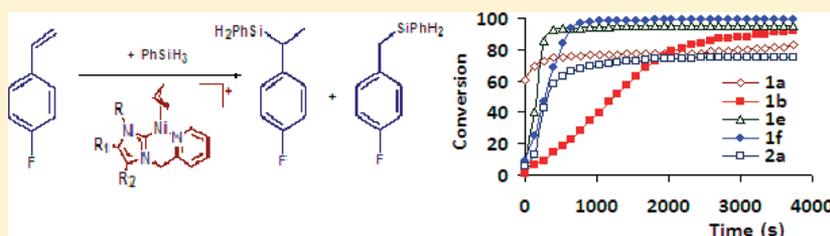


# R-Allyl Nickel(II) Complexes with Chelating N-Heterocyclic Carbenes: Synthesis, Structural Characterization, and Catalytic Activity

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## Supporting Information



**ABSTRACT:** The N-heterocyclic carbene (NHC) nickel complexes  $[(L)Ni(NHC)][BAR^F_4]$  ( $Ar^F = 3,5$ -bis(trifluoromethyl)-phenyl;  $L =$  allyl (**1**), methylallyl (**2**); NHC = 1-(2-picolyl)-3-methylimidazol-2-ylidene (**a**), 1-(2-picolyl)-3-isopropylimidazol-2-ylidene (**b**), 1-(2-picolyl)-3-*n*-butylimidazol-2-ylidene (**c**), 1-(2-picolyl)-3-phenylimidazol-2-ylidene (**d**), 1-(2-picolyl)-3-methylbenzimidazol-2-ylidene (**e**), 1-(2-picolyl)-4,5-dichloro-3-methylimidazol-2-ylidene (**f**)) have been obtained in high yields and characterized by NMR spectroscopy. Furthermore, **1d** was unambiguously characterized by single-crystal X-ray crystallography. Complexes **1a–f/2a–f** have shown catalytic activity toward dimerization and hydrosilylation of styrenes. In particular, **1a** proved to be the most efficient catalyst in the dimerization of styrene derivatives in the absence of cocatalyst. Also, complexes **1a,d** showed high selectivity and moderate to good yields in hydrosilylation reactions.

## INTRODUCTION

The synthesis and isolation of the first N-heterocyclic carbene (NHC) were reported by Wanzlick,<sup>1,2</sup> but until 1991<sup>3</sup> NHCs did not experience a remarkable development. Since then, NHCs have become an important class of ligands in organometallic chemistry and catalysis.<sup>4</sup>

These ligands are often compared to tertiary phosphines because of the similarities in their bonding with transition metals, and in many cases, they have successfully replaced them as auxiliary ligands. However, substantial differences do exist, especially regarding their electron-donating ability. In general, NHCs are stronger Lewis bases and have a reduced  $\pi$ -back-bonding capability in comparison to tertiary phosphines.<sup>5</sup> NHCs show superior performances in many aspects, including higher versatility, easier preparation, thermal, air, and moisture stability, and lower toxicity. Consequently, complexes that incorporate these ligands are more stable toward dissociative and degradative cleavage. The applications of organometallic complexes bearing NHC ligands in catalysis are now well recognized.<sup>3,4</sup>

The use of nickel NHC complexes in catalysis has been eclipsed by the far wider range of applications found for their palladium and ruthenium analogues.<sup>4</sup> However, in the past decade several NHC–Ni(0) and NHC–Ni(II) systems have been reported. NHC–Ni(0) complexes have emerged as efficient catalysts in C–S couplings,<sup>6</sup>  $[2 + 2 + 2]$  cyclo-additions,<sup>7–9</sup> and amination of aryl chlorides.<sup>10</sup> Nevertheless, they are very air sensitive, and their reactions usually require the use of a cocatalyst.<sup>11,12</sup> On the other hand, NHC–Ni(II)

complexes bearing electron-rich ligands have been synthesized to avoid the use of cocatalyst, and they have shown activity in C–C cross-coupling reactions,<sup>11,13</sup> polymerization of styrene,<sup>12</sup> amination of aryl halides,<sup>14</sup> and Suzuki<sup>15,16</sup> and Kumada reactions.<sup>17</sup>

The first Ni(allyl)–NHC complexes were reported by the groups of Sigman et al.,<sup>18</sup> Gomes,<sup>19</sup> and Cámpora.<sup>20</sup> Complexes of the type Ni(allyl)(X)(NHC) ( $X = Cl, Br$ ) have shown activity in several C–C coupling reactions.<sup>14b,20,21</sup> In particular, polymerization reactions are very important, considering the industrial application of the resulting polymers. These reactions have been performed using nickel complexes with MAO (methylalumoxane) as cocatalyst.<sup>22</sup> However, the application of Ni(allyl)–NHC complexes in polymerization has been quite limited. Decomposition of the catalyst due to the cleavage of the Ni–NHC bond, leading to the reductive elimination of the active species,<sup>7a,23</sup> has been proposed to explain the low activity of such complexes. This behavior has mainly been observed in cationic complexes.<sup>24</sup>

Recently, this problem has been avoided by the use of functionalized NHCs, which may act as bidentate ligands due to the presence of additional donor atoms (N, S, O) in the NHC side chains.<sup>25</sup> The hemilabile character of these groups allows additional stabilization of the resulting complexes, whereas they maintain the catalytic activity due to the possibility of

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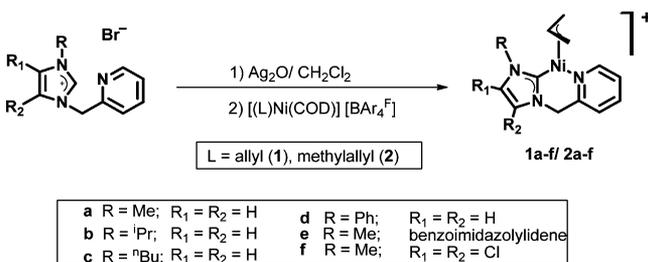
developing a vacant site. On the other hand, the base-promoted C–H activation of a labile acetonitrile ligand on a nickel–NHC center has been recently described.<sup>26,27</sup> An appropriate design of the NHC ligand may also allow tuning of the electronic and steric properties of the ligand.<sup>10,28</sup>

We have previously reported the synthesis and reactivity of allyl–Ni(II) complexes bearing phosphines as auxiliary ligands, and they have shown great activity in alkene polymerization.<sup>29</sup> In this paper, we extend previous studies synthesizing a series of [(L)Ni(NHC)]<sup>+</sup> (L = allyl, methylallyl; NHC = 1-(2-picolyl)-3-(R)-imidazol-2-ylidene (R = Me, *i*Pr, *n*Bu, Ph), 1-(2-picolyl)-3-methylbenzimidazol-2-ylidene, 1-(2-picolyl)-4,5-dichloro-3-methylimidazol-2-ylidene) complexes (**1a–f/2a–f**), reporting the high-yield synthesis of new NHC–Ni(II) complexes and their activity toward styrene polymerization. The wide range of picolyl-NHCs used allowed us to tune the steric and electronic properties of these new Ni complexes and assess the effect on the catalytic activity toward polymerization and hydrosilylation reactions of styrenes. The structure of [(CH<sub>2</sub>CHCH<sub>2</sub>)Ni(1-(2-picolyl)-3-phenylimidazol-2-ylidene)][BAr<sub>4</sub><sup>F</sup>] has been determined by single-crystal X-ray diffraction.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Ni(II)–NHC Complexes.** 2-Picolylimidazolium salts constitute a family of bidentate NHC ligands easily accessible by coupling of 2-(bromomethyl)pyridine with the corresponding imidazole derivative, as described in the literature.<sup>24,30</sup> A series of this type of ligands has been prepared bearing different substituents at the 3-, 4-, and 5-positions on the imidazolium ring (see Scheme 1). Several

**Scheme 1.** Synthesis of R-Allyl–Ni–NHC Complexes

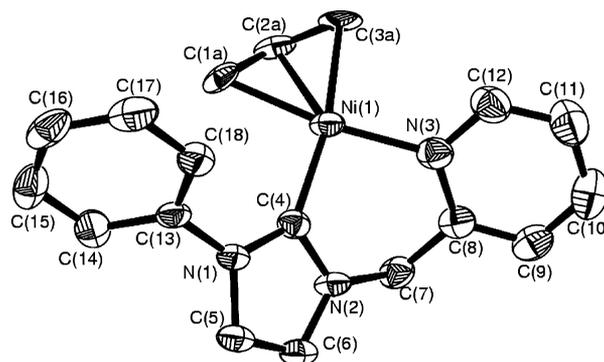


methods can be used to prepare Ni(II)–NHC complexes;<sup>28</sup> among them, transmetalation from a silver precursor has proved to be very efficient. Thus, the Ni(II) complexes [(L)Ni(NHC)][B(Ar<sup>F</sup>)<sub>4</sub>] (L = allyl (**1**), methylallyl (**2**); NHC = 1-(2-picolyl)-3-(R)-imidazol-2-ylidene (R = Me (**a**), *i*Pr (**b**), *n*Bu (**c**), Ph (**d**)), 1-(2-picolyl)-3-methylbenzimidazol-2-ylidene (**e**), 1-(2-picolyl)-4,5-dichloro-3-methylimidazol-2-ylidene (**f**)) have been prepared by transmetalation of the corresponding silver carbenes. Silver species were generated in situ, by treatment of the appropriate 2-picolylimidazolium salt in CH<sub>2</sub>Cl<sub>2</sub> with a slight excess of Ag<sub>2</sub>O. The mixture was filtered through Celite. Then [(L)Ni(COD)][BAr<sub>4</sub><sup>F</sup>] (L = allyl, methylallyl) was added to the previous mixture. After this treatment, complexes **1a–f/2a–f** were obtained in good yields (Scheme 1).

