue was crystallized from THF/hexane at room temperature to give the product as a dark yellow solid (290 mg, 71%). Dark red crystals of **2** were grown from THF at −20 °C. IR (KBr, cm^{-1}): 3055, 2090 (−CC−), 1588, 1488, 1432, 1094, 749, 702, 528. ^{1}H

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NMR (C_6D_6): 7.52−6.78 (m, aromatic protons of PPh_3, CC−Ph, and Ind), 6.09 (br s, H2 and another Ind proton), 3.87 (br, s, H3), 2.18 (br s, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 133.9 (d, $^2J_{P-C}$ = 11.1, *o*-C), 133.0 (d, J_{P-C} = 45.8, *i*-C), 130.9 (s, *p*-C), 129.8 (2 s, *o*- and *m*-C of CC−Ph), 128.5 (d, $^2J_{P-C}$ = 1.4, C1), 128.2, 127.9 (d, $^2J_{P-C}$ = 10.5, *m*-C), 127.2, 124.7, 124.3, 124.2, 123.6, 121.0, 117.7, 116.4, 103.0, 76.9 (s, C3), 12.7 (s, Me). $^{31}P\{^1H\}$ NMR (C_6D_6): 40.4(s). Anal. Calcd for $C_{36}H_{29}NiP$: C 78.43, H 5.32. Found: C 78.06, H 5.27.

(1-Me-Ind)Ni(PCy$_3$)(CC−Ph) (2). A stirring THF (20 mL) solution of PCy_3 (230 mg, 0.82 mmol) was added dropwise to the stirring THF (10 mL) solution of **1** (290 mg, 0.54 mmol). The resultant mixture was stirred for 1 h at room temperature and then evaporated to dryness. The residue was crystallized from EtOH at room temperature to give the product as a dark yellow solid (210 mg, 68%). Dark red crystals of **2** were grown from Et_2O at −20 °C. IR (KBr, cm^{-1}): 2925, 2850, 2091 (−CC−), 1594, 1444, 746. ^1H NMR (C_6D_6): 7.51 (d, $^3J_{H-H}$ = 8.0, H12 and H16), 7.24 (d, $^3J_{H-H}$ = 8.0, H7), 7.06 (m, H13, H14 and H15), 6.92 (d, $^3J_{H-H}$ = 3.2, H4), 6.90 (br s, H6), 6.88 (t, $^3J_{H-H}$ = 1.2, H5), 6.12 (d, $^3J_{H-H}$ = 2.8, H2), 4.64 (s, H3), 2.16 (d, $^4J_{P-H}$ = 4.4, Me), 1.62−1.06 (m, PCy_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 130.8 (s), 129.0 and 125.5 (s, C3a and C7a), 127.5 (s), 124.2, 124.1, 123.7 and 123.3 (s, C6 and C7), 117.6 and 117.4 (s, C4 and C7), 114.7 (s, C10), 103.1 (s, C2), 94.1 (br s, C9), 67.0 (s, C3), 36.0 (d, J_{P-C} = 21.3, C31), 29.6 (d, $^2J_{P-C}$ = 24.4, C32), 27.6 (d, $^3J_{P-C}$ = 10.7, C33), 26.3 (s, C34), 12.7 (d, $^3J_{P-C}$ = 1.5, Me). $^{31}P\{^1H\}$ NMR (C_6D_6): 49.2 (s). Anal. Calcd for $C_{36}H_{47}NiP$: C 75.93, H 8.32. Found: C 75.50, H 8.50.

Polymerization of Phenylacetylene. To a solution of the Ni precatalyst in 2 mL of solvent was added phenylacetylene and then MAO. After stirring for 24 h at room temperature under nitrogen, the quenching/precipitating agent was added to give a yellow solid (PPA), which was washed by hexane and dried in vacuo. ^1H NMR ($CDCl_3$): 6.94 (m, *m- and p*-H), 6.64 (d, $^3J_{H-H}$ = 6.6, *o*-H), 5.85 (s, vinylic H).

X-ray Diffraction Studies. Dark red crystals of **1** and **2** were grown from THF and Et_2O, respectively, at −20 °C. Crystallographic data for these compounds are listed in Table 2. The $\omega/2\theta$ scan mode was used in both cases to measure 30823 reflections for **1** (5307 independent, 2173 observed with $>2\sigma(I)$) and 28169 reflections for **2** (5940 independent, 3370 observed with $>2\sigma(I)$). The structures were solved by direct methods using SHELXS96 and difmap synthesis using SHELXL96; refinement on F^2 by full-matrix least-squares gave the R and R_w values indicated in Table 2.

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Supporting Information Available: Complete details on the X-ray analyses of **1** and **2**, including tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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