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Trimethylsilylated Allyl Complexes of Nickel. The Stabilized Bis(π -allyl)nickel Complex $[\eta^3\text{-}1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Ni}$ and Its Mono(π -allyl)NiX (X = Br, I) Derivatives

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Abstract: Reaction of 2 equiv of $\text{K}[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]$ with $\text{NiBr}_2(\text{dme})$ in THF at -78°C produces the orange π -allyl complex $[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Ni}$ (**1**). Unlike the pyrophoric $(\text{C}_3\text{H}_5)_2\text{Ni}$, the trimethylsilylated derivative only slowly decomposes in air (from hours to days). Both eclipsed (**1a**) and staggered (**1b**) conformations are found in solution; the eclipsed form irreversibly converts to the thermodynamically more stable staggered conformation when heated above 85°C . Single-crystal X-ray structures obtained for both **1a** and **1b** confirm that the allyl ligands are bound in a *trihapto* manner to the metals and that trimethylsilyl substituents are in syn, anti arrangements. Density functional theory calculations performed on the bis(allyl)nickel complexes indicate that the substituents exert little effect on the basic metal–ligand geometries. Trimethylphosphine is converted to tetramethyltetraphosphane, $(\text{MeP})_4$, on reaction with **1**. In toluene, 3-bromo-1,3-bis-(trimethylsilyl)propene reacts with $(\text{COD})_2\text{Ni}$ to produce the dimeric purple complex $\{[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]\text{-NiBr}\}_2$ (**2a**). Both NMR and X-ray crystallographic data establish that the allyl ligands are staggered and that the trimethylsilyl substituents are in a syn, syn conformation. NMR data indicate that the reaction of one equivalent of **1** with Br_2 in benzene produces an analogous complex (**2b**) with the allyl ligand substituents in a syn, anti configuration. When 1 equiv of **1** is treated with I_2 in hexanes, the dark red dimeric complex $\{[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]\text{NiI}\}_2$ (**3**) is formed. Its X-ray crystal structure demonstrates that both eclipsed (**3a**) and staggered (**3b**) allyl conformation are present. The trimethylsilyl groups on the allyl ligands are in syn, anti arrangements in the two forms.

Introduction

Bis(allyl)nickel, $(\text{C}_3\text{H}_5)_2\text{Ni}$, was the first homoleptic transition metal allyl complex to be isolated,¹ and it is still the archetypal example of its class. A variety of both homoleptic and heteroleptic (allyl)nickel complexes have been prepared and studied in the ensuing 40 years,^{2–6} and many of them have found uses in homogeneous catalysis and organic synthesis.^{7–10} Stoichiometric reactions of homoleptic $(\text{allyl})_2\text{Ni}$ complexes with phosphines,⁵ halogens¹¹ and carbon dioxide¹² have also been

examined in detail.^{4,6–10,13} Such studies have been conducted despite the low oxidative and thermal stability of many bis-(allyl)nickel complexes (e.g., the parent $(\text{C}_3\text{H}_5)_2\text{Ni}$ is pyrophoric and decomposes above 20°C). Even physical characterization of these (allyl)nickel compounds can be problematic and has often relied heavily on solution NMR studies^{5,14} or theoretical investigations.^{15–17} The instability of the compounds has made the use of other methods, such as photoelectron spectroscopy,¹⁸ electrochemistry, and in some cases even crystallography¹⁹ problematic.

Sterically bulky cyclopentadienyl rings (e.g., C_5Me_5 , $\text{C}_5\text{H}_3\text{-(SiMe}_3)_2$) are frequently used to synthesize compounds of greater