All of the isolated complexes lack a C2–H imidazolium proton signal at 10–12 ppm, indicating the coordination of the 2-picolylcarbene to the nickel atom. The <sup>1</sup>H NMR spectra of complexes **1a–f** and **2a–f** show characteristic signals corresponding to the diastereotopic methylene protons in the CH<sub>2</sub> bridge of the bidentate ligand, which in its coordinated

form splits and appears as two AB doublets, with typical coupling constants for these systems (*J* = 14.0–15.7 Hz), within the chemical shift range of 6.5–5.5 ppm. However not in all cases were these two signals unambiguously observed. For complexes **1b** and **2b,e**, methylene protons accidentally exhibit a broad singlet. In the case of complex **1e** the two resonances overlap and only a doublet is observed. Complexes **1f** and **2c,f** show two broad singlets. All these assignments of methylene proton resonances have been confirmed by 2D NMR experiments. The <sup>13</sup>C NMR spectra of **1a–f/2a–f** exhibit the resonances of the carbene carbon atoms in the distinctive interval 176–153 ppm, already observed for the carbene carbon signal of Ni–NHC complexes.<sup>17a,19,31,32</sup>

**Crystal Structure of [Ni(η<sup>3</sup>-CH<sub>2</sub>CHCH<sub>2</sub>)(NHC-κ<sup>2</sup>C,N)][B(Ar<sup>F</sup>)<sub>4</sub>] (**1d**).** After recrystallization from a mixture of diethyl ether and petroleum ether, complex **1d** was further characterized by single-crystal X-ray diffraction techniques. The ORTEP drawing of cation complex in **1d** is displayed in Figure 1, along



**Figure 1.** ORTEP view of the cation complex in [Ni(η<sup>3</sup>-CH<sub>2</sub>CHCH<sub>2</sub>)(NHC-κ<sup>2</sup>C,N)][B(Ar<sup>F</sup>)<sub>4</sub>] (**1d**; NHC = 1-(2-picolyl)-3-phenylimidazol-2-ylidene). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. The allyl ligand is represented only in its major orientation (71%). Selected bond lengths (Å) and angles (deg): Ni(1)–C(1a) = 2.049(15), Ni(1)–C(2a) = 2.003(8), Ni(1)–C(3a) = 1.95(2), Ni(1)–C(4) = 1.892(5), Ni(1)–N(3) = 1.946(5), C(1a)–C(2a) = 1.432(17), C(2a)–C(3a) = 1.35(4); C(4)–Ni(1)–N(3) = 92.4(2), C(1a)–C(2a)–C(3a) = 116.9(17). Dihedral angle (deg) between planes C(1a)–C(2a)–C(3a) and C(4)–Ni(1)–N(3): 68.6(10).

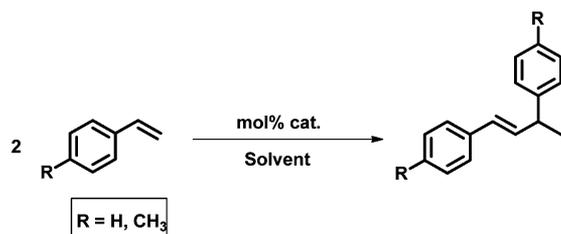
with selected bond lengths and angles. The cation exhibits a classic pseudo-square-planar geometry characteristic of d<sup>8</sup> M(II) allyl complexes. The allyl ligand coordinates to the metal in a η<sup>3</sup> manner. As in other related nickel complexes, the structure reveals that the allyl ligand is disordered. This disorder has been modeled in two opposite orientations of this group relative to the rest of the molecule. Upon refining the occupancy factors, a population ratio of ca. 71:29 was obtained for the two orientations. For clarity, only the major position (approximately 71%) has been represented. The ligand 1-(2-picolyl)-3-phenylimidazol-2-ylidene, binding to the central nickel atom in a bidentate manner, completes the formal tetracoordination. Few structures of cationic allyl nickel complexes containing a κ<sup>1</sup>-NHC ligand have been reported.<sup>18–20,29</sup> None of them contain a chelating κ<sup>2</sup>C,E-NHC ligand. The Ni(1)–C(4) distance of 1.892(5) Å is typical for a Ni–NHC distance and compares well with 1.8780(2) Å for [Ni(η<sup>3</sup>-allyl)(NHC)(NCCCH<sub>3</sub>)<sup>+</sup>] (NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) and 1.909(3) Å for [Ni(η<sup>3</sup>-allyl)(NHC)(NCCCH<sub>3</sub>)<sup>+</sup>] (NHC = 2,5-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).<sup>20</sup> Other related neutral Cp,

Cp\*, or indenyl nickel complexes also show similar parameters: for instance, in  $[\text{Ni}(\text{Me-NHC})\text{I}(\eta^5\text{-C}_5\text{Me}_5)]$ ,  $[\text{Ni}(\text{Me-NHC})\text{I}(\eta^5\text{-C}_5\text{H}_5)]$ , and  $[\text{Ni}(\text{Mes-NHC})\text{Cl}(\eta^5\text{-C}_5\text{Me}_5)]$  the Ni–NHC distances are 1.887(3), 1.880(4), and 1.906(3) Å, respectively.<sup>33</sup> The dihedral angle between planes C(1a)–C(2a)–C(3a) and C(4)–Ni(1)–N(3) matches with the angles in other  $[\text{Ni}(\eta^3\text{-allyl})(\text{NHC})]^+$  systems described in the literature.<sup>18–20</sup>

In neutral complexes  $[\text{NiBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC})]$  Gomes et al.<sup>19</sup> attributed the weakening of the bond between the metal and the allyl atom placed trans to the NHC to a stronger donor ability of the imidazol-2-ylidene ring. In our case, despite the disorder found for the allyl ligand and consequent greater deviations in bond lengths, the pyridyl ring seems to show a greater trans influence, as indicated by the Ni(1)–C(1a) distance (2.049(15) Å) being longer than Ni(1)–C(3a) (1.95(2) Å). It is necessary to take into account this indication in relation to the possibilities of hemilability and chemical reactivity of the chelating ligand.

**Catalytic Oligomerization of Styrenes.** Polymerization of olefins is a very important type of C–C bond coupling reaction, given the wide range of applications of polymers in industrial processes.<sup>11–13,15,16</sup> Many organometallic compounds, especially those of Ni and Pd, have been used as catalysts in such processes.<sup>25</sup> However, a mixture of oligomers and polymers is often observed, due to the low selectivity of the catalysts. Our group has previously reported the oligomerization of styrene derivatives using Ni(II) complexes with good yields.<sup>29</sup> However, it has been very difficult to find highly selective processes for low-molecular-weight oligomers. In this sense, to the best of our knowledge, the new Ni(II)–picolyl-NHC complexes have proved to be more active and selective toward styrene dimer synthesis than any other reported catalytic system (Scheme 2).

### Scheme 2. Catalytic Dimerization of Styrene



The polymerization of styrene using the catalyst **1a** as catalyst precursor was selected as the representative reaction to optimize the system conditions. The results, given in Table 1, show that moderate to high yields were obtained at 60 °C in short reaction times (entries 14–16), especially when low catalyst loadings were used. Another result to note is that the use of a catalytic load of 1 mol % produced the dimer with a selectivity of 100% and high yield in just 1 h (entry 17), while most of the systems previously reported require longer reaction times.<sup>29,35,36</sup> Also, a noncoordinating solvent is needed to prevent solvent coordination to the metal center.<sup>29</sup> It is important to note that, as shown in Table 1, the oligomerization of styrene proceeds with high selectivity toward dimer in all cases.

The oligomerization of styrene was carried out using compounds **1a–f** and **2a–f** to assess the effect of the ligands in the catalytic activity. As shown in Table 2, compounds **1a,b** showed the best catalytic activity, as evidenced by the high yields and selectivity of the reaction (entries 1 and 2).

**Table 1. Dimerization of Styrene: Optimization of Reaction Conditions**

entry	T (°C)	<b>1a</b> (mol %)	t (h)	yield (%)	selectivity dimer/trimer
1	40 <sup>a</sup>	0.1	1	5	100/0
2	40 <sup>a</sup>	0.1	2	6	100/0
3	40 <sup>a</sup>	0.1	3	8	100/0
4	40 <sup>a</sup>	0.5	1	7	98/2
5	40 <sup>a</sup>	0.5	2	30	99/1
6	40 <sup>a</sup>	0.5	3	42	90/10
7	40 <sup>a</sup>	1	1	80	100/0
8	40 <sup>a</sup>	1	4	91	100/0
9	40 <sup>b</sup>	0.5	1	6	100/0
10	40 <sup>b</sup>	0.5	2	25	100/0
11	40 <sup>b</sup>	0.5	3	38	100/0
12	40 <sup>b</sup>	1	1	76	100/0
13	40 <sup>b</sup>	1	4	89	100/0
14	60 <sup>b</sup>	0.5	1	63	100/0
15	60 <sup>b</sup>	0.5	2	74	100/0
16	60 <sup>b</sup>	0.5	3	89	100/0
17	60 <sup>b</sup>	1	1	99	100/0
18	room temp <sup>a</sup>	1	24	6	100/0
19	room temp <sup>a</sup>	0.5	24	3	100/0

<sup>a</sup>Conditions: 10 mmol styrene, 1 mL of dichloroethane. <sup>b</sup>Conditions: 1 mL of dichloroethane.

**Table 2. Catalytic Oligomerization of Styrene**

entry <sup>a</sup>	cat.	yield (%)	dimer (%)	trimer (%)
1 <sup>b</sup>	<b>1a</b>	99	100	
2	<b>1b</b>	99	100	
3	<b>1c</b>	<5		
4	<b>1d</b>	70	100	
5	<b>1e</b>	<5		
6	<b>1f</b>	60	66.7	33.3
7	<b>2a</b>	82	89.4	10.6
8	<b>2b</b>	<5		
9	<b>2c</b>	<5		
10	<b>2d</b>	<5		
11	<b>2e</b>	53	86.2	13.8
12	<b>2f</b>	<5		

<sup>a</sup>Conditions: 10 mmol of styrene, 1 mL of 1,2-dichloroethane at 60 °C, reaction time 4 h. <sup>b</sup>Reaction time 1 h.

