

## Ni(<sup>4-tBu</sup>stb)<sub>3</sub>: A Robust 16-Electron Ni(0) Olefin Complex for Catalysis

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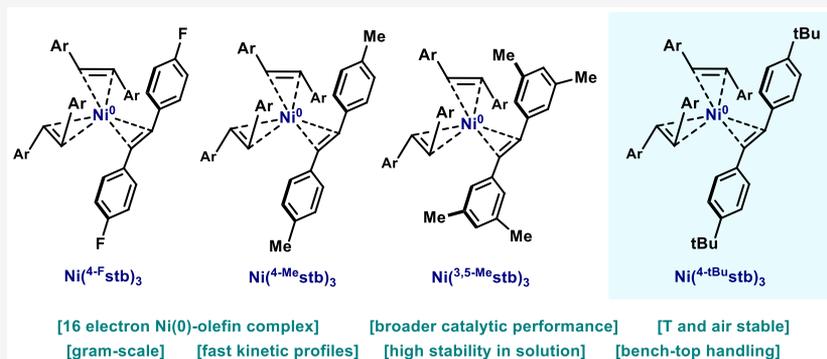
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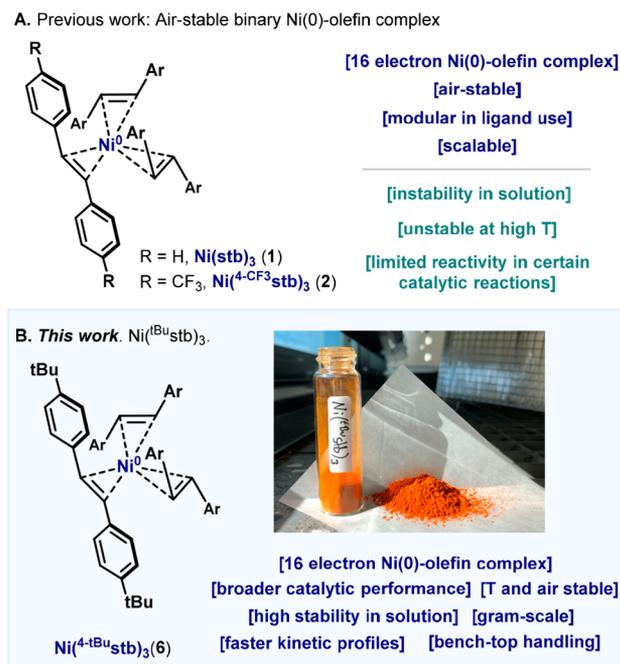
**ABSTRACT:** Sixteen-electron Ni(0) complexes bearing *trans*-stilbene derivative ligands have been shown to display a high degree of stability toward oxidation in the solid state. A structural analysis of a unique family of tris Ni(0) stilbene complexes revealed a remarkable effect of the steric hindrance of the substituents at the *para* position of the stilbene unit to temperature, oxidation, and degradation in solution. From these analyses, Ni(<sup>4-tBu</sup>stb)<sub>3</sub> arose as a long-term air-, bench-, and temperature-stable Ni(0) complex. Importantly, Ni(<sup>4-tBu</sup>stb)<sub>3</sub> presents faster kinetic profiles and a broader scope as a Ni(0) source, thus outperforming the previously described Ni(<sup>4-CF<sub>3</sub></sup>stb)<sub>3</sub> in a variety of relevant Ni-catalyzed transformations.