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diversity and stability than is possible with Cp alone,^{20–22} and a similar approach has recently been found effective with the allyl ligand. In some instances, allyl compounds with ligands substituted by trimethylsilyl and dimethyl(*tert*-butyl)silyl²³ groups represent new classes of metal complexes. Among these are the thermally stable, electron-deficient bis(allyl) compounds [1,3-(SiMe₃)₂C₃H₃]₂M (M = Cr, 12-e⁻;²⁴ Fe, 14-e⁻;²⁵ Co, 15-e⁻;²⁶); they have no monomeric counterparts with unsubstituted ligands. Various lanthanide containing species have also been isolated that have no analogues containing the parent allyl anion (e.g., the neutral monomeric tris(allyl) complexes [1,3-(SiMe₃)₂C₃H₃]₃Ln(thf) (Ln = Ce, Nd, Tb)²⁷ and the tetrametallic salt {K(thf)₂Sm[1,3-(SiMe₃)₂C₃H₃]₃}₂²⁸). In other cases, substituted allyl ligands can provide versions of known compounds that are more robust and easily studied than the unsubstituted species. This situation occurs, for instance, with the homoleptic thorium complexes [(SiMe₃)_nC₃H_{5–n}]₄Th (*n* = 1, 2).²⁹ In contrast to (C₃H₅)₄Th, which decomposes at 0 °C, the trimethylsilylated derivatives are stable up to 90 °C, and their structural authentications were the first for neutral [R_nC₃H_{5–n}]₄M species.

The chemistry already known for (allyl)nickel complexes suggests that the study of their derivatives with bulky allyl ligands should be particularly informative. Previous use of substituted allyl ligands in nickel complexes has been limited to groups such as methyl (e.g., the crotyl anion), ethyl, or phenyl,³⁰ and some of these compounds have been used as catalysts.^{31–33} Modest improvements in thermal stability are observed in several cases (for example, (2-MeC₃H₄)₂Ni decomposes at 33 °C, and the heavily substituted bis(1,1',3,3'-tetraphenylallyl)nickel is stable at room temperature³⁴). The good solubility in hydrocarbons and the typically high thermal stability of known complexes containing trimethylsilylated allyl ligands suggest that nickel species could benefit considerably from their use.

We report here our initial study of the effects of the 1,3-bis(trimethylsilyl)allyl ligand on the synthesis, structure, and reactions of bis(allyl)nickel complexes. As part of this research,

we investigated the related heteroleptic nickel complexes (1,3-bis(trimethylsilyl)allyl)NiX (X = Br, I) and compared their properties with the parent (C₃H₅)NiX species.³⁵

Experimental Section

General Considerations. All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or glovebox techniques. Proton, carbon (¹³C), and phosphorus (³¹P) NMR spectra were obtained on a Bruker DPX-300 spectrometer at 300, 75.5, and 121 MHz, respectively, and were referenced to the residual proton and ¹³C resonances of C₆D₆ (δ 7.15 and 128.0) or to external H₃PO₄ (δ 0.0). NOESY, COSY, and HMQC NMR spectra were recorded on a Bruker DPX-400 spectrometer and were similarly referenced. HSQC NMR spectra were recorded on a Bruker Avance 500 instrument. All NMR data were processed using Bruker XWIN-NMR 3.5 software on an Octane workstation (Silicon Graphics, Mountain View, CA).

UV–vis spectra were obtained on a Cary 50 spectrometer. Infrared data were obtained on an ATI Mattson-Genesis FT-IR spectrometer either neat or as KBr pellets prepared as previously described.³⁶ GC-MS data were obtained with a Hewlett-Packard 5890 Series II gas chromatograph/mass spectrometer with a 5971 Series mass selective detector. Melting points were determined on a Laboratory Devices Mel-Temp apparatus in sealed capillaries. Metal analyses were obtained from complexometric titration;³⁷ combustion analyses were performed by Desert Analytics, Tuscon, AZ.

³¹P Decoupled HSQC Experiments. The phase sensitive ¹H–¹³C HSQC experiments used the following parameters: 1024 data points; a spectral width of 5000 Hz in the acquisition dimension and 1006 Hz in the indirect dimension; an acquisition time of 102 ms with GARP decoupling of the carbons; and two scans for each of the 1024 increments. An echo–antiecho acquisition scheme was employed. Phosphorus decoupling was achieved through an additional 180° hard pulse on the phosphorus resonance using a third channel. All other parameters were kept constant. The data were zero-filled, and a square sinebell apodization was applied in both dimensions.