However, inclusion of Cl or a Ph ring in the imidazole backbone or a phenyl substituent in the imidazole wingtip significantly decreases the reaction yields (entries 4–6). This can be rationalized by the weaker donor properties<sup>34</sup> of the substituents on **1d,e** and, in the case of **1f**, the electron-withdrawing power of the Cl atoms. In any case, this leads to a less electron rich Ni(II) center that hinders the release of the allyl or Me-allyl ligand, which is necessary to complete the catalytic process according to previously published mechanism proposals.<sup>29</sup> On the other hand, Me-allyl–Ni(II) complexes **2a–f** showed less activity and in some cases the absence of activity in comparison with their allyl–Ni(II) counterparts **1a–f**. A similar behavior has been observed for allyl–Ni and methyl-allyl–Ni complexes bearing the chelating phosphine ligand dippe (dippe = <sup>i</sup>Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub><sup>i</sup>Pr<sub>2</sub>), as previously reported by our group.<sup>29</sup>

In addition, the oligomerization of 4-methylstyrene and  $\alpha$ -methylstyrene was carried out to assess the effect of the methyl

substituent on the catalytic system. The reaction mechanism previously proposed for the polymerization of styrene indicates a strong influence of the methyl substituent, given the nature of the allyl intermediates that have to be generated to complete the reaction.<sup>29</sup> The results, given in Table 3, show a decreased

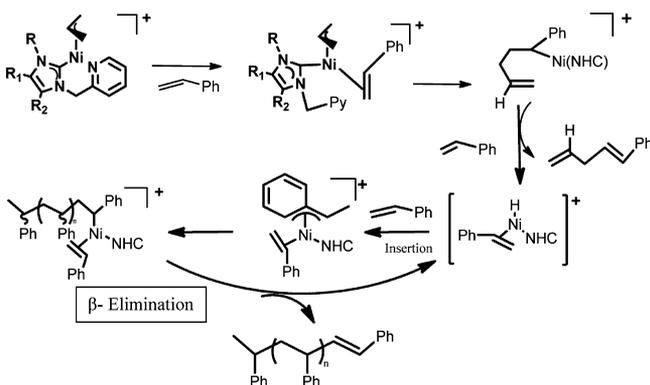
**Table 3. Catalytic Oligomerization of 4-Methylstyrene and  $\alpha$ -Methylstyrene**

entry <sup>a</sup>	cat.	olefin	yield (%)	dimer (%)	trimer (%)
1	1a	4-methylstyrene	87	100	
2	1b	4-methylstyrene	61	84.1	15.9
3	1d	4-methylstyrene	35	100	
4	1f	4-methylstyrene	35	100	
5	2a	4-methylstyrene	77	90.9	9.1
6	2e	4-methylstyrene	35.7	100	
7	1a	$\alpha$ -methylstyrene	72	100	
8	2a	$\alpha$ -methylstyrene	60	100	

<sup>a</sup>Conditions: 10 mmol of olefin, 1 mL of 1,2-dichloroethane at 60 °C, reaction time 4 h.

activity for all the catalysts tested when 4-methylstyrene instead of styrene was used as substrate (entries 1–5). In addition, the use of  $\alpha$ -methylstyrene diminished significantly the activity of all Ni(II)–picolyl–NHC complexes; in most cases no activity was observed. Only 1a and 2a showed catalytic activity toward oligomerization of  $\alpha$ -methylstyrene (entries 7 and 8). These results are in line with those previously published by our group,<sup>29</sup> indicating that the mechanism should be as depicted in Scheme 3, implying a very fast  $\beta$ -elimination step that

**Scheme 3. Mechanism for Oligomerization Reaction of Styrenes**



explains the high selectivity toward dimer formation. It is important to note that the structure of the  $\alpha$ -methylstyrene dimer is not homologous with those of the styrene or 4-methylstyrene dimers. Whereas 4-methylstyrene and styrene dimers have a head-to-tail structure,  $\alpha$ -methylstyrene dimer

produces (4-methylpent-1-ene-2,4-diyl)dibenzene as the only structure. NMR data suggest that  $\alpha$ -methylstyrene dimer is produced by insertion of one  $\alpha$ -methylstyrene into one C–H bond of another  $\alpha$ -methyl substituent.<sup>29</sup>

**Catalytic Hydrosilylation of Styrenes.** Catalytic hydrosilylation of alkenes is one of the most versatile and efficient methods for the synthesis of alkylsilanes and the preparation of organosilicon compounds on an industrial scale.<sup>35</sup> For this reason, it has been widely investigated using several catalytic systems.<sup>29,35</sup> The conventionally accepted mechanism for this reaction includes oxidative addition of substituted silane to a metal–alkene intermediate complex, followed by migratory insertion into a M–H bond and reductive elimination by Si–C bond formation, regenerating the metal–alkene complex. An alternative pathway goes preferentially through an alkene insertion into the M–Si bond. In each case a different metal–hydrido complex is involved.

The addition of Si–H bonds across the C=C double bond can give a mixture of products that follow Markovnikov or anti-Markovnikov rules. This reaction has been already studied by our group<sup>29</sup> and the Zargarian group<sup>35a,b</sup> using nickel(II) complexes bearing phosphine ligands as catalysts. Hence, R-allyl–Ni–NHC complexes (1a–f/2a–f) have been tested in the catalytic hydrosilylation of styrenes (Scheme 4).

As previously stated for the polymerization reactions, our aim has been to study the effect in the catalytic system caused by several substituents on the NHC and the allyl ligand of the Ni complexes. Each catalytic run has been carried out at 60 °C with Ni/R-styrene/PhSiH<sub>3</sub> ratios of 1/100/200, using an excess of PhSiH<sub>3</sub> to prevent oligomerization. Under these conditions, the hydrosilylation product isolated upon purification was either RC<sub>6</sub>H<sub>4</sub>C(R')(CH<sub>3</sub>)SiH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (A) or RC<sub>6</sub>H<sub>4</sub>CH(R')CH<sub>2</sub>SiH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (B). Nevertheless, A was obtained as the major product in all cases. As shown in Table 4, compounds 1a,d were highly selective toward product A when styrene and 4-methylstyrene were used as substrates (entries 1, 3, 10, and 12). However, 1b showed high selectivity in the styrene reaction but lost its reactivity when 4-methylstyrene was used (entries 2 and 11). On the other hand, 1e showed an opposite behavior in comparison with 1b. Compounds 2a–f gave higher yields than their allyl analogues 1a–f but proved to be less selective in all cases. Furthermore, only 2d,e showed activity when  $\alpha$ -methylstyrene was used as substrate, but low yields were obtained. However, in these cases, B was observed as the only product, showing an inversion in the selectivity pattern presented by the other substrates. Also, trisubstituted silanes such as (OEt)<sub>3</sub>SiH and PhMe<sub>2</sub>SiH were tested, but none of them showed activity in the hydrosilylation of styrene.

Furthermore, in order to obtain information regarding the reaction mechanism, the hydrosilylation of three fluoro-substituted styrenes (F at the 2-, 3-, or 4-position of the phenyl ring) was monitored by <sup>19</sup>F NMR and <sup>1</sup>H NMR. The experiments

**Scheme 4. Catalytic Hydrosilylation of Styrenes**

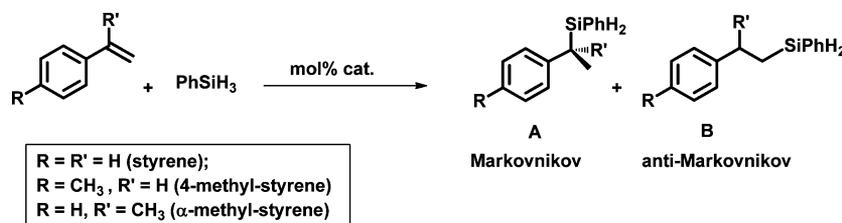


Table 4. Catalytic Hydrosilylation of Styrenes with PhSiH<sub>3</sub>

entry	cat.	olefin	yield (%)	A:	
				Markovnikov product (%)	B: anti-Markovnikov product (%)
1	1a	styrene	40	92.5	7.5
2	1b	styrene	65	96	4
3	1d	styrene	60	96.7	3.3
4	1e	styrene	90.6	65.1	34.9
5	1f	styrene	90	62.8	37.2
6	2a	styrene	79	80.1	19.9
7	2d	styrene	100	85.3	14.7
8	2e	styrene	90	53.8	46.2
9	2f	styrene	100	60.8	39.2
10	1a	4-methylstyrene	60	96.7	3.3
11	1b	4-methylstyrene	53	71.1	28.3
12	1d	4-methylstyrene	60	95	5
13	1e	4-methylstyrene	60	93.3	6.7
14	1f	4-methylstyrene	90	57.3	42.7
15	2a	4-methylstyrene	88.5	73.1	26.9
16	2d	4-methylstyrene	100	76.7	23.3
17	2e	4-methylstyrene	100	76.7	23.3
18	2f	4-methylstyrene	100	54.4	45.6
19	2d	$\alpha$ -methylstyrene	13		100
20	2e	$\alpha$ -methylstyrene	33		100

were carried out with fluorostyrene (1 mmol) and PhSiH<sub>3</sub> (1.3 mmol) using three sets of reaction conditions: (I) 1 mol % of catalyst at 25 °C, (II) 0.5 mol % of catalyst at 60 °C, and (III) 1 mol % of catalyst at 60 °C. Among these experiments, those including 1e as catalyst and 2-fluorostyrene and 4-fluorostyrene as substrates were chosen to rationalize the experimental observations (see the Supporting Information for more details). As shown in Figure 2, when the different sets of

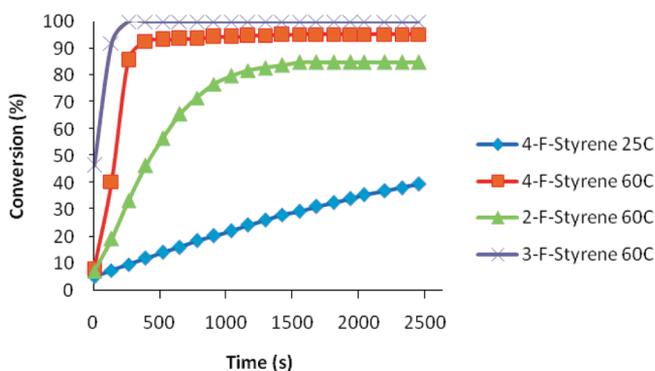


Figure 2. Hydrosilylation of fluorostyrenes with 1 mol % of 1e.

conditions are compared, it is clear that at 60 °C the reaction occurs within minutes. However, at room temperature a lower reaction rate was observed and lower conversions were obtained.

