

Synthesis, Characterization, and Ethylene Polymerization Activities of Neutral Nickel(II) Complexes Derived from Anilino-Substituted Enone Ligands Bearing Trifluoromethyl and Trifluoroacetyl Substituents

Lei Zhang, Maurice Brookhart,* and Peter S. White

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599

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A series of neutral Ni(II) complexes derived from anilino-substituted enone ligands bearing electron-withdrawing trifluoromethyl and trifluoroacetyl groups have been synthesized and characterized: $[\eta^2\text{-ArNC(R}_1\text{)C=C(R}_2\text{)C(O)CF}_3]\text{Ni(PPh}_3\text{)Ph}$ (**3a**, Ar = 3,5-*i*-Pr₂C₆H₃, R₁ = H, R₂ = COCF₃; **3b**, Ar = 3,5-*i*-Pr₂C₆H₃, R₁ = Me, R₂ = COCF₃; **3c**, Ar = 3,5-*i*-Pr₂C₆H₃, R₁ = Me, R₂ = H; **3d**, Ar = 3,5-Me₂C₆H₃, R₁ = Me, R₂ = COCF₃). When they are activated with either Ni(COD)₂ or B(C₆F₅)₃, these complexes are active for the polymerization of ethylene to branched polyethylenes. Complex **3a** is especially active and long-lived, with a turnover frequency of 5×10^5 at 60 °C and 200 psig of ethylene, a half-life exceeding 15 h at 35 °C, and a total turnover number exceeding 10^6 at 35 °C and 200 psig. Molecular weights and degrees of branching of polyethylenes obtained from **3a** are reported as a function of reaction temperature and ethylene pressure.

Introduction

In 1995 cationic Ni(II) and Pd(II) catalysts derived from bulky aryl-substituted α -diimines were reported to convert ethylene and α -olefins to high-molecular-weight polyolefins.¹ These materials exhibited unique microstructures due primarily to the now well-established ability of the metal to migrate along the polymer chain via β -hydride elimination/reinsertion reactions without undergoing chain transfer.^{2–7} This discovery was followed by intense collaborative activities between the UNC and DuPont Versipol groups, and later by other groups, in developing the catalytic chemistry and related mechanistic understanding of the diimine systems and related catalysts.^{8–21}

A particular appeal of examining late-metal catalysts was the potential to copolymerize ethylene and polar monomers such as alkyl acrylates.^{22–24} While a limited set of polar monomers were successful in copolymerizations using the diimine systems, even the successful polar monomers exhibited reduced rates, due to the substantial electrophilicity of the cationic metal center and the propensity to form stable chelate structures following polar monomer incorporation.^{8,11,25} In addition, these cationic catalysts were sensitive to polar additives such as water and alcohols. For these reasons, considerable attention turned to developing neutral catalysts based on Ni(II) which should have reduced electrophilicity and thus reduced sensitivity to polar groups.

The first neutral Ni(II) catalysts for ethylene polymerizations were reported in the 1980s.^{22,26–28} These catalysts were primarily based on modifications of the SHOP systems and incorporated anionic phosphino-enolate ligands. Such systems normally provided low-molecular-weight linear polyethylene at modest rates. Incorporation of bulky substituents²⁹ or perfluoroalkyl

* To whom correspondence should be addressed. E-mail: mbrookhart@unc.edu.

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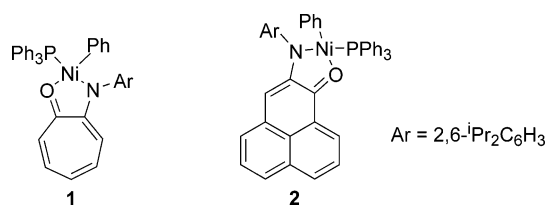
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groups³⁰ in the backbone of the P,O chelates greatly accelerated the polymerization rates, but molecular weights of the linear PE were modest. Claverie³¹ and Mecking^{32,33} have shown that neutral P,O chelate Ni complexes bearing perfluoroalkyl or hydrophilic groups can be used for emulsion polymerizations of ethylene in water. Other interesting SHOP-type derivatives, though mainly used for oligomerization, are zwitterionic Ni(II) complexes developed recently by the Bazan group.³⁴

Neutral ligands based on bidentate anionic N,O ligands have received considerable recent attention since incorporation of a bulky ortho-substituted aryl-N functionality, modeled after the diimine systems, results in substantial increases in polymer molecular weights as well as incorporation of branching due to chain walking.^{35–40} Early prominent examples were based on salicylaldimines formed from ortho-disubstituted anilines and first reported by the DuPont³⁹ and Grubbs groups.⁴⁰ These systems were shown to copolymerize ethylene and norbornene derivatives containing polar functionalities;⁴⁰ Mecking demonstrated that related Ni(II) catalysts were effective for the aqueous emulsion polymerization of ethylene.^{32,41}

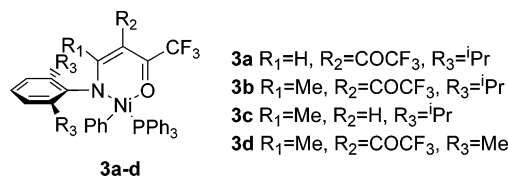
This laboratory has reported the synthesis of anionic five-membered N,O chelates derived from bulky anilinetropones^{35–37} and anilino-perinaphthenone⁴² for preparation of Ni(II) catalysts of types **1** and **2**. These systems proved to be compatible with



polar solvents and highly active for formation of branched PEs. Mechanistic studies established the nature of the catalyst resting state(s) and the mechanisms of chain transfer and decomposition.³⁷ DFT studies of both the salicylaldimine and anilino-tropone systems have been reported.^{17,43}

We report here our efforts to further enhance the activity of neutral Ni(II) catalysts through synthesis and screening of a series of catalysts **3a–d**, which incorporate the strongly electron withdrawing $-\text{CF}_3$ and $-\text{C}(\text{O})\text{CF}_3$ groups in the ligand

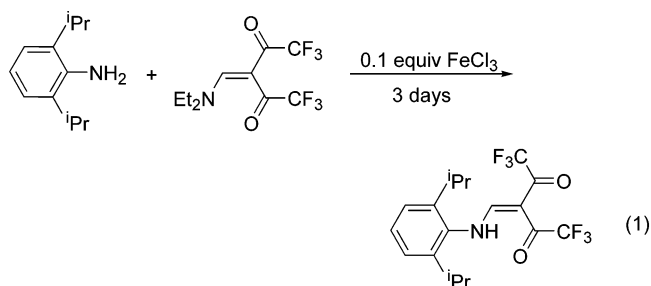
backbone. Complex **3a** shows especially high activity and long lifetime when activated with $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Ni}(\text{COD})_2$.