Materials. 1-(SiMe₃)C₃H₅ and (C₆H₅COO)₂ were purchased from Acros, (COD)₂Ni was obtained from Strem, and NiCl₂, NiBr₂, NiBr₂(dme), NiI₂, and [AgI·PMe₃]₄ were purchased from Aldrich; all were used as received. 1,3-(SiMe₃)₂C₃H₄ and Li[1,3-(SiMe₃)₂C₃H₃] were synthesized according to literature procedures.³⁸ K[1,3-(SiMe₃)₂C₃H₃] was prepared by transmetalation of Li[1,3-(SiMe₃)₂C₃H₃] with potassium *tert*-butoxide in hexanes solution. THF, toluene, and hexanes were distilled under nitrogen from potassium benzophenone ketyl.³⁹ Deuterated solvents were vacuum distilled from Na/K (22/78) alloy prior to use.

Attempted Synthesis of [1,3-(SiMe₃)₂C₃H₃]₂Ni from NiCl₂ and K[1,3-(SiMe₃)₂C₃H₃]. Formation of 1,3,4,6-Tetrakis(trimethylsilyl)-1,5-hexadiene. A 125 mL Schlenk flask containing a magnetic stirring bar and fitted with an addition funnel was charged with NiCl₂ (0.288 g; 2.22 mmol) in 10 mL of THF. K[1,3-(SiMe₃)₂C₃H₃] (1.00 g; 4.45 mmol) dissolved in 15 mL of THF was placed in the addition funnel. The apparatus was cooled to –78 °C using a dry ice/acetone bath. The THF solution of K[1,3-(SiMe₃)₂C₃H₃] was added dropwise with stirring over the course of 30 min. The solution was allowed to warm to room temperature overnight, after which the THF was removed under vacuum. The residue was extracted with hexanes, and the extract was

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filtered over a medium porosity glass frit. Removal of the hexanes under vacuum afforded a dark oil. Under reduced pressure (10^{-3} Torr) at 55 °C, a white, waxy solid (mp 44–46 °C) sublimed from the oil; it was identified as 1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene (0.192 g, 23% yield). The product could be obtained as colorless crystals from hexanes. Anal. Calcd for $C_{18}H_{42}Si_4$: C, 58.29; H, 11.41. Found: C, 58.44; H, 11.74. MS (*m/e*) 370 (M^+), 355 ($M^+ - Me$), 297 ($M^+ - SiMe_3$), 73 ($SiMe_3$). Principle IR bands (KBr, cm^{-1}): 2959 (s), 2898 (m), 2390 (w), 1600 (w), 1449 (m), 1250 (s), 1248 (s), 1082 (s), 1028 (s), 850 (s), 803 (s), 734 (w), 687 (m), 402 (m). Two diastereomers were identified in NMR spectra; their ratios varied somewhat from reaction to reaction, but the same one was always present in larger amounts. Major product diastereomer: 1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.14 (s, 36H, $SiMe_3$); 2.01 (mult, 2H, $C_{(3,4)}-H$); 5.47 (d, 2H, $J = 18.3$ Hz, $C_{(1,6)}-H$); 5.90 (mult, 2H, $C_{(2,5)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -1.05 ($SiMe_3$); -0.88 ($SiMe_3$); 39.89 ($C_{(3,4)}$); 127.20 ($C_{(2,5)}$); 149.38 ($C_{(1,6)}$). Minor product diastereomer: 1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.068 (s, 18H, $SiMe_3$); 0.084 (s, 18H, $SiMe_3$); 2.01 (mult, 2H, $C_{(3,4)}-H$); 5.60 (d, 2H, $J = 18.3$ Hz, $C_{(1,6)}-H$); 6.37 (dd, 2H, $J = 18.3$ Hz, $J = 9.9$ Hz, $C_{(2,5)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -2.16 ($SiMe_3$); -1.05 ($SiMe_3$); 39.50 ($C_{(3,4)}$); 128.76 ($C_{(2,5)}$); 146.88 ($C_{(1,6)}$).

Attempted Synthesis of [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni from NiBr $_2$ and NiI $_2$. The preparation of [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni was attempted as described above from K[1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] and either NiBr $_2$ or NiI $_2$ in THF. Workup in both cases afforded dark oils, which yielded crystalline 1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene on standing for several days (78% from NiBr $_2$ and 39% from NiI $_2$), identified from NMR spectra.