The use of nickel (Ni) to catalyze organic transformations has gained tremendous momentum as a sustainable alternative to more noble metals.<sup>1</sup> Indeed, the breadth of redox manipulations in Ni complexes opened the door to reactivity that exponentially expanded the palette of opportunities for bond formation.<sup>1,2</sup> Within this vast realm of transformations, reactions catalyzed by Ni(0) complexes have played a crucial role in enabling new catalytic activation modes.<sup>3</sup> In this context, the 18-electron binary complex Ni(COD)<sub>2</sub> represented the most versatile and modular Ni(0) source for reaction discovery.<sup>4</sup> This is primarily due to the high lability of the olefin ligands toward ligand exchange with a wide variety of ligands—a reactivity feature which Wilke referred to as “naked nickel”.<sup>5</sup> In spite of these advantages, the sensitivity to air of Ni(COD)<sub>2</sub> requires its handling under an inert atmosphere using gloveboxes or Schlenk techniques. Moreover, Ni(COD)<sub>2</sub> is temperature-sensitive and will eventually decompose if not stored at low temperatures (<−20 °C). These drawbacks have partially been circumvented by the use of air-stable Ni(II) and Ni(0) ligand precursors<sup>6,7</sup> and the development of paraffin capsules for Ni(COD)<sub>2</sub>,<sup>8</sup> which afford the desired Ni species under aerobic conditions. Recently, Engle and co-workers have shown that the Schrauzer complex (COD)Ni(DQ)<sup>9</sup> (DQ = duroquinone) can be used as an air-stable Ni source. Yet, catalysis is limited to its combination with strongly nucleophilic ligands, due to the highly coordinating DQ.<sup>10</sup> Consequently, the development of a simple, scalable, and

modular Ni(0) source which is bench-, air-, and temperature-stable but retains the levels of reactivity demonstrated by Ni(COD)<sub>2</sub> is still highly desirable. As part of our ongoing program on the study of low-valent Ni complexes,<sup>11</sup> our group has recently reported the air-stable, 16-electron binary Ni(0) olefin complexes Ni(stb)<sub>3</sub> (1) and Ni(<sup>4-CF<sub>3</sub></sup>stb)<sub>3</sub> (2) (Figure 1A).<sup>12</sup> In contrast to other 16-electron Ni(0) olefin compounds,<sup>5</sup> complex 2 can be stored in air in the freezer for long periods of time before showing signs of decomposition. Importantly, complex 2 was shown to be an alternative to Ni(COD)<sub>2</sub> in a variety of Ni-catalyzed transformations. However, in the absence of nucleophilic ligands, complex 2 was shown to be unstable in solution at room temperature, with fast exchange of the <sup>4-CF<sub>3</sub></sup>stb ligand with the solvent, ultimately leading to Ni black.

With the aim of providing a solution to these drawbacks and to elucidate the origin of the unusual stability of tris-stilbene Ni(0) derivatives, herein we report a structural analysis of different 16-electron binary Ni(0) complexes bearing distinct