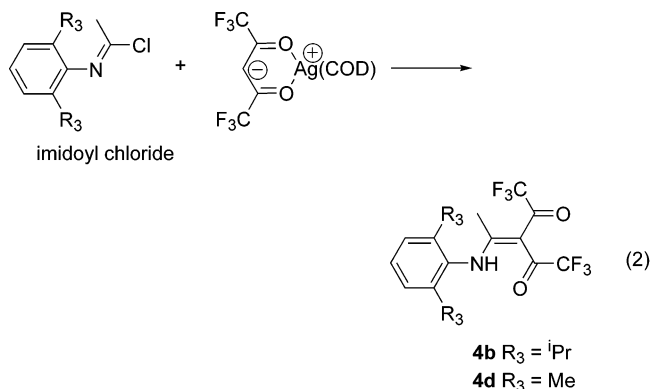
Results and Discussion

Ligand Syntheses. Complexes **3a–d** all share a common five-membered N,O chelate backbone and differ only in the substitution patterns along the backbone. As noted in the Introduction, the rationale for preparing these complexes with highly electron-withdrawing fluoroalkyl substituents was the expectation, based on analogy to P,O chelates, that such complexes may exhibit significantly enhanced activities in ethylene polymerization. All of the complexes **3a–d** are prepared from the corresponding acyl-substituted enamine ligands **4a–d**. However, despite the similarities in structure, different synthetic routes must be employed to access these ligands.

Ligand **4a** is prepared by displacement of the $\text{Et}_2\text{N}-$ group in ((diethylamino)methylene)-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA) by 2,6-diisopropylaniline catalyzed by the Lewis acid FeCl_3 (eq 1), in analogy with the known chemistry of DMAFA. Following chromatographic purification, **4a** was isolated in good yields and high purity.



Ligands **4b** and **4d** were prepared by the reaction of the corresponding imido chloride with silver cyclooctadiene hexafluoroacetylacetonate in toluene at 25 °C (eq 2). Crystal-



lizations from CH_2Cl_2 /hexane at lower temperature afford the pure ligands in excellent yields. Use of the silver enolate is required, since the lithium enolate results in substantial imidoylation at oxygen.

In analogy with the preparation of ligand **4a**, ligand **4c** was prepared by displacement of the methoxy group from the enol

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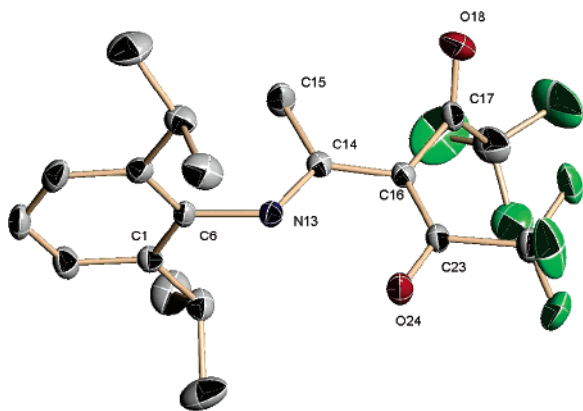
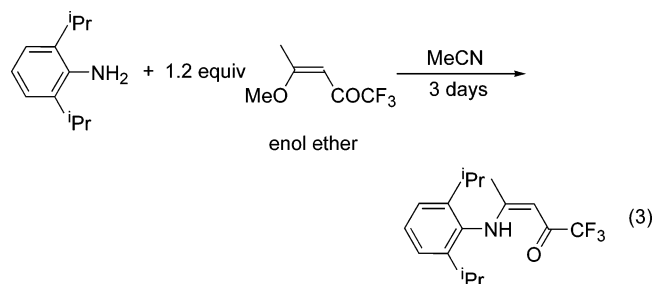


Figure 1. ORTEP view of **4b**. Selected interatomic distances (Å) and angles (deg): C(6)–N(13) = 1.4475(17), N(13)–C(14) = 1.3241(6), C(14)–C(16) = 1.4167(18), C(16)–C(23) = 1.4170(19), C(16)–C(17) = 1.4957(18), C(23)–O(24) = 1.2415(16), C(17)–O(18) = 1.2014(19); C(1)–C(6)–N(13)–C(14) = 86.86(16), N(13)–C(14)–C(16)–C(23) = –0.62(10), C(14)–C(16)–C(23)–O(24) = 1.51(9), C(6)–N(13)–C(14)–C(15) = 5.99(11).

ether (4-methoxy-1,1,1-trifluoro-3-penten-2-one) by 2,6-diisopropylaniline (eq 3). High yields of pure product are obtained in acetonitrile after 3 days at 25 °C.



Ligands **4a–d** were fully characterized by ^1H , ^{13}C , and ^{19}F NMR spectroscopy. All exist in the enamine form rather than the imine form and exhibit a broad N–H signal at ca. 12 ppm. This low-field shift suggests that the preferred geometries are U-shaped to accommodate H-bonding between N–H and the carbonyl oxygen. Consistent with the enamine structure, complexes **4a** and **4c** display vinylic resonances at 7.93 and 5.55 ppm, respectively.

Solid-state structures of ligands **4b** and **4d** have been determined by single-crystal X-ray diffraction (Figures 1 and 2). As anticipated from ^1H NMR data, both ligands exist in the U form appropriate for intramolecular hydrogen bonding and the five atoms of the chelate backbones of both ligands are in the same plane, within a couple of degrees. The aryl rings lie roughly perpendicular to the plane of these chelate backbones. The slight difference between the dihedral angle C(1)–C(6)–N(13)–C(14) of **4b**, 86.9°, and C(5)–C(6)–N(7)–C(8) of **4d**, 81.5°, can be attributed to the steric effect of the bulkier isopropyl group in **4b**. The isopropyl methyl groups of **4b** (and **4c**) exhibit two sets of resonances, indicating that rotation around of the aryl ring is slow on the NMR time scale. Complex **4a**, which lacks a vinylic methyl group, shows a single resonance for the isopropyl methyl group, indicating rapid rotation of the aryl group on the NMR time scale.