The fast conversion of 2-fluorostyrene in 1-(2-fluorophenyl)ethyl)diphenylsilane (A) can be observed in Figure 3. Also, it is important to note that the main signals in the <sup>19</sup>F NMR

spectrum at -119.7, -121.2, and -121.6 ppm are from the major reaction product FC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)SiH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (A), 2-fluorostyrene, and the minor reaction product FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (B), respectively. However, a fourth signal in the <sup>19</sup>F NMR spectrum at -122.1 ppm is observed that may correspond to a catalytically active species. In addition, the <sup>1</sup>H NMR of the reaction (Figure 4) clearly showed distinctive signals in the metal-hydride region at -29.28 and -29.29 ppm, indicating the presence of Ni-H intermediates. These experimental data are consistent with the participation of nickel-silyl and a nickel-hydride intermediates, as suggested by Zargarian et al.<sup>35</sup> However, these data are insufficient to support a complete mechanistic proposal. They also illustrate that, as a result of the weakening of the double bond in the fluorinated styrenes, the hydrosilylation processes are faster in comparison with those for the non-fluorinated analogues.

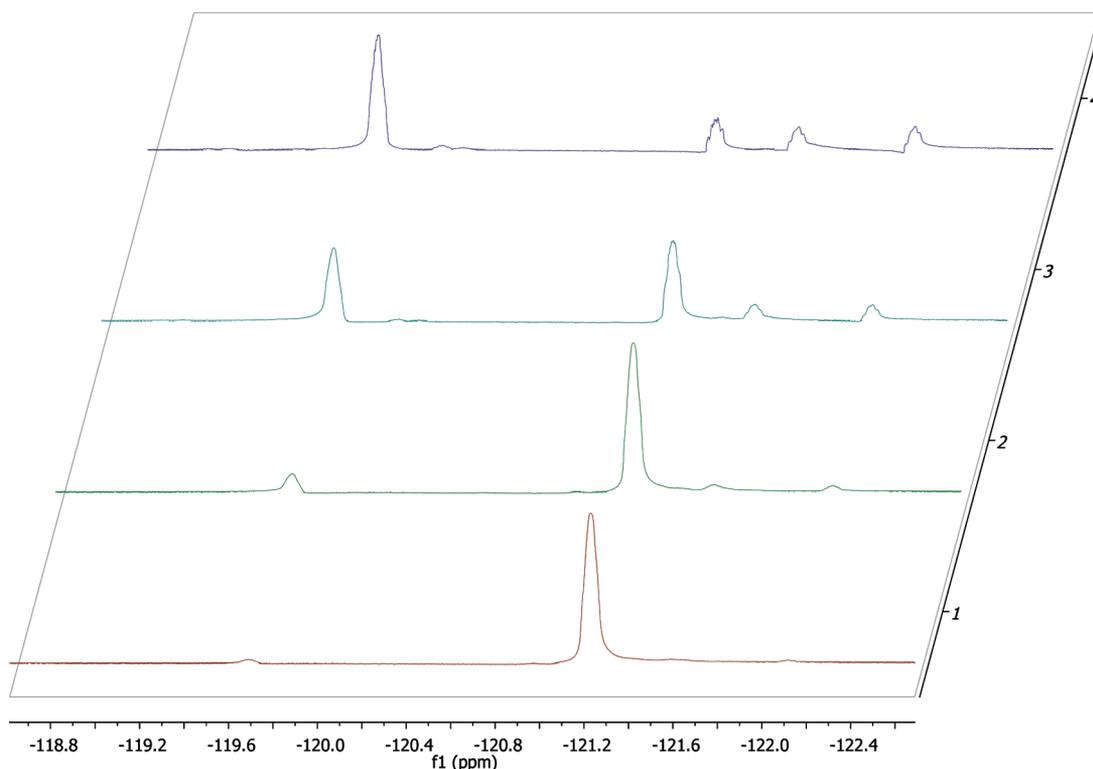
## CONCLUSION

We have reported the synthesis of novel allyl- and methylallyl-nickel complexes bearing hemilabile picolyl-NHC carbene ligands using the transmetalation method from silver precursors. These compounds have proved to be catalytically active toward dimerization of styrenes without the use of any cocatalyst, especially 1a. The dimerization reactions were highly selective toward styrene dimers and occurred with moderate to good yields. Also, the new nickel compounds showed activity in hydrosilylation reactions of styrenes. The silylated products were mainly the Markovnikov addition products when styrene and 4-methylstyrene were used but anti-Markovnikov products when  $\alpha$ -methylstyrene was the chosen substrate. The use of <sup>19</sup>F NMR and <sup>1</sup>H NMR with fluorinated substrates allowed us to observe some reaction intermediates, and we propose that the possible reaction mechanism is similar to that previously reported by Zargarian.<sup>35</sup> These catalysts have the potential to be active in other reactions, and further studies are underway.

## EXPERIMENTAL SECTION

**General Procedures.** All reactions were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Dry and oxygen-free solvents were always used unless otherwise stated. The starting materials Ni(COD)<sub>2</sub>,<sup>37</sup> [(allyl)Ni(COD)][BAR<sub>4</sub><sup>F</sup>],<sup>38</sup> [(Methyl)Ni(COD)][BAR<sub>4</sub><sup>F</sup>],<sup>38</sup> 1-methyl-3-(2-picolyl)imidazolium bromide (a),<sup>24</sup> 1-isopropyl-3-(2-picolyl)imidazolium bromide (b),<sup>30a</sup> 1-butyl-3-(2-picolyl)imidazolium bromide (c),<sup>30a</sup> 1-phenyl-3-(2-picolyl)imidazolium bromide (d),<sup>34</sup> 1-methyl-3-(2-picolyl)benzoimidazolium bromide (e),<sup>30b</sup> and 1-methyl-3-(2-picolyl)-4,5-dichloroimidazolium bromide (f)<sup>34</sup> were prepared according to the literature methods. NMR spectra were recorded using Varian INOVA 600 and 400 MHz spectrometers. Chemical shifts are given in ppm from TMS (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) and J values in Hz; NMR signal assignments were confirmed by 2D NMR experiments. Microanalysis was performed on a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz. The GC/MS analyses of the catalytic mixtures were performed using an Agilent 6890N system.

**Preparation of Allyl-Nickel Complexes 1a–f.** Imidazolium salts of the ligands a–f (1.0 mmol) and silver oxide (0.12 g, 0.5 mmol) were stirred in dichloromethane (25 mL) at room temperature for 3 h. The resulting mixture was then filtered through Celite. [(allyl)Ni(COD)][BAR<sub>4</sub><sup>F</sup>] (0.91 g, 0.85 mmol) was added to the solution, and the mixture was stirred at room temperature for 3 h. After removal of the formed silver halide by filtration through Celite, the solvent was evaporated under vacuum. The residual orange-brown oil was washed with petroleum ether and dried under vacuum to give an orange-brown solid.