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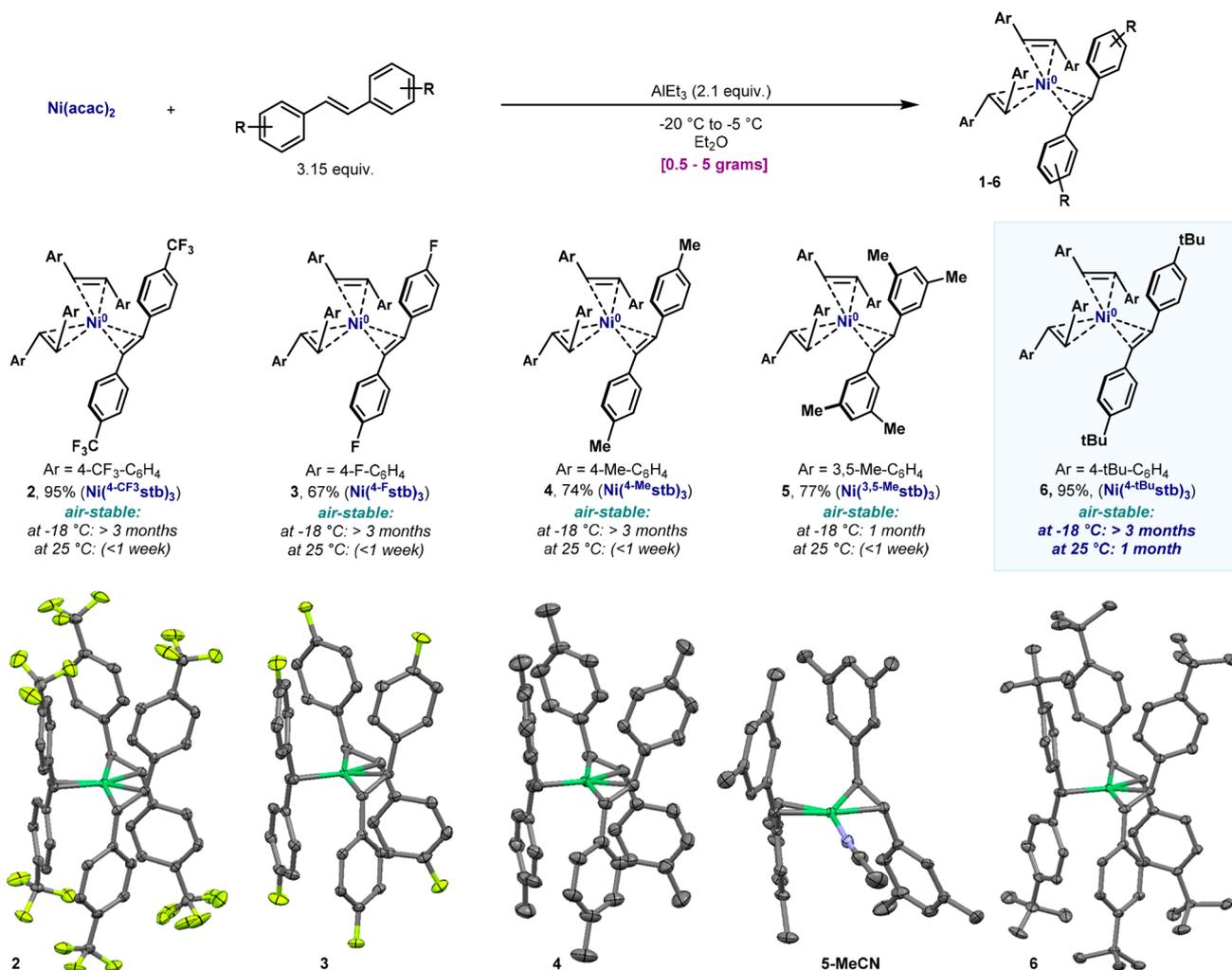
**Figure 1.** (A) Ni(<sup>4</sup>CF<sub>3</sub>stb)<sub>3</sub>: advantages and drawbacks. (B) Ni(<sup>4-t</sup>Bustb)<sub>3</sub>: a superior Ni(0) source for Ni catalysis.

stilbene derivatives as ligands. A survey of the substitution pattern of the aryl groups revealed that steric hindrance play a fundamental role toward protecting the Ni(0) center from oxidation. The stability and catalytic activity of these new complexes were benchmarked with complexes 1 and 2. From this analysis, Ni(<sup>4-t</sup>Bustb)<sub>3</sub> (6) was identified as an extremely superior Ni(0) complex, with features that circumvent the limitations of 2 (Figure 1B). Hence, 6 (1) is stable at room temperature and can be stored opened to air on the bench for long periods of time (ca. 1 month), (2) displays higher stability in solution with various solvents, (3) presents faster kinetic profiles than 2, (4) is catalytically competent in reactions where 2 was proven to be either inefficient or inactive, and (5) can be prepared in multigram quantities with high yields (95%).

The unexpectedly high stability toward oxidation observed in our previous work for complex 2 over that of 1<sup>12</sup> posed the question as to whether this is the result of steric factors rendered by the CF<sub>3</sub> groups or is a consequence of the electron-withdrawing effect posed by this group on the stilbene unit. To shed light on this question, we synthesized various binary 16-electron complexes, featuring different steric and electronic substitutions at the *meta* and *para* positions of the stilbene. The procedure previously optimized for the multigram synthesis for 2 (Ni(acac)<sub>2</sub>, stilbene, and AlEt<sub>3</sub>)<sup>12</sup> proved successful for the preparation of complexes 3–6 (Figure 2, top). At the onset, we prepared complex 3, bearing fluorine atoms at both *para* positions of the phenyl rings, which render the stilbene unit slightly electron deficient (67% yield). When the fluorine atoms were replaced by a more electron donating group such as Me, complex 4 was obtained in good yield (74%). At this point, we questioned whether the highly compact arrangement of the stilbenes around the Ni would permit substitution at the *meta* position of the aryl ring. Gratifyingly, the corresponding Ni(0) complex bearing three (*E*)-1,2-bis(3,5-dimethylphenyl)ethene ligands (5) could be successfully synthesized in high yield. Although several