Synthesis of Nickel Complexes 3a–d. Complexes **3a–d** were synthesized as shown in Scheme 1. The enamines **4a–d** were readily deprotonated with excess sodium hydride in THF to yield the corresponding sodium salts. In situ reactions of these

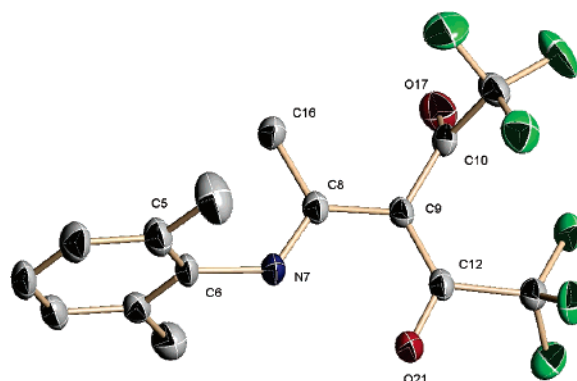
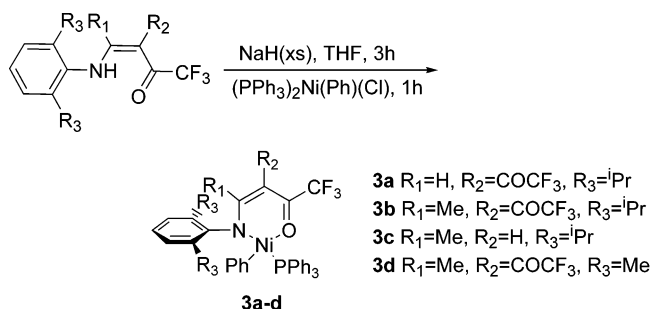


Figure 2. ORTEP view of **4d**. Selected interatomic distances (Å) and angles (deg): C(6)–N(7) = 1.4497(19), N(7)–C(8) = 1.3200(19), C(8)–C(9) = 1.4231(20), C(9)–C(12) = 1.4160(21), C(12)–O(21) = 1.2373(18), C(9)–C(10) = 1.4862(20); C(5)–C(6)–N(7)–C(8) = –81.5(3), C(6)–N(7)–C(8)–C(16) = –6.60(19), N(7)–C(8)–C(9)–C(12) = 2.50(18), C(8)–C(9)–C(12)–O(21) = –2.88(17).

Scheme 1



sodium salts with $(\text{PPh}_3)_2\text{Ni}(\text{Ph})(\text{Cl})$ at 25 °C generated the desired Ni(II) complexes. Following filtration and removal of THF, crystallization of the resulting crude mixtures from toluene/pentane at –30 °C gave crystalline complexes suitable for X-ray diffraction in 33–68% yield.

These complexes were fully characterized by ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectroscopy (see Experimental Section). For complex **3a**, the coordination of the ligand to the Ni(II) center slows the rotation around the N–aryl bond and results in the observation of two magnetically inequivalent isopropyl methyl doublets in the ^1H NMR spectrum. The methine signals in **3a–c** shift to lower fields by ca. 0.6 ppm (3.60 ppm for **3a**, 3.34 ppm for **3b**, and 3.36 ppm for **3c**) compared with the signals for the corresponding free ligands **4a–c**. The ^{13}C resonances of the coordinated carbonyl groups shift to higher fields upon complexation; e.g., the ^{13}C signal in **4b** appears at 176.6 ppm and shifts to 161.4 ppm in **3b**.

Complex **3b** was characterized by single-crystal X-ray diffraction (Figure 3). The complex is square planar, with all L–Ni–L bond angles very close to 90°. As expected on the basis of electronic considerations, the PPh_3 ligand is trans to the better donor amido nitrogen. The diisopropyl-substituted aryl ring is nearly perpendicular to the coordination square plane, as shown by the Ni(1)–N(6)–C(18)–C(19) dihedral angle of –90.1°. There is a slight twist in the ligand backbone to accommodate the square-planar coordination, as illustrated by the C(3)–C(4)–C(5)–N(6) dihedral angle of –28.2°. (Compare this to the N(13)–C(14)–C(16)–C(23) dihedral angle of –0.62° in the ligand **4b**.)

The differing substitution patterns along the ligand backbone significantly affects the steric and electronic properties of the

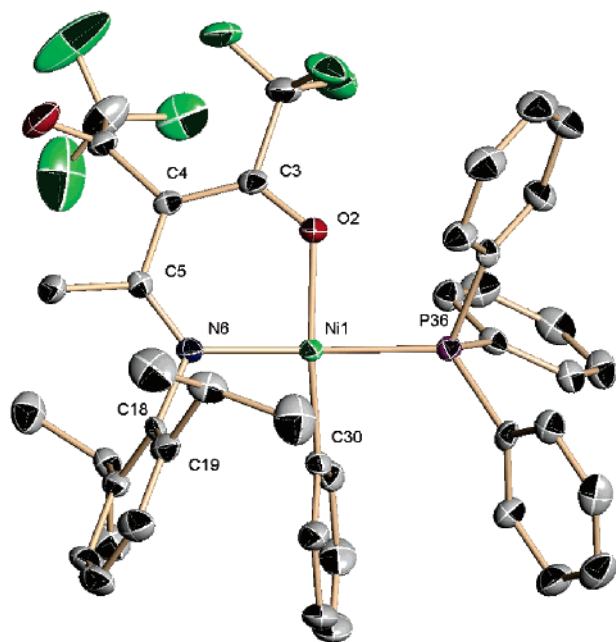


Figure 3. ORTEP view of **3b**. Selected interatomic distances (Å) and angles (deg): Ni(1)–N(6) = 1.953(3), Ni(1)–O(2) = 1.907(2), Ni(1)–C(30) = 1.900(3), Ni(1)–P(36) = 2.1884(9), C(3)–O(2) = 1.269(4), C(3)–C(4) = 1.388(5), C(4)–C(5) = 1.460(5), C(5)–N(6) = 1.308(4); N(6)–Ni(1)–O(2) = 90.42(11), C(30)–Ni(1)–P(36) = 86.97(10), Ni(1)–N(6)–C(18)–C(19) = –90.1, C(3)–C(4)–C(5)–N(6) = –28.2, Ni(1)–O(2)–C(3)–C(4) = 23.9.

Ni(II) centers and in turn their behavior as catalysts for ethylene polymerizations, results of which are summarized below.

Ethylene Polymerizations Catalyzed by 3a–d. To initiate polymerization, ethylene must replace PPh₃ to yield a Ni(phenyl)(ethylene) complex, which then undergoes migratory insertion to yield a Ni–alkyl species that propagates through a series of migratory insertion reactions. The propagating nickel alkyl species can “rest” as a Ni(PPh₃)(alkyl) complex, a Ni(ethylene)(alkyl) complex or a Ni(alkyl) complex, which would most likely exist as a β -agostic structure.^{37,44} For catalysts of type **1** there exists an equilibrium between the (N,O)Ni(PPh₃)-alkyl and the (N,O)Ni(ethylene)alkyl complexes. At high pressures the ethylene complex is the major species and the turnover frequency becomes independent of ethylene pressure.