**Figure 3.**  $^{19}\text{F}$  NMR spectra ( $\text{C}_6\text{D}_6$ ,  $60\text{ }^\circ\text{C}$ ) with 1 mmol of 2-fluorostyrene, 1.3 mmol of  $\text{PhSiH}_3$ , and 1 mol % of **1e**: (1) 0.13 min; (2) 2.28 min; (3) 6.56 min; (4) 12.68 min.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1a**). Yield: 0.67 g, 70%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.022 (d, 1H,  $^3J_{\text{H-H}} = 5.28$ ,  $1\text{H}_{\text{py}}$ ), 8.091 (vt, 1H,  $^3J_{\text{H-H}} = 5.28$ ,  $J_{\text{H-H}} = 1.46$ ,  $1\text{H}_{\text{py}}$ ), 7.875 (d, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $1\text{H}_{\text{py}}$ ), 7.804 (s, 8H,  $\text{BAr}_4^F$ ), 7.667 (s, 4H,  $\text{BAr}_4^F$ ), 7.555 (t, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $J_{\text{H-H}} = 1.46$ ,  $1\text{H}_{\text{py}}$ ), 7.540 (d, 1H,  $^3J_{\text{H-H}} = 1.76$ ,  $1\text{H}_{\text{Im}}$ ), 7.307 (d, 1H,  $^3J_{\text{H-H}} = 1.76$ ,  $1\text{H}_{\text{Im}}$ ), 5.798 (d, 1H,  $^2J_{\text{H-H}} = 14.94$ ,  $\text{CH}_2$  bridge), 5.798 (q, 1H,  $1\text{H}_{\text{allyl CH}}$ ), 5.611 (d, 1H,  $^2J_{\text{H-H}} = 14.94$ ,  $\text{CH}_2$  bridge); 3.882 (s, 3H,  $\text{CH}_3$ ), 3.849 (d, 1H,  $^3J_{\text{H-H}} = 2.34$ ,  $1\text{H}_{\text{allyl}}$ ), 3.513 (d, 1H,  $^3J_{\text{H-H}} = 7.04$ ,  $1\text{H}_{\text{allyl}}$ ), 3.241 (d, 1H,  $^3J_{\text{H-H}} = 14.35$ ,  $1\text{H}_{\text{allyl}}$ ), 2.504 (d, 1H,  $^3J_{\text{H-H}} = 13.19$ ,  $1\text{H}_{\text{allyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  176.05 ( $\text{C}_{\text{Im}}$ ), 162.54 ( $\text{BAr}_4^F$ ), 155.49 ( $\text{C}_{\text{py}}$ ), 155.29 ( $\text{C}_{\text{ipso}}$ ), 140.38 ( $\text{C}_{\text{py}}$ ), 135.46 ( $\text{BAr}_4^F$ ), 129.81 ( $\text{BAr}_4^F$ ), 125.69 ( $\text{C}_{\text{py}}$ ), 124.78 ( $\text{C}_{\text{Im}}$ ), 124.45 ( $\text{C}_{\text{py}}$ ), 122.68 ( $\text{C}_{\text{Im}}$ ), 118.28 ( $\text{BAr}_4^F$ ), 116.81 ( $\text{C}_{12}$ ), 70.93 ( $\text{C}_{\text{allyl}}$ ), 54.29 ( $\text{C}_{\text{CH}_2}$  bridge), 48.32 ( $\text{C}_{\text{allyl}}$ ), 37.75 ( $\text{C}_{\text{CH}_3}$ ). Anal. Calcd for  $\text{C}_{45}\text{H}_{28}\text{BF}_2\text{N}_3\text{Ni}$ : C, 47.57; H, 2.48; N, 3.70. Found: C, 47.69; H, 2.54; N, 3.58.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1b**). Yield: 0.49 g, 50%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  8.74 (d, 1H,  $^3J_{\text{H-H}} = 5.45$ ,  $1\text{H}_{\text{py}}$ ), 7.79 (vt, 1H,  $^3J_{\text{H-H}} = 7.57$ ,  $1\text{H}_{\text{py}}$ ), 7.62 (d, 1H,  $^3J_{\text{H-H}} = 8.03$ ,  $1\text{H}_{\text{py}}$ ), 7.36 (vs, 1H,  $1\text{H}_{\text{Im}}$ ), 7.25 (t, 1H,  $^3J_{\text{H-H}} = 7.76$ ,  $1\text{H}_{\text{py}}$ ), 7.11 (vs, 1H,  $1\text{H}_{\text{Im}}$ ), 5.45 ( $s_{\text{broad}}$ , 2H,  $\text{CH}_2$  bridge), 5.23 (m, 1H,  $1\text{H}_{\text{allyl}}$ ), 4.53 (m, 1H,  $1\text{H}_{\text{isp}}$ ), 1.93 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.33 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.20 (s, 6H,  $2 \times \text{CH}_3$   $\text{isp}$ ), 0.58 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ); 0.57 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  175.19 ( $\text{C}_{\text{Im}}$ ), 154.84 ( $\text{C}_{\text{py}}$ ), 150.90 ( $\text{C}_{\text{ipso}}$ ), 139.74 ( $\text{C}_{\text{py}}$ ), 128.43 ( $\text{C}_{\text{allyl}}$ ), 125.86 ( $\text{C}_{\text{py}}$ ), 124.72 ( $\text{C}_{\text{py}}$ ), 124.00 ( $\text{C}_{\text{Im}}$ ), 123.11 ( $\text{C}_{\text{Im}}$ ), 54.10 ( $\text{CH}_2$  bridge), 52.50 ( $\text{C}_{\text{isp}}$ ), 27.82 ( $\text{C}_{\text{allyl}}$ ), 22.82 ( $\text{C}_{\text{isp}}$ ), 22.08 ( $\text{C}_{\text{allyl}}$ ). Anal. Calcd for  $\text{C}_{47}\text{H}_{32}\text{BF}_2\text{N}_3\text{Ni}$ : C, 48.49; H, 2.77; N, 3.61. Found: C, 48.57; H, 2.65; N, 3.47.

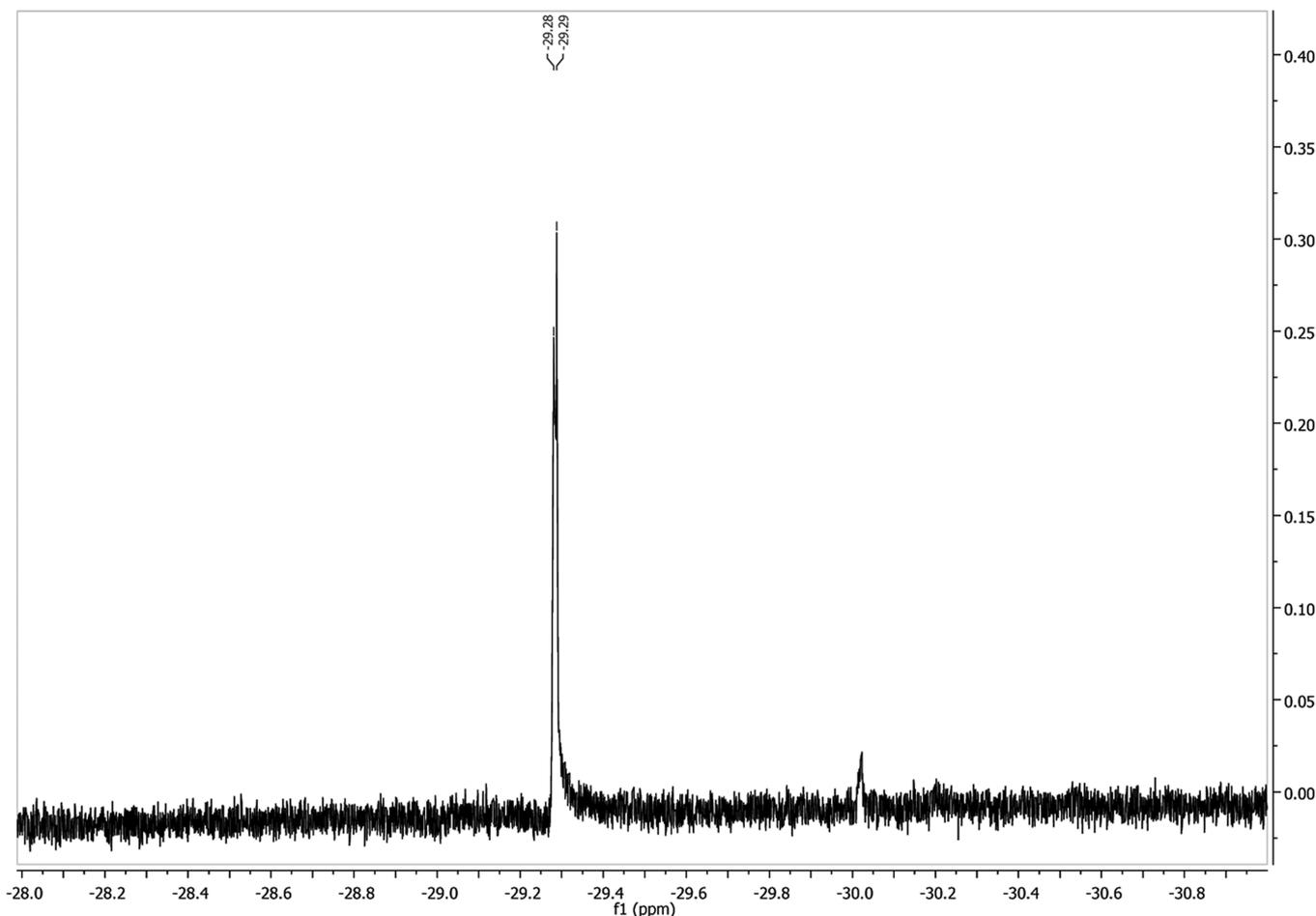
$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1c**). Yield: 0.40 g, 40%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.19 (d, 1H,  $^3J_{\text{H-H}} = 4.4$ ,  $1\text{H}_{\text{py}}$ ), 8.25 (vt, 1H,  $^3J_{\text{H-H}} = 7.33$ ,  $1\text{H}_{\text{py}}$ ), 8.05 (d, 1H,  $^3J_{\text{H-H}} = 7.33$ ,  $1\text{H}_{\text{py}}$ ), 7.74 (s, 1H,  $1\text{H}_{\text{Im}}$ ), 7.72 (t, 1H,  $^3J_{\text{H-H}} = 6.16$ ,  $1\text{H}_{\text{py}}$ ), 7.55 (s, 1H,  $1\text{H}_{\text{Im}}$ ), 6.01 ( $s_{\text{overlapped}}$ , 1H,  $\text{CH}_2$  bridge), 5.83 (d, 1H,  $^2J_{\text{H-H}} = 14.08$ ,  $\text{CH}_2$  bridge), 4.35 (t, 2H,  $^3J_{\text{H-H}} = 7.04$ ,  $\text{CH}_2\text{Bu}$ ), 4.02 (d, 1H,  $^3J_{\text{H-H}} = 6.74$ ,  $1\text{H}_{\text{allyl}}$ ), 3.65 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 3.46 (d, 1H,  $^3J_{\text{H-H}} = 14.08$ ,  $1\text{H}_{\text{allyl}}$ ), 2.62 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.53 (m, 2H,  $\text{CH}_2\text{Bu}$ ), 1.09 (t, 3H,  $^3J_{\text{H-H}} = 7.23$ ,  $\text{CH}_3$   $\text{Bu}$ ), 1.01