crystallization attempts were unsuccessful, compound 5 was successfully characterized by NMR spectroscopy and elemental analysis.<sup>13</sup> Yet, when 5 was dissolved in Et<sub>2</sub>O/MeCN 10/1, small crystals of 5-MeCN were obtained. This is in line with previous observations in our group about the facile displacement of one of the stilbene units in nucleophilic coordinating solvents.<sup>12,13</sup> Interestingly, complexes 3–5 have stability comparable to that of complex 2: they are stable for months in air if stored in the freezer (−18 °C); however, signs of decomposition could be observed after several days if they were left opened to air in the benchtop.<sup>13</sup> Despite their similarities in structure, complexes 2–5 have severe differences in electronics; yet, a clear trend in their stability toward oxidation could not be clearly deduced. Then, we speculated that the steric contribution of these substituents could play a major role. To validate this hypothesis, we increased the bulk at the *para* positions of the stilbene by introducing a <sup>t</sup>Bu group. Following the general procedure as for 1–5, Ni(<sup>4-t</sup>Bustb)<sub>3</sub> (6) was obtained as a yellow-orange solid in gram quantities and in high yield (95%, Figures 1B and 2). To our delight, 6 exhibited a remarkable stability to temperature and oxidation, and it could simply be stored in air on the benchtop (1 month). In contrast to 1–5, complex 6 also displayed high stability in solution, showing no signs of decomposition in a variety of solvents. Strikingly, in the solid state, this 16-electron complex could be heated up to 60 °C for 1 h, showing no visual signs of decomposition. Finally, X-ray photoelectron spectroscopy (XPS) unequivocally confirmed that the oxidation state of Ni in complex 6 is Ni(0).<sup>13</sup> Such outstanding physical properties highlight the robustness of 6 and certify its superior stability in comparison to the other binary 16-electron Ni(0) olefin complexes known.<sup>14</sup> Figure 2 (bottom) shows the ORTEP drawings of these family of complexes. Complexes 2–4 and 6 reveal certain common features in the solid state: three stilbene units are wrapped around the Ni center in a propeller arrangement, rendering a distorted-trigonal-planar geometry resembling that of 1, 2 and *t,t,t*-Ni(CDT).<sup>14c</sup>

A detailed analysis of the solid-state structures revealed *a priori* unexpected features (Figure 3). Although the stilbene ligands are electronically different among themselves, similar C1=C2 distances of the ethene moiety coordinated to Ni were observed (1.39 Å)—comparing well with the distance in *t,t,t*-Ni(CDT) (1.37 Å)<sup>14c</sup> and coinciding with that of Ni(COD)<sub>2</sub> (1.39 Å) (Figure 3).<sup>15</sup> This striking observation suggests a comparable  $\pi$  back-donation from the d orbitals of the Ni to the empty  $\pi^*$  orbital of the stilbenes in 1–4 and 6. Moreover, similar geometries for the propeller structure were observed, with torsion angles ( $\theta$  = C2–C1–Ni–C3 = 28.3–30.3°) slightly lower than that of *t,t,t*-Ni(CDT) (32.0°).<sup>14c</sup> Yet, differences could be observed in the torsion between the ethene moiety and the *ipso* carbons of the aryl groups ( $\psi$  = C1–C2 = C3–C4). Indeed, these angles range from 158.4 to 161.7° in complexes 1–4; however, complex 6 presents a much higher torsion ( $\psi$  = 156.2°), which is ascribed to the repulsion between the three <sup>t</sup>Bu units pointing outward at the edges of the complex. This structural feature suggests that the <sup>t</sup>Bu groups are experiencing an extreme steric situation and, as a result, they are offering minimal space available for oxygen to go through, thus profoundly protecting the Ni center. Although speculative at this point, the origin of the superior stability of 6 could be the result of attractive London dispersion forces (LDF) by the <sup>t</sup>Bu units, which hold the stilbenes together in the solid state.<sup>16</sup>