Polymerizations of ethylene catalyzed by **3a–d** were generally carried out in 80 mL of toluene in a 300 mL reactor, except for catalyst **3a**, for which ethylene polymerizations, when using B(C₆F₅)₃ as activator, were conducted in 200 mL of toluene in a 1 L reactor due to a mass transport problem of ethylene (vide infra). Ethylene pressures varied between 100 and 400 psig; temperatures varied between 25 and 80 °C. Low catalyst loadings were employed so that reaction exotherms could be controlled. Internal temperatures of the autoclaves did not vary more than ca. ± 2 °C. Results for the ethylene polymerization are summarized in Table 1 (for complex **3a**) and Table 2 (for complexes **3b–d**). Turnover numbers as a function of time and temperature are given in the tables and relate to productivities. Since catalyst decay often occurs during polymerization runs, the intrinsic activities are best judged by calculating turnover frequencies at early times.

Without the addition of an activator to sequester PPh₃ and drive the equilibrium toward the Ni(ethylene)(alkyl) complex,

Table 1. Ethylene Polymerization Results Using Catalyst **3a**^a

entry	cat. (μ mol)	cocat. (μ mol)	T (°C)	psig	t (h)	TON ^b	M _w	MWD	Br ^c / 1000C
1 ^d	3.9	0	70	100	1	4 700			
2 ^d	1.5	3.8	70	200	1	123 000	23 000	2.4	42
3 ^d	1.5	3.8	60	200	1	188 000	27 000	2.3	39
4 ^d	1.5	3.8	60	400	1	287 000	29 000	2.2	35
5 ^d	1.5	3.8	50	200	1	142 000	34 000	2.1	35
6 ^e	1.2	4.8	70	200	1	384 000	23 000	3.1	45
7 ^e	1.5	6.0	60	200	1	506 000	25 000	3.7	41
8 ^e	1.2	4.8	35	200	1.7	336 000	115 000	6.0	35
9 ^e	1.2	4.8	35	200	5	990 000	100 000	5.4	34
10 ^e	1.2	4.8	35	200	9	1 349 000			46
11 ^e	1.2	4.8	60	200	1	437 000			49
12 ^e	1.2	4.8	60	200	1	164 000			47

^a All polymerization temperatures are well-controlled with variation less than ± 2 °C. ^b In units of mol of C₂H₄ (mol of Ni)^{–1}. ^c Branching numbers were measured by ¹H NMR spectroscopy in C₆D₅Br at 120 °C. ^d Polymerization was carried out in 80 mL of toluene in a 300 mL reactor with 2.5 equiv of Ni(COD)₂. ^e Polymerization was carried out in 200 mL of toluene in a 1 L reactor with 4.0 equiv of B(C₆F₅)₃.

Table 2. Ethylene Polymerization Results Using Catalysts **3b–d**^a

entry	cat.	cat. (μ mol)	T (°C)	psig	t (h)	TON ^b	M _w	MWD	Br ^c / 1000C
1	3b	8	70	100	3		1 500 ^d		79
2	3b	5	60	200	1	78 000	17 000	4.9	65
3	3b	2.5	50	100	1	52 000	19 000	3.6	54
4	3b	2.3	50	200	1	106 000	27 000	3.3	58
5	3b	3.9	50	200	0.5	48 000	20 000	3.5	56
6	3b	3.2	50	300	1	87 000	24 000	3.2	53
7	3b	1.7	40	200	1	32 000	21 000	3.0	55
8	3c	5.0	60	200	1	37 000	13 000	3.0	56
9	3c	5.0	50	200	1	32 000	17 000	2.3	41
10	3c	3.5	50	300	1	48 000	18 000	3.7	34
11	3c	11.3	25	200	3	3 000	59 000	2.8	
12	3d	12.5	60	200	1	30 000	3 000	1.5	

^a Polymerization was carried out in 80 mL of toluene in a 300 mL reactor with 2.5 equiv of Ni(COD)₂. The temperature is well-controlled with variation less than ± 2 °C. ^b In units of mol of C₂H₄ (mol of Ni)^{–1}. ^c Branching numbers were measured by ¹H NMR spectroscopy in C₆D₅Br at 120 °C. ^d M_n was measured by ¹H NMR.

low productivities are observed for complexes **3a,b** (see Table 1, entry 1 and Table 2, entry 1) and no polymer is obtained for **3c,d** even at 200 psig of ethylene. This implies, in contrast to catalysts of type **1**, that the equilibria lie in favor of the PPh₃ complexes even at high ethylene pressures. Subsequent ethylene polymerizations were conducted using 2–4 equiv of phosphine scavengers to activate these complexes.

For the most active catalyst studied, **3a**, the productivity is greatly enhanced from a TON of only ca. 4700 after 1 h and 100 psig at 70 °C without an activator to 1.23×10^5 at 200 psig with 2.5 equiv of Ni(COD)₂ and 3.84×10^5 with 4 equiv of B(C₆F₅)₃ (compare entries 1, 2, and 6). The optimal productivity for ethylene polymerization is reached at 60 °C (compare entry 3 with entries 2 and 5 and compare entry 7 with entries 6 and 8); the catalyst productivity increases as the ethylene pressure increases (compare entries 3 and 4). BPh₃ and Rh(acac)₂(C₂H₄)₂ were also studied as activators. BPh₃ appears to be nearly as effective as B(C₆F₅)₃ (compare entries 11 and 7; 4.37×10^5 TON versus 5.06×10^5 TON), but Rh(acac)₂(C₂H₄)₂ is clearly much less effective (see entries 11 and 12 vs entry 7). At 60 °C, complex **3a** activated by Ni(COD)₂ or B(C₆F₅)₃ forms a catalyst system with a short lifetime: $t_{1/2} < 20$ min. However, experiments at 35 °C have shown the catalyst is remarkably long-lived (entries 8–10). Between 1.7 and 5.0 h the TON increases linearly with time and shows a calculated TOF of 2.0×10^5 at each time. The TON number at 9 h is less than the extrapolated value (1.35×10^6 vs 1.8×10^6), but at

(44) Wiencko, H. L.; Kogut, E.; Warren, T. H. *Inorg. Chim. Acta* **2003**, *345*, 199.

that time, the reactor is completely filled with solvent-swollen polyethylene and ethylene uptake is clearly limited by mass transfer. On the basis of these observations, conservatively the catalyst half-life must be greater than 15 h and likely is much more.