Synthesis of [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni (1). A 125 mL Schlenk flask containing a magnetic stirring bar and fitted with an addition funnel was charged with NiBr $_2$ ·DME (1.002 g; 3.224 mmol) in 10 mL of THF. K[1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] (1.457 g; 6.490 mmol), dissolved in 15 mL of THF, was added to the addition funnel. The apparatus was cooled to -78 °C using a dry ice/acetone bath. The THF solution of K[1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] was added dropwise with stirring over the course of 30 min. The solution was allowed to warm to room temperature overnight. THF was removed under vacuum, and the residue was extracted with hexanes. The extract was filtered over a medium porosity glass frit, and hexanes were removed under vacuum to afford a nearly black oil that appeared dark red when transilluminated. Over a period of days, orange needles grew (1.00 g, 72% yield), mp 64–66 °C. The compound sublimates at 0.01 Torr and 45 °C. Anal. Calcd for $C_{18}H_{42}NiSi_4$: C, 50.33; H, 9.85; Ni, 13.7. Found: C, 49.24; H, 9.85; Ni (complexometric), 13.4. Principle IR bands (KBr, cm^{-1}): 2959 (s), 2898 (m), 2390 (w), 1600 (w), 1449 (m), 1250 (s), 1248 (s), 1082 (s), 1028 (s), 850 (s), 803 (s), 734 (w), 687 (m), 402 (m). UV-vis (THF): 318 nm ($\epsilon = 4100$), 330 nm ($\epsilon = 2500$), 411 nm ($\epsilon = 540$). Magnetic susceptibility measurements (toluene- d_8) indicate that the compound is diamagnetic. Two diastereomers (in variable ratio) were identified in NMR spectra. Major product diastereomer (1a): 1H NMR (300 MHz, C_6D_6 , 298 K) δ 0.151 (s, 18H, $SiMe_3$); 0.156 (s, 18H, $SiMe_3$); 2.67 (d, $J = 16.0$ Hz, 2H, anti C-H); 3.60 (d, $J = 10.4$ Hz, 2H, syn C-H); 4.96 (dd, $J = 16.0$ Hz, $J = 10.4$ Hz, 2H, $C_{(2)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K) δ 0.41 ($SiMe_3$); 1.88 ($SiMe_3$); 63.67 (anti C-H); 67.02 (syn C-H); 125.60 ($C_{(2)}$). Minor product diastereomer (1b): 1H NMR (300 MHz, C_6D_6 , 298 K) δ -0.055 (s, 18H, $SiMe_3$); 0.29 (s, 18H, $SiMe_3$); 2.07 (d, $J = 16.4$ Hz, 2H, anti C-H); 3.63 (d, $J = 10.0$ Hz, 2H, syn C-H); 5.62 (dd, $J = 16.4$ Hz, $J = 10.0$ Hz, 2H, $C_{(2)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ 1.06 ($SiMe_3$); 1.27 ($SiMe_3$); 63.14 (anti C-H); 63.49 (syn C-H); 123.79 ($C_{(2)}$).

Reaction of 1 with PMe_3 . In a 125 mL Schlenk flask, a solution of 1 (60% 1a) (0.064 g; 0.15 mmol) in hexanes (10 mL) was cooled to -78 °C in a dry ice/acetone bath. The flask was connected to a glass tube containing [AgI· PMe_3] $_4$ (0.190 g; 0.153 mmol). The glass tube was heated with a heat gun; after the PMe_3 was released, the initial

dark red solution turned yellow-brown. The reaction was filtered, and hexanes were removed under vacuum leaving an orange oil that crystallized and was identified with NMR data as containing staggered [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni (>95% 1b). Several crystals obtained from the concentrated reaction mixtures were examined with X-ray diffraction and were found to have unit cells matching only 1b. The organophosphorus compound tetramethyltetraphosphane was also detected in the oil. For it, 1H NMR (300 MHz, C_6D_6 , 298 K): δ 1.15 (s). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ 25.1 (apparent quintet, $J \approx 10.1$ Hz). 1H - ^{13}C HSQC [1H , ^{31}P] NMR (C_6D_6 , 298 K): δ 25.1 (s). ^{31}P NMR (121 MHz, C_6D_6 , 298 K): δ -21.6 (s). The same products were detected when the reaction was repeated with a 1:0.25 ratio of 1 and [AgI· PMe_3] $_4$ (i.e., a 1:1 ratio of 1 to PMe_3).