**Figure 2.** (top) Synthesis of 16-electron Ni(0) stilbene complexes 1–6. (bottom) ORTEP drawings of complexes 2–4, 5-MeCN, and 6 and analysis of their physical properties. Color code: green, Ni; black, C; yellow, F; purple, N. Hydrogen atoms are omitted for clarity. See the Supporting Information for complete descriptions of the XRD structures. The stability of the complexes 1–6 to air in the solid state was judged by a clear visual color change on oxidation; color fading is a good indicator of decomposition. For example, after >1 month, complex 6 showed noticeable color fading after being exposed to air. Stoichiometric exchange experiments with phosphine revealed a 20% decomposition after this time.<sup>13</sup>

Complex	olefin distance (Å) C1–C2	torsion of propeller (°) C2–C1–Ni–C3	torsion of stilbene (°) C1–C2–C3–C4
<i>tt</i> -Ni(CDT)	1.37	32.0	169.5
1	1.39	28.9	161.7
2	1.39	29.2	160.1
3	1.39	30.2	158.6
4	1.39	28.3	159.4
6	1.39	30.3	<b>156.2</b>

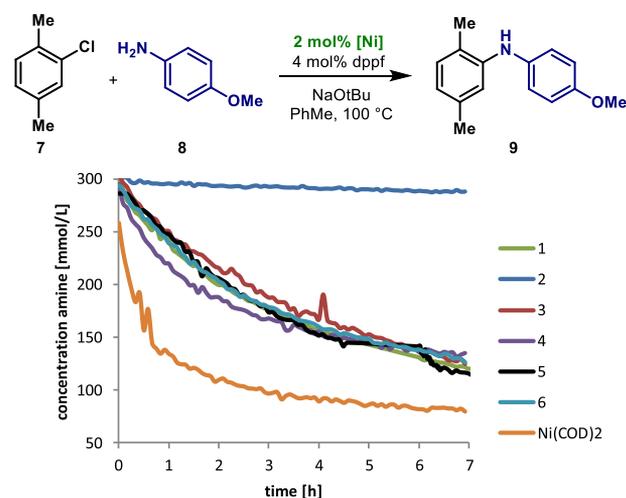
**Figure 3.** Characteristic features of the solid state X-ray for complexes 1–4 and 6. Color code: green; Ni; black, C. Hydrogen atoms are omitted for clarity.

Having identified complex 6 ( $\text{Ni}(\text{}^4\text{-tBuStb})_3$ ) as a superior Ni(0) complex in terms of stability, we decided to study its performance as a catalyst. Although the differences in electronics on the stilbene units are not reflected in the C=C distance (2 compared to 6), we speculated that in catalysis

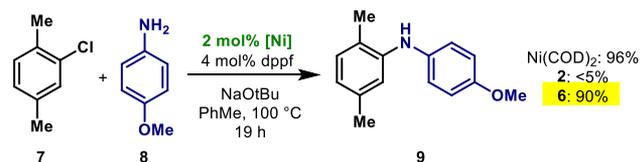
such properties could become important and dramatically influence the catalytic kinetic profiles.<sup>17</sup> Hence, we focused our attention on the venerable Ni-catalyzed Buchwald–Hartwig amination reaction (Figure 4A), where the presence of  $\pi$  acceptors has been shown to influence the kinetic profiles due to competing ligation to the (bis-phosphine)Ni(0) active species.<sup>18</sup> Whereas this transformation proceeds efficiently with  $\text{Ni}(\text{COD})_2$  at  $100\text{ }^\circ\text{C}$ ,<sup>18a</sup> complex 2 ( $\text{Ni}(\text{}^4\text{-CF}_3\text{stb})_3$ ) required  $130\text{ }^\circ\text{C}$  to proceed to full conversion.<sup>12</sup> As shown in Figure 4A, when complex 2 was used as a catalyst at  $100\text{ }^\circ\text{C}$ , extremely slow kinetic profiles were observed (dark blue line), with almost no conversion of 8 after 7 h. However, complexes 1 and 3–6 bearing more electron rich stilbenes exhibit much faster performances, with virtually identical profiles. In light of these results, we attempted a batch reaction using complex 6 at the reported temperature, and after 19 h reaction time, an excellent yield of 9 was obtained (Figure 4B, 90%).