Polymers produced using either $\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$ as the activator are quite similar. Monomodal GPC traces are observed with molecular weight distributions (MWD) generally in the range of 2–4, indicating a single-site catalytic species is involved for ethylene polymerization. (MWD values above 2 occur in cases exhibiting high total TOs. As noted above, under these conditions the autoclave is filled with solvent-swollen polymer and mass transfer effects likely result in an increase of the MWD value above 2.) M_n values are limited by chain transfer to the monomer, as is supported by entries 3 and 4, showing that an increase of ethylene pressure does not result in a significant increase of PE molecular weight. M_w values lie in the range of 23–100 K and decrease as expected at higher temperatures. Total branching numbers, as measured by ^1H NMR spectroscopy,⁴⁵ fall between 35 and 45 branches per 1000 carbons. Higher temperatures (60–70 °C) produce polymers with branching numbers in the high end of this range, while lower temperatures (35–50 °C) show branching numbers in the low end of the range. (Compare entries 2 and 6 with entries 8 and 9.) The degree of branching of PE produced by complex **3a** with $\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$ as activator is higher than that from catalysts of type **1** or type **2**, where generally 10 branches per 1000 C are observed for type **1** and 17–34 branches for type **2**. The 9 h run at 35 °C produces PE with an unusually high branching number, in comparison to the number for runs at shorter time (entry 10). We ascribe the high branching to the fact that the reactor was filled with solvent-swollen polyethylene, causing slow mass transport of ethylene to the Ni center and thus a reduced polymerization rate vs the polymer chain β -hydride elimination/reinsertion rate responsible for branching. While standard runs were carried out at 200 psig, a 400 psig experiment (entry 4, Table 1) shows that branching is decreased at higher pressures. Both the increase in branching with an increase in temperature and the decrease in branching at higher pressures are consistent with behavior noted previously for the diimine and related systems.^{4,12,36,37} A detailed mechanistic explanation of these effects has been advanced.^{12,13}

Complexes **3b–d** are active ethylene polymerization catalysts in the presence of 2.5 equiv of $\text{Ni}(\text{COD})_2$ as activator, but all are less productive than **3a** (Table 2). Polyethylenes produced by **3b–d** have lower molecular weights and are more highly branched when compared to polymers produced by **3a** under similar conditions (200 psig of ethylene, 60 °C; compare entries 2, 8, and 12 of Table 2 with entry 3 of Table 1). As seen from entries 2 and 12, decreasing the steric bulk around $\text{Ni}(\text{II})$ by replacing ortho isopropyl groups with methyl groups has dramatically decreased the polymer molecular weight and catalyst productivity from $M_w = 17\,000$, TON = 78 000 for **3b** to $M_w = 3000$, TON = 30 000 for **3d**. Entries 4 and 5 show the lifetime of catalytic species generated from **3b**/ $\text{Ni}(\text{COD})_2$ is long, with $t_{1/2} > 60\text{ min}$ at 50 °C. The polymerization results follow the trend observed with complex **3a** (vide supra).

Conclusions

A series of new neutral (N,O) chelated $\text{Ni}(\text{II})$ complexes derived from anilino-substituted enone ligands bearing electron-

withdrawing trifluoromethyl and trifluoroacetyl groups have been synthesized and characterized. These complexes are active for ethylene polymerization in the presence of an activator ($\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$) to sequester PPh_3 . Moderately branched polyethylenes, generally in the range of 35–55 branches per 1000 carbons, are produced, consistent with expectations based on the presence of ortho-disubstituted aryl groups on nitrogen. The productivity ranking under standard conditions (200 psig, 60 °C, $\text{Ni}(\text{COD})_2$ activator) follows the order **3a** > **3b** > **3c** $\approx$ **3d**. The spread in productivities is modest but significant (188 000 TOs for **3a** to 30 000 TOs for **3d**). The rationale for these productivity differences is not obvious. Variations could result from not only differences in intrinsic turnover frequencies but also variable lifetimes. We do note that **3a**, the most productive catalyst, is the only one which bears no methyl substituent α to nitrogen. A notable feature of **3a**, the catalyst we investigated most thoroughly, is not only the excellent productivity at 60 °C but also the very long lifetime at 35 °C. Judging from entries 8–10 in Table 1, the half-life must exceed many hours, since no decrease in activity after 5 h is seen, while the productivity at 9 h was limited by reactor capacity. Further studies of **3a** are underway concerning the detailed mechanism of chain propagation and transfer and the catalyst decay pathway, as well as the use of **3a** for copolymerizations of ethylene and polar monomers.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled drybox and, unless stated otherwise, were stored at room temperature. The ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra were acquired using Bruker 300 and 400 MHz spectrometers. Chemical shifts were reported in δ units as parts per million (ppm) and referenced against residual deuterated solvent peaks (^1H , ^{13}C) or the external standards CF_3COOH (^{19}F) and H_3PO_4 (^{31}P). Flash chromatography was performed using 60 Å silica gel (SAI). High-temperature gel permeation chromatography (GPC) was performed by DuPont (Wilmington, DE) in 1,2,4-trichlorobenzene at 135 °C using a Waters HPLC 150C chromatograph equipped with Shodex columns. All calibration curves were established with polystyrene standards, and universal calibration was applied using Mark–Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Elemental analyses were performed by Altantic Microlab Inc. of Norcross, GA.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum-transferred from CaH_2 , degassed by repeated freeze–pump–thaw cycles, and stored over 4 Å molecular sieves. 2,6-Diisopropylaniline, FeCl_3 , NaH, and $\text{Ni}(\text{COD})_2$ were used as received. Polymer-grade ethylene was used as received for bulk polymerizations and NMR experiments. The following starting materials were prepared according to literature procedures: $(\text{PPh}_3)_2\text{-Ni}(\text{Ph})(\text{Cl})$,⁴⁶ *N*-(2,6-diisopropylphenyl)acetimidoyl chloride,⁴⁷ *N*-(2,6-dimethylphenyl)acetimidoyl chloride,⁴⁷ $\text{Ag}(\text{COD})(\text{hfacac})$,⁴⁸ ((diethylamino)methylene)-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA),⁴⁹ and 4-methoxy-1,1,1-trifluoro-3-penten-2-one.⁵⁰ Yields

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refer to isolated yields of compounds of greater than 95% purity, as estimated by ^1H NMR analysis and elemental analysis.