Synthesis of 1,3-($SiMe_3$) $_2$ C $_3$ H $_3$ Br. A 500 mL Schlenk flask containing a magnetic stirring bar and fitted with a reflux condenser was charged with 1,3-($SiMe_3$) $_2$ C $_3$ H $_4$ (7.01 g; 37.6 mmol) and NBS (6.60 g; 37.1 mmol) in 200 mL of CCl_4 . The solution turned pale yellow upon mixing. Benzoyl peroxide, (C_6H_5COO) $_2$, (0.104 g; 0.429 mmol) was added, and the solution was refluxed overnight. The resulting dark yellow solution was cooled to room temperature, and then was filtered to remove NHS. Removal of CCl_4 under vacuum afforded a dark yellow oil, which upon vacuum distillation (200 mTorr) at 40 °C afforded 1,3-($SiMe_3$) $_2$ C $_3$ H $_3$ Br as a colorless liquid (6.98 g) in 70% yield. Anal. Calcd for $C_9H_{21}BrSi_2$: C, 40.74; H, 7.98. Found: C, 40.60; H, 7.76. MS (*m/e*) 266/264 (M^+), 251/249 ($M^+ - Me$), 178/176 ($M^+ - SiMe_3$, - Me), 139/137 (HC($Si(Me)H_2$)Br), 97 (C(C) $SiMe_3$), 73 ($SiMe_3$). Principle IR bands (neat, cm^{-1}): 3059 (m), 2957 (s), 2898 (m), 2484 (w), 2263 (w), 1697 (m), 1604 (m), 1409 (m), 1287 (m), 1250 (s), 1138 (m), 991 (m), 908 (m), 840 (s), 752 (m), 694 (m), 475 (m), 409 (m). 1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.025 (s, 9H, vinylic $SiMe_3$); 0.044 (s, 9H, $SiMe_3$); 3.65 (d, $J = 8.8$ Hz, 1H, sp^3 -C-H); 5.71 (d, $J = 18.0$ Hz, 1H, anti C-H); 6.26 (dd, $J = 18.0$ Hz, $J = 8.8$ Hz, 1H, $C_{(2)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -3.28 (vinylic $SiMe_3$); -1.29 ($SiMe_3$); 45.83 (sp^3 -C); 131.13 (anti C-H); 143.78 ($C_{(2)}$).

Synthesis of [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ NiBr (2a) from 1,3-($SiMe_3$) $_2$ C $_3$ H $_3$ Br and Ni(COD) $_2$. A 125 mL Schlenk flask containing a magnetic stirring bar and fitted with a septum was charged with Ni(COD) $_2$ (2.00 g; 7.27 mmol) in 30 mL of toluene. The apparatus was cooled to -78 °C using a dry ice/acetone bath. To the stirred solution, 1,3-($SiMe_3$) $_2$ C $_3$ H $_3$ Br (1.99 g; 7.50 mmol) was delivered with a syringe. The solution was allowed to warm to room temperature overnight and became deep red-purple upon warming. Toluene was removed under vacuum, and the residue was extracted with hexanes. The reaction was filtered, and the hexanes were removed under vacuum to afford a deep purple solid (1.94 g, 82% yield). Purple plates could be obtained on recrystallization from hexanes. Anal. Calcd for $C_9H_{21}BrNiSi_2$: Ni, 18.1. Found: Ni (complexometric), 17.4. Principle IR bands (KBr, cm^{-1}): 2960 (s), 2898 (m), 2358 (w), 2341 (w), 1600 (w), 1260 (s), 1099 (s), 1086 (s), 1019 (s), 850 (s), 801 (s), 693 (m), 424 (m). Magnetic susceptibility measurements (toluene- d_8) indicate the compound is diamagnetic. 1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.22 (s, 18H, $SiMe_3$); 1.93 (d, $J = 14.4$ Hz, 2H, anti C-H); 5.27 (t, $J = 14.4$ Hz, 1H, $C_{(2)}-H$). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -0.53 ($SiMe_3$); 68.70 ($C_{(1,3)}$); 114.65 ($C_{(2)}$).