The stability in solution and kinetic profile observed for  $\text{Ni}(\text{}^4\text{-tBuStb})_3$  (6) led us to speculate that this complex might prove superior in other catalytic domains. Specifically, we focused our attention in reactions where complex 2 struggled

## A. Ni(0)-catalyzed amination of aryl chlorides: a kinetic analysis



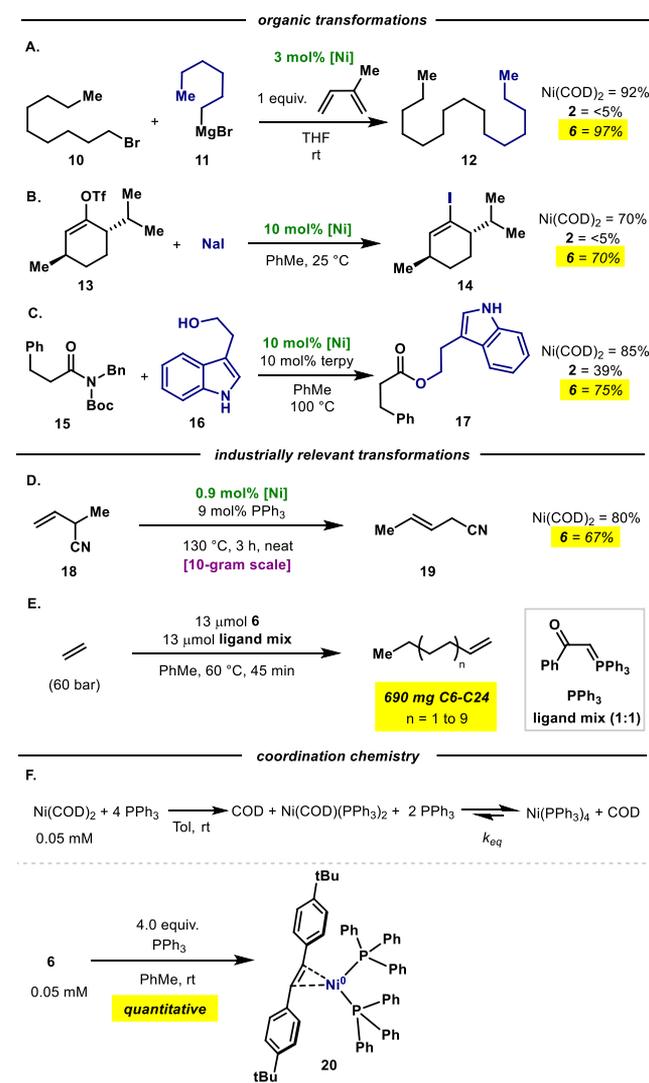
## B. Comparison on the catalytic activity with different Ni(0) catalysts



**Figure 4.** (A) Kinetic profiles of the consumption of the aryl chloride in the Buchwald–Hartwig amination reaction. (B) Batch experiment at 19 h reaction time.

to perform or was not stable, due to the absence of supporting ligands. For example, we examined the alkyl–alkyl cross-coupling developed by Kambe between alkyl bromides (**10**) and alkyl Grignard reagents (**11**), which requires the use of dienes as ligands for Ni (Scheme 1A).<sup>19</sup> In our previous work, we showed that complex **2** was completely inactive and resulted in fast decomposition of **2** in solution.<sup>12</sup> However, in a remarkable example of superior reactivity, Ni(<sup>4-tBu</sup>stb)<sub>3</sub> (**6**) performed at the same level as Ni(COD)<sub>2</sub>, affording a >95% yield of **12**. A similar situation was found in the conversion of vinyl triflates to vinyl halides developed by Reisman (Scheme 1B).<sup>20</sup> In this case, no external supporting ligand was required and Ni(<sup>4-CF<sub>3</sub></sup>stb)<sub>3</sub> (**2**) did not show any catalytic activity. However, when Ni(<sup>4-tBu</sup>stb)<sub>3</sub> was used instead, smooth formation of vinyl iodide **14** was obtained in 70% yield. The amide activation protocol developed by Garg is another example of this different reactivity (Scheme 1C).<sup>21</sup> Previously, our Ni(<sup>4-CF<sub>3</sub></sup>stb)<sub>3</sub> (**2**) required forcing conditions (130 °C versus 100 °C) to facilitate the formation of **17**. The use of complex **6** surpasses these limitations and delivers **17** in 75% yield at 100 °C.