(m, 2H,  $\text{CH}_2$   $\text{Bu}$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  175.87 ( $\text{C}_{\text{Im}}$ ), 155.49 ( $\text{C}_{\text{py}}$ ), 155.44 ( $\text{C}_{\text{ipso}}$ ), 140.43 ( $\text{C}_{\text{py}}$ ), 126.41 ( $\text{C}_{\text{py}}$ ), 125.28 ( $\text{C}_{\text{py}}$ ), 123.04 ( $\text{C}_{\text{Im}}$ ), 121.76 ( $\text{C}_{\text{Im}}$ ), 116.57 ( $\text{C}_{\text{allyl}}$ ), 71.14 ( $\text{C}_{\text{allyl}}$ ), 54.28 ( $\text{CH}_2$  bridge), 47.96 ( $\text{C}_{\text{allyl}}$ ). Anal. Calcd for  $\text{C}_{48}\text{H}_{34}\text{BF}_2\text{N}_3\text{Ni}$ : C, 48.93; H, 2.91; N, 3.57. Found: C, 48.81; H, 3.00; N, 3.49.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1d**). Yield: 0.61 g, 60%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.167 (d, 1H,  $^3J_{\text{H-H}} = 4.68$ ,  $1\text{H}_{\text{py}}$ ), 8.129 (t, 1H,  $^3J_{\text{H-H}} = 7.03$ ,  $1\text{H}_{\text{py}}$ ), 8.004 (d, 1H,  $^3J_{\text{H-H}} = 7.91$ ,  $1\text{H}_{\text{py}}$ ), overlapped with the  $\text{BAr}_4^F$  ( $2 \times 1\text{H}_{\text{Im}}$ ), 7.574 (vt, 1H,  $^3J_{\text{H-H}} = 7.61$ ,  $1\text{H}_{\text{py}}$ ), 6.122 (d, 1H,  $^2J_{\text{H-H}} = 14.65$ ,  $\text{CH}_2$  bridge), 5.885 (d, 1H,  $^2J_{\text{H-H}} = 14.65$ ,  $\text{CH}_2$  bridge), 5.656 (q, 1H,  $1\text{H}_{\text{allyl}}$ ), 3.874 (d, 1H,  $^3J_{\text{H-H}} = 7.03$ ,  $1\text{H}_{\text{allyl}}$ ), 3.175 (d, 1H,  $^3J_{\text{H-H}} = 14.36$ ,  $1\text{H}_{\text{allyl}}$ ), 2.414 ( $s_{\text{broad}}$ , 1H,  $1\text{H}_{\text{allyl}}$ ), 1.933 (d, 1H,  $^3J_{\text{H-H}} = 13.48$ ,  $1\text{H}_{\text{allyl}}$ ), phenyl group signals are between 7 and 8 ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  176.40 ( $\text{C}_{\text{Im}}$ ), 155.05 ( $\text{C}_{\text{py}}$ ), 154.26 ( $\text{C}_{\text{ipso}}$ ), 139.71 ( $\text{C}_{\text{py}}$ ), 139.64 ( $\text{C}_{\text{py}}$ ), 124.74 ( $\text{C}_{\text{py}}$ ), overlapped with the  $\text{BAr}_4^F$  ( $\text{C}_{4\text{-Im}}$ ) and ( $\text{C}_{5\text{-Im}}$ ), 115.52 ( $\text{C}_{\text{allyl}}$ ), 69.52 ( $\text{C}_{\text{allyl}}$ ), 53.94 ( $\text{CH}_2$  bridge), 49.22 ( $\text{C}_{\text{allyl}}$ ), phenyl group signals are between 120 and 130 ppm. Anal. Calcd for  $\text{C}_{50}\text{H}_{30}\text{BF}_2\text{N}_3\text{Ni}$ : C, 50.12; H, 2.52; N, 3.51. Found: C, 49.98; H, 2.30; N, 3.29.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1e**). Yield: 0.50 g, 50%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.08 (d, 1H,  $^3J_{\text{H-H}} = 5.27$ ,  $1\text{H}_{\text{py}}$ ), 8.08 (s, 2H,  $2\text{H}_{\text{benzo}}$ ), 7.95 (t, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $1\text{H}_{\text{py}}$ ), 7.67 (d, 1H,  $^3J_{\text{H-H}} = 7.91$ ,  $1\text{H}_{\text{py}}$ ), 7.57 (s, 2H,  $2\text{H}_{\text{benzo}}$ ), 7.43 (vt, 1H,  $^3J_{\text{H-H}} = 8.8$ ,  $1\text{H}_{\text{py}}$ ), 6.097 (d, 2H,  $^2J_{\text{H-H}} = 15.66$ ,  $\text{CH}_2$  bridge), 5.954 (q, 1H,  $1\text{H}_{\text{allyl}}$ ), 4.53 ( $s_{\text{broad}}$ , 1H,  $1\text{H}_{\text{allyl}}$ ), 4.12 (s, 3H,  $\text{CH}_3$ ), 2.30 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 2.23 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.46 (s, 1H,  $1\text{H}_{\text{allyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  155.03 ( $\text{C}_{\text{py}}$ ), 154.48 ( $\text{C}_{\text{ipso}}$ ), 153.31 ( $\text{C}_{\text{Im}}$ ), 139.98 ( $\text{C}_{\text{benzo}}$ ), 126.09 ( $\text{C}_{\text{benzo}}$ ), 124.94 ( $\text{C}_{\text{py}}$ ), 123.87 ( $\text{C}_{\text{py}}$ ), 123.40 ( $\text{C}_{\text{Im}}$ ), 120.67 ( $\text{C}_{\text{Im}}$ ), 111.24 ( $\text{C}_{\text{allyl}}$ ), 110.60 ( $\text{C}_{\text{py}}$ ), 50.10 ( $\text{CH}_2$  bridge), 34.24 ( $\text{CH}_3$ ), 32.09 ( $\text{C}_{\text{allyl}}$ ), 27.93 ( $\text{C}_{\text{allyl}}$ ). Anal. Calcd for  $\text{C}_{49}\text{H}_{30}\text{BF}_2\text{N}_3\text{Ni}$ : C, 49.61; H, 2.55; N, 3.54. Found: C, 49.78; H, 2.60; N, 3.48.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NHC-}\kappa^2\text{C,N})][\text{B}(\text{Ar}^F)_4]$  (**1f**). Yield: 0.61 g, 60%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  8.85 (d, 1H,  $^3J_{\text{H-H}} = 3.81$ ,  $1\text{H}_{\text{py}}$ ), 7.909 (t, 1H,  $^3J_{\text{H-H}} = 7.33$ ,  $1\text{H}_{\text{py}}$ ), 7.83 (d, 1H,  $^3J_{\text{H-H}} = 7.04$ ,  $1\text{H}_{\text{py}}$ ), 7.39 (t, 1H,  $1\text{H}_{\text{py}}$ ), 5.95 (s, 1H,  $\text{CH}_2$  bridge), 5.80 ( $s_{\text{broad}}$ , 1H,  $\text{CH}_2$  bridge), 5.48 (m, 1H,  $1\text{H}_{\text{allyl}}$ ), 3.95 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 3.69 (s, 3H,  $\text{CH}_3$ ), 3.36 (vs, 1H,



**Figure 4.**  $^1\text{H}$  NMR spectrum after reaction of 2-fluorostyrene with  $\text{PhSiH}_3$  catalyzed by **1e**.

$1\text{H}_{\text{allyl}}$ ), 2.38 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 0.86 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  155.36 ( $\text{C}_{\text{py}}$ ), 155.30 ( $\text{C}_{\text{ipso}}$ ), 153.59 ( $\text{C}_{\text{im}}$ ), 139.31 ( $\text{C}_{\text{py}}$ ), 126.03 ( $\text{C}_{\text{py}}$ ), 125.32 ( $\text{C}_{\text{py}}$ ), 124.18 ( $\text{C}_{\text{im}}$ ), 122.30 ( $\text{C}_{\text{im}}$ ), 116.79 ( $\text{C}_{\text{allyl}}$ ), 70.48 ( $\text{C}_{\text{allyl}}$ ), 51.56 ( $\text{CH}_2$  bridge), 35.86 ( $\text{CH}_3$ ), 28.23 ( $\text{C}_{\text{allyl}}$ ). Anal. Calcd for  $\text{C}_{43}\text{H}_{26}\text{BCl}_2\text{F}_{24}\text{N}_3\text{Ni}$ : C, 44.85; H, 2.17; N, 3.49. Found: C, 45.04; H, 2.28; N, 3.38.