Analysis of Polymer Branching by ^1H NMR Spectroscopy. ^1H NMR spectra were recorded in either CDCl_3 at room temperature or in $\text{C}_6\text{D}_5\text{Br}$ at 120°C . Assignment of peaks and calculation of polymer branching were carried out by following the previously published method.⁵¹

General Polymerization Procedure. Polymerizations were carried out in a mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was heated under vacuum at 120°C for 1–2 h and then back-filled with Ar, cooled to the desired reaction temperature. A 70 mL portion of toluene was injected, and the reactor was purged with ethylene (3×100 psig). A solution of the catalyst in 10 mL of toluene was added to the vented reactor via cannula. The reactor was sealed and pressurized with ethylene to the desired pressure, and the stirring motor was engaged. When the reaction time was reached, the ethylene pressure was released, and the reaction was quenched with 120 mL of MeOH. Polymer was collected and weighed after removing the volatiles in vacuo and dried in a vacuum oven overnight at 80°C .

A 1 L Parr reactor with external heating and cooling control was also used for polymerizations. A procedure similar to that for the 300 mL Parr reactor was used, but 190 mL of toluene was injected before ethylene purging and the reaction was quenched with 250 mL of MeOH instead.

For cocatalyst studies, the catalyst solution was prepared by dissolving both catalyst and cocatalyst in 10 mL of toluene at room temperature, except for $\text{Ni}(\text{COD})_2$, where the catalyst solution was prepared at -20°C .

3-[(2,6-Diisopropylphenyl)amino)methylene]-1,1,1,5,5,5-hexafluoropentane-2,4-dione (4a). A Schlenk tube flame-dried under vacuum was charged with ((diethylamino)methylene)-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA; 3.577 g, 12.3 mmol) and FeCl_3 (0.1982 g, 1.2 mmol) under argon. Dry toluene (10 mL) was added, followed by 2,6-diisopropylaniline (2.8 mL 14.8 mmol). After it was refluxed for 3 days, the mixture was cooled to room temperature, quenched with 1 N HCl (10 mL), extracted with ether (3×10 mL), and washed with saturated NaHCO_3 (50 mL) and brine (50 mL). After drying over Mg_2SO_4 , volatiles were removed under reduced pressure and pure product was obtained by silica gel chromatography with ethyl acetate–hexane (1:16 v:v) as eluent. Yield: 2.230 g (46%). ^1H NMR (400 MHz, CDCl_3): δ 12.01 (br s, 1H, NH), 7.93 (br s, 1H, vinylic H), 7.41 (t, $J = 7.6$ Hz, 1H, Ar *p*-H), 7.26 (d, $J = 7.6$ Hz, 2H, Ar *m*-H), 2.97 (septet, $J = 6.8$ Hz, 2H, *i*Pr CH), 1.23 (d, $J = 6.8$ Hz, 12H, *i*Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 181.4 (q, $J = 37.6$ Hz, CO), 175.1 (q, $J = 34.4$ Hz, CO), 162.5 (vinylic C=CH), 143.9 (Ar C–N), 133.5, 130.0, 124.6 (Ar C), 116.8 (q, $J = 292.4$ Hz, CF_3), 116.4 (q, $J = 287.6$ Hz, CF_3), 101.6 (vinylic C=CH), 28.6 (*i*Pr CH), 23.6 (*i*Pr CH_3). ^{19}F NMR (376 MHz, CDCl_3): δ -72.68, -68.88. Anal. Calcd ($\text{C}_{18}\text{H}_{19}\text{NO}_2\text{F}_6$): C, 54.7; H, 4.84; N, 3.54. Found: C, 55.8; H, 5.04; N, 3.69.

3-[1-((2,6-Diisopropylphenyl)amino)ethylidene]-1,1,1,5,5,5-hexafluoropentane-2,4-dione (4b) and 3-[1-((2,6-Dimethylphenyl)amino)ethylidene]-1,1,1,5,5,5-hexafluoropentane-2,4-dione (4d). (a) **General Procedure.** A toluene solution of $\text{Ag}(\text{COD})$ -(hfacac) was added to imidoyl chloride in toluene via cannula at room temperature. AgCl rapidly precipitated from the solution. The mixture was further stirred for 2 h at room temperature and then filtered through a pad of Celite and washed two times with toluene. After removal of solvent in vacuo, products were recrystallized from toluene and pentane to yield clear crystals.

(b) **Synthesis of 4b.** This compound was prepared from $\text{Ag}(\text{COD})$ -(hfacac) (3.568 g, 8.4 mmol) in 50 mL of toluene and *N*-(2,6-diisopropylphenyl)acetimidoyl chloride (2.000 g, 8.4 mmol) in 30

mL of toluene. Yield: 3.310 g (96%). ^1H NMR (400 MHz, CDCl_3): δ 13.07 (br s, 1H, NH), 7.39 (t, $J = 7.6$ Hz, 1H, Ar *p*-H), 7.25 (d, $J = 7.6$ Hz, 2H, Ar *m*-H), 2.78 (septet, $J = 6.8$ Hz, 2H, *i*Pr CH), 1.87 (s, 3H, vinylic CH_3), 1.16 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3), 1.21 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 184.8 (br s, CO), 176.6 (br s, CO), 171.6 (vinylic CCH_3), 144.9 (Ar C–N), 130.9, 130.0, 124.4 (Ar C), 116.5 (br q, $J = 300$ Hz, 2CF_3), 100.4 (vinylic C=CCH₃), 28.9 (*i*Pr CH₃), 22.5 (*i*Pr CH₃), 24.3 (*i*Pr CH), 17.8 (vinylic CCH_3). ^{19}F NMR (376 MHz, CDCl_3): δ -75.38, -71.57. Anal. Calcd ($\text{C}_{19}\text{H}_{21}\text{F}_6\text{NO}_2$): C, 55.7; H, 5.17; N, 3.42. Found: C, 55.6; H, 5.02; N, 3.38.