Synthesis of [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ NiBr (2b) from [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni and Br $_2$. A 125 mL Schlenk flask containing a magnetic stirring bar and fitted with an addition funnel was charged with [1,3-($SiMe_3$) $_2$ C $_3$ H $_3$] $_2$ Ni (0.302 g; 0.703 mmol) in 15 mL of benzene. Bromine (0.112 g; 0.701 mmol) and benzene (15 mL) were added to the addition funnel. The apparatus was cooled to 0 °C using an ice bath. The bromine solution was added dropwise with stirring over a period of 30 min, and the reaction was stirred at room temperature overnight. The mixture was then filtered, and benzene was removed from the filtrate under vacuum to yield a red-purple solid (0.21 g, 92%). Two isomers (2:1 ratio) were identified in NMR spectra. Major product isomer: 1H NMR (300 MHz, C_6D_6 , 298 K) δ 0.067 (s, 9H, $SiMe_3$); 0.13 (s, 9H, $SiMe_3$); 2.00 (d, $J = 10.0$ Hz, 1H, syn C-H); 5.58 (d, $J = 18.4$ Hz, 1H, anti

C–H); 6.34 (dd, $J = 18.4$ Hz, $J = 10.0$ Hz, 1H, $C_{(2)}$ –H). ^{13}C NMR (75 MHz, C_6D_6 , 298 K) δ –2.11 (SiMe₃); –0.98 (SiMe₃); 39.52 (syn C–H); 128.77 (anti C–H); 146.88 ($C_{(2)}$). Minor product isomer: ^1H NMR (300 MHz, C_6D_6 , 298 K) δ 0.023 (s, 9H, SiMe₃); 0.044 (s, 9H, SiMe₃); 2.96 (d, $J = 9$ Hz, 1H, syn C–H); 5.46 (d, $J = 18.4$ Hz, 1H, anti C–H); 6.10 (dd, $J = 18.4$ Hz, $J = 9$ Hz, 1H, $C_{(2)}$ –H). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ –3.23 (SiMe₃); –1.24 (SiMe₃); 30.48 (syn C–H); 131.52 (anti C–H); 145.70 ($C_{(2)}$).

Attempted Synthesis of [1,3-(SiMe₃)₂C₃H₃]NiBr from NiBr₂(dme) and K[1,3-(SiMe₃)₂C₃H₃]. A three-neck flask containing a magnetic stirring bar and fitted with a stopper, gas inlet, and addition funnel was charged with NiBr₂(dme) (1.236 g; 4.004 mmol) in 50 mL of THF. K[1,3-(SiMe₃)₂C₃H₃] (0.900 g; 4.00 mmol) was added in 10 mL of THF to the addition funnel. The apparatus was cooled to –78 °C using a dry ice/acetone bath. The THF solution of K[1,3-(SiMe₃)₂C₃H₃] was added dropwise with stirring over the course of 30 min. The solution was allowed to warm to room temperature overnight. THF was removed under vacuum, and the residue was extracted with the hexanes. The extract was filtered over a medium porosity glass frit, and hexanes were removed under vacuum to afford a nearly black solid. The solid was identified as [1,3-(SiMe₃)₂C₃H₃]₂Ni (1) from its NMR data and melting point.

Attempted Synthesis of [1,3-(SiMe₃)₂C₃H₃]NiBr from NiBr₂(dme) and Li[1,3-(SiMe₃)₂C₃H₃]. The preparation of [1,3-(SiMe₃)₂C₃H₃]NiBr was attempted as described above from Li[1,3-(SiMe₃)₂C₃H₃] and NiBr₂(dme) in toluene. Workup afforded a dark oil, which crystallized on standing for several days. The solid was identified as [1,3-(SiMe₃)₂C₃H₃]₂Ni (1) (73% yield) from its NMR data and melting point.