**Preparation of Methylallyl–Nickel Complexes 2a–f.** Imidazolium salts of the ligands **a–f** (1.0 mmol) and silver oxide (0.12 g, 0.5 mmol) in dichloromethane (25 mL) were stirred at room temperature for 3 h. The resulting mixture was then filtered through Celite.  $[\text{Me}(\text{allyl})\text{Ni}(\text{COD})][\text{BAR}_4^{\text{F}}]$  (0.92 g, 0.85 mmol) was added to the solution, and the mixture was stirred at room temperature for 3 h. After removal of the formed silver halide by filtration through Celite, the solvent was evaporated under vacuum. The residual orange-brown oil was washed with petroleum ether and dried under vacuum to give an orange-brown solid.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)(\text{NHC-}\kappa^2\text{C}_2\text{N})][\text{B}(\text{Ar}^{\text{F}})_4]$  (**2a**). Yield: 0.64 g, 65%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.030 (d, 1H,  $^3J_{\text{H-H}} = 5.12$ ,  $1\text{H}_{\text{py}}$ ), 8.076 (t, 1H,  $J_{\text{H-H}} = 5.12$ ,  $J_{\text{H-H}} = 1.76$ ,  $1\text{H}_{\text{py}}$ ), 7.857 (d, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $1\text{H}_{\text{py}}$ ), 7.547 (t, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $J_{\text{H-H}} = 1.76$ ,  $1\text{H}_{\text{py}}$ ), 7.527 (d, 1H,  $^3J_{\text{H-H}} = 1.75$ ,  $1\text{H}_{\text{im}}$ ), 7.303 (d, 1H,  $^3J_{\text{H-H}} = 1.75$ ,  $1\text{H}_{\text{im}}$ ), 5.757 (d, 1H,  $^2J_{\text{H-H}} = 15.24$ ,  $\text{CH}_2$  bridge), 5.561 (d, 1H,  $^2J_{\text{H-H}} = 15.24$ ,  $\text{CH}_2$  bridge), 3.888 (s, 3H,  $\text{CH}_3$ ), 3.619 (d, 1H,  $^3J_{\text{H-H}} = 3.23$ ,  $1\text{H}_{\text{allyl}}$ ); 3.224 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 3.133 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 2.312 (vs, 1H,  $1\text{H}_{\text{allyl}}$ ), 2.190 (s, 1H,  $\text{CH}_3$  allyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  176.53 ( $\text{C}_{\text{im}}$ ), 155.68 ( $\text{C}_{\text{py}}$ ), 155.38 ( $\text{C}_{\text{ipso}}$ ), 140.52 ( $\text{C}_{\text{py}}$ ), 126.72 ( $\text{C}_{\text{py}}$ ), 125.47 ( $\text{C}_{\text{py}}$ ), 124.02 ( $\text{C}_{\text{im}}$ ), 123.84 ( $\text{C}_{\text{im}}$ ), 121.31 ( $\text{C}_{\text{allyl}}$ ), 70.12 ( $\text{C}_{\text{allyl}}$ ), 54.49 ( $\text{CH}_2$  bridge), 48.78 ( $\text{C}_{\text{allyl}}$ ), 37.95 ( $\text{CH}_3$ ), 23.49 ( $\text{CH}_3$  allyl). Anal. Calcd for  $\text{C}_{46}\text{H}_{30}\text{BF}_{24}\text{N}_3\text{Ni}$ : C, 48.03; H, 2.63; N, 3.65. Found: C, 47.79; H, 2.55; N, 3.72.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)(\text{NHC-}\kappa^2\text{C}_2\text{N})][\text{B}(\text{Ar}^{\text{F}})_4]$  (**2b**). Yield: 0.45 g, 45%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.01 (d, 1H,  $^3J_{\text{H-H}} = 5.28$ ,  $1\text{H}_{\text{py}}$ ), 7.84 (d, 1H,  $^3J_{\text{H-H}} = 7.74$ ,  $1\text{H}_{\text{py}}$ ), 7.57 (t, 1H,  $J_{\text{H-H}} = 7.62$ ,  $J_{\text{H-H}} = 1.76$ ,  $1\text{H}_{\text{py}}$ ), 7.44 (t, 1H,  $^3J_{\text{H-H}} = 6.83$ ,  $1\text{H}_{\text{py}}$ ), 7.38 (d, 1H,  $^3J_{\text{H-H}} = 1.75$ ,  $1\text{H}_{\text{im}}$ ), overlapped with the  $\text{BAR}_4^{\text{F}}$  ( $1\text{H}_{\text{im}}$ ), 5.51 (s, broad, 2H,  $\text{CH}_2$  bridge), 4.84 (m, 1H,  $1\text{H}_{\text{isp}}$ ), 2.07 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.68 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.50 (d, 6H,  $2 \times \text{CH}_3$  isp), 0.87 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 0.84 (s, 1H,  $1\text{H}_{\text{allyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  178.56 ( $\text{C}_{\text{im}}$ ), 154.71 ( $\text{C}_{\text{py}}$ ), 150.02 ( $\text{C}_{\text{ipso}}$ ), 128.47 ( $\text{C}_{\text{allyl}}$ ), 126.14 ( $\text{C}_{\text{py}}$ ), 125.66 ( $\text{C}_{\text{py}}$ ), 124.64 ( $\text{C}_{\text{py}}$ ), 123.08 ( $\text{C}_{\text{im}}$ ), 120.72 ( $\text{C}_{\text{im}}$ ), 53.85 ( $\text{CH}_2$  bridge), 52.61 ( $\text{C}_{\text{isp}}$ ), 28.98 ( $\text{C}_{\text{allyl}}$ ), 27.81 ( $\text{CH}_3$  allyl), 22.73 ( $\text{CH}_3$  isp), 21.95 ( $\text{C}_{\text{allyl}}$ ). Anal. Calcd for  $\text{C}_{48}\text{H}_{34}\text{BF}_{24}\text{N}_3\text{Ni}$ : C, 48.93; H, 2.91; N, 3.57. Found: C, 49.03; H, 3.09; N, 3.64.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)(\text{NHC-}\kappa^2\text{C}_2\text{N})][\text{B}(\text{Ar}^{\text{F}})_4]$  (**2c**). Yield: 0.35 g, 35%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  8.84 (d, 1H,  $^3J_{\text{H-H}} = 5.28$ ,  $1\text{H}_{\text{py}}$ ), 7.81 (t, 1H,  $^3J_{\text{H-H}} = 7.69$ ,  $1\text{H}_{\text{py}}$ ), 7.72 (d, 1H,  $^3J_{\text{H-H}} = 7.69$ ,  $1\text{H}_{\text{py}}$ ), 7.72 (s, 1H,  $1\text{H}_{\text{im}}$ ), 7.37 (s, 1H,  $1\text{H}_{\text{im}}$ ), 7.29 (t, 1H,  $^3J_{\text{H-H}} = 6.59$ ,  $1\text{H}_{\text{py}}$ ), 6.66 (s, broad, 1H,  $\text{CH}_2$  bridge), 5.46 (s, broad, 1H,  $\text{CH}_2$  bridge), 4.03 (t, 2H,  $J_{\text{H-H}} = 7.26$ ,  $2\text{H}_{\text{butyl}}$ ), 3.45 (s, 3H,  $3\text{H}_{\text{CH}_3\text{allyl}}$ ), 3.00 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 2.24 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.58 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 1.21 (m, 2H,  $2\text{H}_{\text{butyl}}$ ), 0.71 (s, 1H,  $1\text{H}_{\text{allyl}}$ ), 0.75 (t, 3H,  $J_{\text{H-H}} = 7.25$ ,  $3\text{H}_{\text{butyl}}$ ), 0.67 (m, 2H,  $2\text{H}_{\text{butyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  175.45 ( $\text{C}_{\text{im}}$ ), 154.52 ( $\text{C}_{\text{py}}$ ), 154.50 ( $\text{C}_{\text{ipso}}$ ), 139.47 ( $\text{C}_{\text{py}}$ ), 128.25 ( $\text{C}_{\text{allyl}}$ ), 125.39 ( $\text{C}_{\text{im}}$ ), 124.50 ( $\text{C}_{\text{py}}$ ), 122.12 ( $\text{C}_{\text{im}}$ ), 121.24 ( $\text{C}_{\text{im}}$ ); 66.61 ( $\text{CH}_3$  allyl), 53.70 ( $\text{CH}_2$  bridge), 49.87 ( $\text{C}_{\text{butyl}}$ ), 47.49 ( $\text{C}_{\text{allyl}}$ ), 27.32 ( $\text{C}_{\text{butyl}}$ ), 21.55 ( $\text{C}_{\text{allyl}}$ ), 21.19 ( $\text{C}_{\text{butyl}}$ ), 12.02 ( $\text{C}_{\text{butyl}}$ ). Anal. Calcd for  $\text{C}_{49}\text{H}_{36}\text{BF}_{24}\text{N}_3\text{Ni}$ : C, 49.36; H, 3.04; N, 3.52. Found: C, 49.25; H, 3.57; N, 3.40.

$[\text{Ni}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)(\text{NHC-}\kappa^2\text{C}_2\text{N})][\text{B}(\text{Ar}^{\text{F}})_4]$  (**2d**). Yield: 0.62 g, 60%.  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K):  $\delta$  9.006 (d, 1H,  $^3J_{\text{H-H}} = 5.56$ ,  $1\text{H}_{\text{py}}$ ), 8.012 (d, 1H,  $^3J_{\text{H-H}} = 7.62$ ,  $1\text{H}_{\text{py}}$ ), 7.993 (t, 1H,  $^3J_{\text{H-H}} = 7.61$ ,  $1\text{H}_{\text{py}}$ ),

7.501 (t, 1H,  $^3J_{\text{H-H}} = 7.03$ , 1H<sub>py</sub>), overlapped with the BAR<sub>4</sub><sup>F</sup> (2 × 1H<sub>im</sub>), 5.897 (d, 1H,  $^2J_{\text{H-H}} = 14.95$ , CH<sub>2</sub> bridge), 5.660 (d, 1H,  $^2J_{\text{H-H}} = 14.65$ , CH<sub>2</sub> bridge), 3.486 (vs, 1H, 1H<sub>allyl</sub>), 2.039 (vs, 1H, 1H<sub>allyl</sub>), 1.634 (vs, 1H, 1H<sub>allyl</sub>), 1.943 (s, 3H, CH<sub>3</sub> allyl), phenyl group signals are between 7 and 8 ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, 298 K): δ 177.68 (C<sub>im</sub>), 155.93 (C<sub>py</sub>), 155.14 (C<sub>ipso</sub>), 140.56 (C<sub>py</sub>), 135.62 (C<sub>py</sub>), 131.18 (C<sub>py</sub>), overlapped with the BAR<sub>4</sub><sup>F</sup> (C<sub>4-im</sub>) and (C<sub>5-im</sub>), 121.38 (C<sub>allyl</sub>), 54.92 (CH<sub>2</sub> bridge), 31.17 (C<sub>allyl</sub>), 28.59 (C<sub>allyl</sub>), 23.28 (CH<sub>3</sub> allyl), phenyl group signals are between 120 and 130 ppm. Anal. Calcd for C<sub>51</sub>H<sub>32</sub>BF<sub>24</sub>N<sub>3</sub>Ni: C, 50.53; H, 2.66; N, 3.47. Found: C, 50.70; H, 2.78; N, 3.62.