The stability and facility of ligand exchange with other olefins has also been demonstrated in two industrially relevant transformations which require Ni(COD)<sub>2</sub>: for example, the Ni-catalyzed isomerization of 2M3BN (2-methyl-3-butenitrile, **18**) to 3PN (3-pentenitrile, **19**) (Scheme 1D),<sup>22</sup> which is crucial in the efficient synthesis of adiponitrile from butadiene.<sup>23</sup> This transformation proceeds under neat conditions with the aid of PPh<sub>3</sub> and affords comparable levels of reactivity toward **19** (67%). Another process is the Ni-catalyzed SHOP (Shell Higher Olefin Process),<sup>24</sup> which enables the oligomerization of ethylene to obtain higher-molecular-weight  $\alpha$ -olefins. Under the reported conditions and

Scheme 1. Comparison of the Reactivity among Ni(COD)<sub>2</sub>, Ni(<sup>4-CF<sub>3</sub></sup>stb)<sub>3</sub> (**2**), and Ni(<sup>4-tBu</sup>stb)<sub>3</sub> (**6**)<sup>a</sup>

<sup>a</sup>The use of complex **6** permits the use of an air- and bench-stable Ni(0) source in a broader range of Ni(0)-catalyzed transformations. See the Supporting Information for experimental details.

without precatalyst isolation, complex **6** together with the ligand mixture depicted in Scheme 1E successfully catalyzed the formation of a mixture of  $\alpha$ -olefins with high efficiency.<sup>25</sup> These results highlight the potential of **6** in industrially relevant settings, thus providing an air- and temperature-stable alternative to current Ni(0) catalysts. Although Ni(<sup>4-tBu</sup>stb)<sub>3</sub> (**6**) might be regarded as an air-stable Ni(COD)<sub>2</sub> surrogate, the fundamental coordination chemistries of both complexes differ significantly. For example, when Ni(COD)<sub>2</sub> is mixed with 4.0 equiv of PPh<sub>3</sub>, a mixture of Ni(PPh<sub>3</sub>)<sub>4</sub> and (PPh<sub>3</sub>)<sub>2</sub>Ni(COD) is commonly obtained (Scheme 1F, top), with a calculated  $k_{eq}$  value of 7.5 at 25 °C.<sup>13</sup> On the other hand, when **6** is used instead, clean conversion to the 16-electron compound **20** is formed (Scheme 1F, bottom). These differences in coordination chemistry provide an orthogonal tool to existing strategies for the synthesis of well-defined L–Ni(0)–olefin complexes.<sup>26,17b</sup>

Overall, this report presents the synthesis of a family of air-stable 16-electron tris-olefin Ni(0) complexes. A systematic study of the substituents enabled us to establish that the origin of the high stability toward oxidation is the result of a steric demand imbued by the substituents at the *para* position of the stilbene ligands. This fundamental observation permitted the rational design of Ni(<sup>4-tBu</sup>stb)<sub>3</sub> (**6**), which proved to be a superior Ni(0) source with remarkable physical properties. Complex **6** has been shown to perform at the same level as Ni(COD)<sub>2</sub> in challenging catalytic transformations. The high resemblance in reactivity to Ni(COD)<sub>2</sub>, the broad applicability, high practicality, and robustness of complex **6** lead us to believe that such a complex will find rapid application in the field of Ni catalysis. Studies toward studying the origin of such remarkable stability are currently ongoing in our laboratory.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00485>.

Experimental procedures and analytical data (<sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR, HRMS) for all new compounds (PDF)

### Accession Codes

CCDC 2004460–2004464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare the following competing financial interest(s): A patent application, being directed to the catalysts and the synthesis and the use thereof, has been filed with the European patent office under application No. EP19189236.3 and subsequently as PCT-application under application No. PCT/EP2020/069898.

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