Synthesis of [1,3-(SiMe₃)₂C₃H₃]NiI (3). A 125 mL Erlenmeyer flask containing a magnetic stirring bar and fitted with a septum was charged with [1,3-(SiMe₃)₂C₃H₃]₂Ni (0.335 g; 0.780 mmol) in 20 mL of hexanes. Iodine (0.098 g; 0.78 mmol) in hexanes (20 mL) was cannulated into the stirred solution at room temperature. The color of the solution changed from red to dark red-purple with the addition of the iodine solution. After being stirred overnight, the hexanes were removed under vacuum to yield a red-purple solid (0.205 g) in 71% yield. Recrystallization from hexanes afforded dark red blocks. The compound decomposes at 130 °C, giving off purple vapor (presumably I₂). Anal. Calcd for C₉H₂₁INiSi₂: C, 29.13; H, 5.70. Found: C, 30.19; H, 5.60. Principle IR bands (KBr, cm^{–1}): 2956 (s), 2897 (m), 2390 (w), 1600 (w), 1470 (w), 1259 (s), 1250 (s), 1099 (s), 1087 (s), 1021 (s), 854 (s), 808 (s), 742 (w), 693 (m), 420 (m). Two isomers (1.6:1 ratio) were identified in NMR spectra. Isomer 1: ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.011 (s, 9H, SiMe₃); 0.060 (s, 9H, SiMe₃); 3.60 (d, $J = 10.0$ Hz, 1H, syn C–H); 5.57 (d, $J = 18.0$ Hz, 1H, anti C–H); 6.09 (dd, $J = 18.0$ Hz, $J = 10.0$ Hz, 1H, $C_{(2)}$ –H). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ –2.47 (SiMe₃); –1.33 (SiMe₃); 23.12 (syn C–H); 131.20 (anti C–H); 145.30 ($C_{(2)}$).

Isomer 2: ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 0.078 (s, 9H, SiMe₃); 0.13 (s, 9H, SiMe₃); 2.01 (d, $J = 10.0$ Hz, 1H, syn C–H); 5.59 (d, $J = 18.0$ Hz, 1H, anti C–H); 6.36 (dd, $J = 18.0$ Hz, $J = 10.0$ Hz, 1H, $C_{(2)}$ –H). ^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ –2.14 (SiMe₃); –1.02 (SiMe₃); δ 39.51 (syn C–H); 128.77 (anti C–H); 146.88 ($C_{(2)}$).

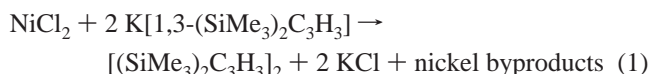
General Procedures for X-ray Crystallography. Data collection and structure solution were conducted at the X-ray Crystallographic Laboratory at the University of Minnesota. All calculations were performed using the current SHELXTL⁴⁰ suite of programs. Suitable crystals were located and attached to the tip of a glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. Data collection of a randomly oriented region of reciprocal space was carried out using Mo K α radiation (graphite

monochromator). Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration. Relevant crystal and collection data parameters can be found in Table 1. Additional details can be found in the Supporting Information.

Computational Details. Geometry optimization calculations were performed using the Gaussian 03W suite of programs.⁴¹ Both the B3LYP functional, which incorporates Becke's three-parameter exchange functional⁴² and the correlation functional of Lee, Yang, and Parr,^{43,44} and the B3PW91 functional, which employs the 1991 gradient-corrected correlation functional of Perdew and Wang, were used.⁴⁵ The DFT-optimized double- ζ polarized basis sets DGDZVP2 and DGDZVP (for Br, I) of Godbout⁴⁶ were used for geometry optimizations and energy calculations of the allyl complexes. The standard Pople basis sets 6-311G(d,p) and 6-311+G(2d,p) were used for other calculations.⁴⁷ Stationary points were characterized by the calculation of vibrational frequencies, and unless otherwise noted, all geometries were found to be minima ($N_{\text{imag}} = 0$).