[Ni( $\eta^3$ -CH<sub>2</sub>CCH<sub>3</sub>CH<sub>2</sub>)(NHC-κ<sup>2</sup>C,N)](BAR<sub>4</sub><sup>F</sup>) (2e). Yield: 0.51 g, 50%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 298 K): δ 8.87 (d, 1H,  $^3J_{\text{H-H}} = 5.11$ , H<sub>py</sub>), 7.72 (t, 1H,  $^3J_{\text{H-H}} = 7.95$ , H<sub>py</sub>), 7.45 (d, 1H,  $^3J_{\text{H-H}} = 7.72$ , H<sub>py</sub>), 7.34 (m, 1H, H<sub>py</sub>), 7.86 (m, 2H, H<sub>benzo</sub>), 7.21 (d-t, 2H,  $^3J_{\text{H-H}} = 7.51$ , H<sub>benzo</sub>), 5.89 (s<sub>broad</sub>, 2H, CH<sub>2</sub> bridge), 3.38 (s, 3H, CH<sub>3</sub>), 3.92 (s, 3H, CH<sub>3</sub> allyl), 2.10 (s, 1H, 1H<sub>allyl</sub>), 2.05 (s, 1H, 1H<sub>allyl</sub>), 0.65 (s, 1H, 1H<sub>allyl</sub>), 0.64 (s, 1H, 1H<sub>allyl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, 298 K): δ 155.56 (C<sub>py</sub>), 155.11 (C<sub>ipso</sub>), 153.58 (C<sub>im</sub>), 140.50 (C<sub>benzo</sub>), 129.12 (C<sub>im</sub>), 128.08 (C<sub>im</sub>), 126.56 (C<sub>allyl</sub>), 126.28 (C<sub>benzo</sub>), 125.55 (C<sub>py</sub>), 124.46 (C<sub>benzo</sub>), 111.82 (C<sub>py</sub>), 111.18 (C<sub>py</sub>), 67.52 (CH<sub>3</sub>), 50.83 (CH<sub>2</sub> bridge), 34.65 (CH<sub>3</sub> allyl); 28.52 (C<sub>allyl</sub>), 23.46 (C<sub>allyl</sub>). Anal. Calcd for C<sub>50</sub>H<sub>32</sub>BF<sub>24</sub>N<sub>3</sub>Ni: C, 50.03; H, 2.69; N, 3.50. Found: C, 49.91; H, 2.51; N, 3.33.

[Ni( $\eta^3$ -CH<sub>2</sub>CCH<sub>3</sub>CH<sub>2</sub>)(NHC-κ<sup>2</sup>C,N)](BAR<sub>4</sub><sup>F</sup>) (2f). Yield: 0.57 g, 55%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 298 K): δ 9.05 (d, 1H,  $^3J_{\text{H-H}} = 4.69$ , 1H<sub>py</sub>), 8.09 (t, 1H,  $J_{\text{H-H}} = 7.92$ ,  $J_{\text{H-H}} = 1.76$ , 1H<sub>py</sub>), 8.00 (d, 1H,  $^3J_{\text{H-H}} = 7.92$ , 1H<sub>py</sub>), 7.58 (t, 1H,  $J_{\text{H-H}} = 5.57$ ,  $J_{\text{H-H}} = 1.47$  Hz 1H<sub>py</sub>), 5.83 (s<sub>broad</sub>, 1H, CH<sub>2</sub> bridge), 5.00 (s<sub>broad</sub>, 1H, CH<sub>2</sub> bridge), 3.88 (s, 3H, CH<sub>3</sub>), 3.87 (vs, 1H, 1H<sub>allyl</sub>), 3.66 (vs, 1H, 1H<sub>allyl</sub>), 2.31 (vs, 1H, 1H<sub>allyl</sub>), 2.21 (s, 3H, CH<sub>3</sub> allyl), 0.83 (vs, 1H, 1H<sub>allyl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, 298 K): δ 158.79 (C<sub>im</sub>), 155.36 (C<sub>py</sub>), 154.70 (C<sub>ipso</sub>), 140.70 (C<sub>py</sub>), 129.81 (BAR<sub>4</sub><sup>F</sup>), 128.14 (C<sub>allyl</sub>), 126.81 (C<sub>py</sub>), 125.53 (C<sub>py</sub>), 124.86 (C<sub>im</sub>), 123.59 (C<sub>im</sub>), 51.46 (CH<sub>2</sub> bridge), 36.16 (CH<sub>3</sub>), 36.00 (C<sub>allyl</sub>), 28.27 (C<sub>allyl</sub>), 23.24 (CH<sub>3</sub> allyl). Anal. Calcd for C<sub>46</sub>H<sub>28</sub>BCl<sub>2</sub>F<sub>24</sub>N<sub>3</sub>Ni: C, 45.32; H, 2.31; N, 3.45. Found: C, 45.37; H, 2.46; N, 3.63.

**Crystal Structure Analysis.** A sample of **1d** was recrystallized from a mixture of diethyl ether and petroleum ether (bp 40–60 °C) at –20 °C. A crystal of **1d** suitable for X-ray structural determination was mounted on a glass fiber and then transferred to the cold nitrogen gas stream of a Bruker Smart APEX CCD three-circle diffractometer (*T* = 100 K) with a sealed-tube source and graphite-monochromated Mo *K*α radiation (*λ* = 0.71073 Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Four sets of frames were recorded over a hemisphere of the reciprocal space by *ω* scans with *δ*(*ω*) = 0.30 and an exposure of 10 s per frame. Correction for absorption was applied by scans of equivalents using the SADABS program.<sup>39</sup> An insignificant crystal decay correction was also applied. The structure was solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least squares (SHELX97)<sup>40</sup> by using all unique data. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in calculated positions (riding model). The allyl ligand was refined split in two complementary orientations with site occupation factors of 0.71 and 0.29, respectively. Also, three disordered CF<sub>3</sub> groups in the anion were refined split into two complementary orientations using displacement parameter restraints. The program ORTEP-3 was used for plotting.<sup>41</sup> Table 5 summarizes the crystal data and data collection and refinement details for **1d**. CCDC 836795 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Catalytic Oligomerization Studies.** A Schlenk tube was loaded with styrene, 4-methylstyrene, or *α*-methylstyrene (10 mmol), 1,2-dichloroethane (1 mL), and the corresponding catalyst (1 mol %) under argon. The system was heated to 60 °C using a paraffin bath. The reaction time was measured from the moment the compounds were introduced at 60 °C. The reaction was quenched by addition of methanol. The volatiles were pumped off, and the residue was treated with methanol to yield a white oil of but-1-ene-1,3-diylidbenzene, which was dried under vacuum. The distyrene was dissolved in

Table 5. Summary of Crystallographic Data for **1d**

formula	C <sub>54</sub> H <sub>40</sub> BF <sub>24</sub> N <sub>3</sub> NiO
fw	1272.41
<i>T</i> (K)	100
cryst size (mm)	0.59 × 0.54 × 0.27
cryst system	monoclinic
space group	C2/c
cell params (Å, deg)	
<i>a</i> , Å	30.180(6)
<i>b</i> , Å	12.912(3)
<i>c</i> , Å	28.568(6)
β, deg	93.67(3)
<i>V</i> (Å <sup>3</sup> )	11 109(4)
<i>Z</i>	8
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.522
μ(Mo <i>K</i> α) (mm <sup>-1</sup> )	0.472
<i>F</i> (000)	5136
max–min transmissn factors	1.000–0.737
range for data collection (deg)	1.43 < <i>θ</i> < 25.14
index ranges	–35 < <i>h</i> < 34; –15 < <i>k</i> < 14; –32 < <i>l</i> < 33
no. of rflns collected	36 542
no. of unique rflns	9795
no. of obsd rflns ( <i>I</i> > 2σ <sub><i>i</i></sub> )	8795
no. of params	774
final R1, wR2 values ( <i>I</i> > 2σ <sub><i>i</i></sub> )	0.0982, 0.2305
final R1, wR2 values (all data)	0.1076, 0.2373
residual electron density peaks (e Å <sup>-3</sup> )	1.681, –0.767

petroleum ether (10 mL) and filtered through a silica gel plug. The silica gel was washed with several small portions of petroleum ether in order to remove all traces of but-1-ene-1,3-diylidbenzene. The resulting residue was dried under vacuum to constant weight.

**Catalytic Hydrosilylation Studies.** A Schlenk tube was loaded with olefin (10 mmol), PhSiH<sub>3</sub> (20 mmol), 1,2-dichloroethane (1 mL), and the corresponding catalyst (1 mol %) under argon. The system was heated to 60 °C using a paraffin bath over 4 h. The reaction time was measured from the moment it was introduced at 60 °C. After this period of time, a dark brown solution was obtained. The volatiles were pumped off, and the residue was treated with petroleum ether, which was filtered through a silica gel plug. The silica gel was washed with several small portions. The resulting residue was dried under vacuum, and the corresponding hydrosilylation products were observed in the form of yellowish oils. Their NMR properties were compared with data in the literature.<sup>35a,36</sup>

**4-Fluorostyrene Hydrosilylation Kinetic Studies.** In a NMR tube was prepared a mixture of 4-fluorostyrene (0.5 mmol), PhSiH<sub>3</sub> (1 mmol), 1,2-dichloroethane (300 μL), benzene-*d*<sub>6</sub> (100 μL), and the corresponding catalyst (1 mol %) under argon in a bath containing N<sub>2</sub>(l)/EtOH. This mixture was monitored by NMR at 60 °C: <sup>19</sup>F NMR spectra were measured every 180 s during 1 h. Their NMR properties were compared with data in the literature and confirmed by CG-MS.

<sup>1</sup>H NMR for {1-(4-fluorophenyl)ethyl}phenylsilane (benzene-*d*<sub>6</sub>, 298 K): δ 1.19 (d, 3H,  $J_{\text{H-H}} = 6.8$ , CH<sub>3</sub>), 2.73 (m, 2H, CH<sub>2</sub>), 4.15 (vd, SiH<sub>2</sub>), aromatic signals 7.6–7.0 ppm.

<sup>1</sup>H NMR (4-fluorophenylethyl)phenylsilane (benzene-*d*<sub>6</sub>, 298 K): δ 1.25 (m, 2H, CH<sub>2</sub>), δ: 2.63 (m, 2H, CH<sub>2</sub>), 4.21 (vd, SiH<sub>2</sub>), aromatic signals 7.6–7.0 ppm.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures, tables, and a CIF file giving catalytic screening results and crystallographic data for compound **1d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.



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## Notes

The authors declare no competing financial interest.

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