(c) **Synthesis of 4d.** This compound was prepared from $\text{Ag}(\text{COD})$ -(hfacac) (2.328, 1.1 mmol) in 25 mL of toluene and *N*-(2,6-dimethylphenyl)acetimidoyl chloride (1.000 g, 1.1 mmol) in 25 mL of toluene. Yield: 1.543 g (79%). ^1H NMR (400 MHz, CD_2Cl_2): δ 12.98 (br s, 1H, NH), 7.26 (t, $J = 7.6$ Hz, 1H, Ar *p*-H), 7.20 (d, $J = 7.6$ Hz, 2H, Ar *m*-H), 2.20 (s, 6H, Ar 2,6-*o*-CH₃), 1.89 (s, 3H, vinylic CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.8 (br s, CO), 177.2 (br s, 2CO), 171.2 (vinylic CCH_3), 134.6, 133.8, 129.2, 129.0 (Ar C), 116.3 (q, $J = 288$ Hz, 2CF_3), 100.4 (vinylic C=CCH₃), 18.0 (Ar 2,6-*o*-CH₃), 17.2 (vinylic CH_3). ^{19}F NMR (376 MHz, CD_2Cl_2): δ -77.2, -73.6. Anal. Calcd ($\text{C}_{19}\text{H}_{21}\text{F}_6\text{NO}_2$): C, 51.0; H, 3.71; N, 3.96. Found: C, 51.0; H, 3.62; N, 3.75.

4-((2,6-Diisopropylphenyl)amino)-1,1,1-trifluoro-pent-3-en-2-one (4c). A solution of 2,6-diisopropylaniline (1.63 mL, 8.7 mmol) and 4-methoxy-1,1,1-trifluoro-3-penten-2-one (1.746 g, 10.4 mmol) in MeCN (8 mL) was stirred at room temperature for a prolonged time (monitored by silica TLC, about 3 days). The solvent was removed under reduced pressure after the completion of reaction as judged by TLC. The crude product was redissolved in Et_2O (20 mL) and was washed with 1 N HCl and then saturated aqueous NaHCO_3 . After drying over Na_2SO_4 , Et_2O was removed to provide 2.537 g of pure product (93%). ^1H NMR (400 MHz, CDCl_3): δ 12.17 (br s, 1H, NH), 7.34 (t, $J = 7.6$ Hz, 1H, Ar *p*-H), 7.20 (d, $J = 7.6$ Hz, 2H, Ar *m*-H), 5.55 (s, 1H, vinylic H), 2.91 (septet, $J = 6.8$ Hz, 2H, *i*Pr CH), 1.80 (s, 3H, vinylic CH_3), 1.21 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3), 1.14 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 176.7 (q, $J = 33$ Hz, C=O), 170.4 (vinylic CCH_3), 145.5 (Ar C–N), 132.1, 129.2, 124.0 (Ar C), 117.6 (q, $J = 287$ Hz, CF_3), 89.5 (vinylic CH), 28.6 (*i*Pr CH_3), 22.6 (*i*Pr CH_3), 24.5 (*i*Pr CH), 19.7 (vinylic CH_3). ^{19}F NMR (376 MHz, CDCl_3): δ -75.35. Anal. Calcd ($\text{C}_{17}\text{H}_{22}\text{F}_3\text{NO}$): C, 65.2; H, 7.08; N, 4.47. Found: C, 64.6; H, 6.94; N, 4.27.

Synthesis of Complexes 3a–d. (a) **General Procedure.** A Schlenk tube flame-dried under vacuum was charged with ligands **4a–d** and NaH (3 equiv) under argon. THF was added, and the mixture was stirred at room temperature for 3 h. This solution containing deprotonated ligand was transferred via cannula to another flame-dried Schlenk flask containing $(\text{PPh}_3)_2\text{Ni}(\text{Ph})(\text{Cl})$. After 1 h of reaction, the mixture was filtered through a pad of dry Celite and solvent was removed under vacuum. Crystals suitable for single-crystal X-ray diffraction were obtained by slow diffusion of pentane into a toluene solution (1:10 v:v) in the freezer ($\sim -30^\circ\text{C}$).

(b) **Synthesis of 3a.** This compound was prepared from ligand **4a** (0.218 g, 0.55 mmol) and NaH (39.8 mg, 1.66 mmol) in 10 mL of THF and $(\text{PPh}_3)_2\text{Ni}(\text{Ph})(\text{Cl})$ (0.384 g, 0.56 mmol). Yield: 0.133 g (33%). ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 8$ Hz, 1H, vinylic CH), 7.39–7.23 (m, 15H, PPh₃), 6.91 (t, $J = 7.6$ Hz, 1H, Ar *p*-H), 6.80 (d, $J = 7.6$ Hz, 2H, Ar *m*-H), 6.52 (d, $J = 7.6$ Hz, 2H, Ni–Ph *o*-H), 6.25 (t, $J = 7.6$ Hz, 1H, Ni–Ph *p*-H), 6.12 (t, $J = 7.6$ Hz, 2H, Ni–Ph *m*-H), 3.60 (septet, $J = 6.8$ Hz, 2H, *i*Pr CH), 1.13 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3), 1.01 (d, $J = 6.8$ Hz, 6H, *i*Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 177.9 (q, $J = 34.4$ Hz, C=O), 161.6 (vinylic CH), 148.4, 142.5, 140.4, 136.6, 133.8, 130.2, 129.5, 128.2, 125.9, 122.7, 121.8 (Ar C), 118.0 (q, $J = 300$ Hz, CF_3), 116.5 (q, $J = 300$ Hz, CF_3), 105.4 (vinylic C=CH), 28.6

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Table 3. Crystallographic Data Collection Parameters for **4b,d** and **3b**

	4b	4d	3b
formula	C ₁₉ H ₂₁ F ₆ NO ₂	C ₁₅ H ₁₃ F ₆ NO ₂	C ₄₃ H ₄₀ F ₆ NNiO ₂ P
mol wt	409.37	353.26	806.47
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.5817(4)	7.7190(12)	13.7411(7)
<i>b</i> (Å)	10.9073(5)	9.4574(15)	15.0842(8)
<i>c</i> (Å)	10.9450(5)	11.3047(17)	18.7681(13)
α (deg)	111.170(3)	75.083(6)	90
β (deg)	108.944(3)	78.299(6)	93.375(3)
γ (deg)	97.324(3)	81.459(7)	90
<i>V</i> (Å ³)	969.28	776.82(21)	3883.4(4)
<i>D</i> _{calcd} (Mg/m ³)	1.403	1.510	1.38
scan mode	ω - ψ	ω	φ - ω
μ (mm ⁻¹)	0.13	0.15	0.607
cryst dims (mm)	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.25	0.20 × 0.20 × 0.10
2 θ range (deg)	5.00–56.00	5.00–56.00	3–25
no. of rflns	25 391	17 608	22 578
no. of unique rflns	4647	3371	9345
no. of obsd data (<i>I</i> > 2.5 σ (<i>I</i>))	3773	2833	4530
no. of refined params	338	269	487
<i>hkl</i> range	–12 to +12, 0–14, –14 to +13	–9 to +10, 0–12, –14 to +14	–17 to +18, –19 to +16, –24 to +18
<i>R</i> _F , %	0.043	0.041	0.046
<i>R</i> _w , %	0.051	0.050	0.049
GOF	2.8941	2.3672	1.134
<i>Z</i>	2	2	4

(*i*Pr CH), 25.3 (*i*Pr CH₃), 22.5 (*i*Pr CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ –71.59, –71.21. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 27.26. Anal. Calcd (C₄₂H₃₈NO₂F₆PNi): C, 63.7; H, 4.83; N, 1.77. Found: C, 63.9; H, 4.86; N, 1.79.

(c) Synthesis of 3b. This compound was prepared from ligand **4b** (0.300 g, 0.73 mmol) with NaH (52.8 mg, 2.2 mmol) in 60 mL in THF and (PPh₃)₂Ni(Ph)(Cl) (0.510 g, 0.73 mmol). Yield: 0.263 g (49%). ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.19 (m, 15H, PPh₃), 6.97 (t, *J* = 7.6 Hz, 1H, Ar *p*-H), 6.87 (d, *J* = 7.6 Hz, 2H, Ar *m*-H), 6.37 (d, *J* = 7.6 Hz, 2H, Ni–Ph *o*-H), 6.29 (t, *J* = 7.6 Hz, 1H, Ni–Ph *p*-H), 6.11 (t, *J* = 7.6 Hz, 2H, Ni–Ph *m*-H), 3.34 (septet, *J* = 6.8 Hz, 2H, *i*Pr CH), 1.68 (s, 3H, vinylic CH₃), 1.05 (d, *J* = 6.8 Hz, 6H, *i*Pr CH₃), 0.99 (d, *J* = 6.8 Hz, 12H, *i*Pr CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 185.8 (q, *J* = 34 Hz, C=O), 161.4 (q, *J* = 34 Hz, C=O), 166.4 (vinylic CCH₃), 145.2, 141.4, 139.6, 137.0, 133.8, 130.0, 129.5, 127.9, 126.0, 125.3, 123.4, 121.6 (Ar C), 118.7 (q, *J* = 300 Hz, 2CF₃), 105.6 (vinylic C=CCH₃), 28.6 (*i*Pr CH), 24.0 (allylic CH₃), 24.3 (*i*Pr CH₃), 23.9 (*i*Pr CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ –76.57, –70.27. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 24.11. Anal. Calcd (C₄₃H₄₀NO₂F₆PNi): C, 64.0; H, 5.00; N, 1.74. Found: C, 63.8; H, 4.70; N, 1.86.

(d) Synthesis of 3c. This compound was prepared from ligand **4c** (0.200 g, 0.64 mmol) with NaH (46.0 mg, 1.92 mmol) in 40 mL of THF and (PPh₃)₂Ni(Ph)(Cl) (0.444 g, 0.64 mmol). Yield: 0.222 g (50%). ¹H NMR (400 MHz, CDCl₃): δ 7.33–7.16 (m, 15H, PPh₃), 6.92 (t, *J* = 7.6 Hz, 1H, Ar *p*-H), 6.80 (d, *J* = 7.6 Hz, 2H, Ar *m*-H), 6.43 (d, *J* = 7.6 Hz, 2H, Ni–Ph *o*-H), 6.25 (t, *J* = 7.6 Hz, 1H, Ni–Ph *p*-H), 6.07 (t, *J* = 7.6 Hz, 2H, Ni–Ph *m*-H), 5.49 (s, 1H, vinylic CH), 3.36 (septet, *J* = 6.8 Hz, 2H, *i*Pr CH), 1.67 (s, 3H, vinylic CH₃), 1.07 (d, *J* = 6.8 Hz, 6H, *i*Pr CH₃), 0.99 (d, *J* = 6.8 Hz, 12H, *i*Pr CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 168.5 (vinylic CCH₃), 158.8 (q, *J* = 30.4 Hz, CO), 146.6, 143.0, 140.0, 137.0, 133.9, 130.8, 129.5, 127.6, 125.2, 124.8, 122.9, 121.0 (Ar C), 119.0 (q, *J* = 286 Hz, CF₃), 94.6 (vinylic CH), 28.3 (*i*Pr CH), 25.8 (vinylic CH₃), 24.38 (*i*Pr CH₃), 23.80 (*i*Pr CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ –75.01 (CF₃). ³¹P{¹H} NMR (162 MHz,

CDCl₃): δ 22.50. Anal. Calcd (C₄₁H₄₁NOF₃PNi): C, 69.3; H, 5.82; N, 1.97. Found: C, 69.5; H, 5.88; N, 2.13.

(e) Synthesis of 3d. This compound was prepared from ligand **4d** (0.300 g, 0.85 mmol) with NaH (61.2 g, 2.55 mmol) in 50 mL of THF and (PPh₃)₂Ni(Ph)(Cl) (0.591 g, 0.85 mmol). Yield: 0.430 g (68%). ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.20 (m, 15H, PPh₃), 6.62 (br s, 3H, Ar H), 6.53 (d, *J* = 7.6 Hz, 2H, Ni–Ph *o*-H), 6.24 (t, *J* = 7.6 Hz, 1H, Ni–Ph *p*-H), 6.05 (t, *J* = 7.6 Hz, 2H, Ni–Ph *m*-H), 2.18 (s, 6H, CH₃), 1.54 (s, 3H, vinylic CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 185.7 (q, *J* = 35.2 Hz, CO), 165.7 (vinylic CCH₃), 161.9 (q, *J* = 34.4 Hz, CO), 147.7 (Ar C–N), 144.5, 136.5, 130.0, 129.9, 128.9, 127.9, 127.8, 125.0, 124.9, 121.4 (Ar C), 118.4 (q, *J* = 283 Hz, CF₃), 116.0 (q, *J* = 293 Hz, CF₃), 105.6 (vinylic C=CCH₃), 21.8 (vinylic CH₃), 18.9 (Ar CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ –76.7, –70.2. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 27.6. Anal. Calcd (C₃₉H₃₂NO₂F₆PNi): C, 62.4; H, 4.30; N, 1.87. Found: C, 64.0; H, 4.95; N, 1.76.

X-ray Crystal Structures. Diffraction data were collected on a Bruker SMART 1K diffractometer, at –100 °C. Refinement was carried out with the full-matrix least-squares method based on *F* (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection for **4a,d** and **3b** are given in Table 3.

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Supporting Information Available: CIF files giving crystallographic data for **4b,d** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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