Results and Discussion

Synthesis of a Trimethylsilylated Bis(allyl)nickel Complex. In a reaction modeled after that used for preparing the substituted chromium, iron, and cobalt complexes,^{24–26} an attempt was made to synthesize a trimethylsilylated bis(allyl)nickel complex from the reaction of NiCl₂ and the substituted potassium allyl K[1,3-(SiMe₃)₂C₃H₃] in THF. On workup of the reaction mixture, however, the dimerized ligand (1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene) was isolated instead (eq 1).



Similar attempts to synthesize the bis(allyl)nickel complex from the reaction of NiBr₂ or NiI₂ with K[1,3-(SiMe₃)₂C₃H₃] also resulted in the formation of the trimethylsilylated hexadiene. Coupling of allyl ligands on a nickel center is well-documented,⁵ and it may be that oxidative coupling of the allyl anion is occurring at the surface of these relatively insoluble nickel starting materials.

NMR studies indicate that the hexadiene is found in two forms with an average ratio of 1.7:1, although it ranges from 1.3:1 to 2.5:1. The patterns in the NMR spectra are consistent with two diastereomers of *C_i* (meso) and *C₂* (rac) symmetry (Figure 1). DFT calculations (B3PW91/6-311G(d,p)) indicate that the *C_i*

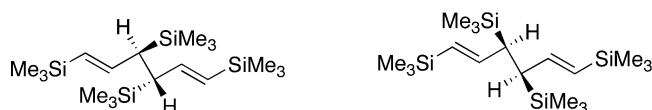
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Table 1. Crystal Data and Summary of X-ray Data Collection

compound	[1,3-(SiMe ₃) ₂ C ₃ H ₃] ₂ Ni (eclipsed) (1a)	[1,3-(SiMe ₃) ₂ C ₃ H ₃] ₂ Ni (staggered) (1b)	[1,3-(SiMe ₃) ₂ C ₃ H ₃ NiBr] ₂ (2a)	[1,3-(SiMe ₃) ₂ C ₃ H ₃ NiI] ₂ (3)
formula	C ₁₈ H ₄₂ NiSi ₄	C ₁₈ H ₄₂ NiSi ₄	C ₁₈ H ₄₂ Br ₂ Ni ₂ Si ₄	C ₁₈ H ₄₂ I ₂ Ni ₂ Si ₄
formula weight	429.59	429.59	648.12	742.10
color of cryst	orange	yellow	purple	dark red
cryst dims, mm ³	0.32 × 0.12 × 0.08	0.29 × 0.21 × 0.14	0.24 × 0.14 × 0.04	0.24 × 0.16 × 0.12
space group	C2/c	C2/c	C2/c	C222 ₁
cell dims				
<i>a</i> , Å	16.537(5)	10.969(1)	14.819(7)	16.448(4)
<i>b</i> , Å	12.438(4)	19.144(2)	23.37(1)	19.038(4)
<i>c</i> , Å	12.723(4)	12.491(2)	11.251(5)	19.669(4)
β, deg	90.1555(5)	103.151(2)	130.197(8)	90.000
volume, Å ³	2617.0(14)	2554.1(5)	2976(2)	6159(2)
<i>Z</i>	4	4	4	8
calcd density, Mg/m ³	1.090	1.117	1.447	1.601
abs coeff, mm ⁻¹	0.924	0.946	4.115	3.387
<i>F</i> (000)	936	936	1328	2944
radiation type	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
temperature, K	173(2)	173(2)	173(2)	173(2)
limits of data collection	1.60° ≤ θ ≤ 25.06°	2.13° ≤ θ ≤ 27.53°	1.74° ≤ θ ≤ 25.05°	1.94° ≤ θ ≤ 25.05°
index ranges	−19 ≤ <i>h</i> ≤ 19, −13 ≤ <i>k</i> ≤ 14, −15 ≤ <i>l</i> ≤ 15	−14 ≤ <i>h</i> ≤ 14, −24 ≤ <i>k</i> ≤ 24, −16 ≤ <i>l</i> ≤ 16	−17 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 27, 0 ≤ <i>l</i> ≤ 13	−19 ≤ <i>h</i> ≤ 19, −15 ≤ <i>k</i> ≤ 22, −22 ≤ <i>l</i> ≤ 23
total reflns collected	8667	11,447	6593	15,491
unique reflns	2315 (<i>R</i> _{int} = 0.0311)	2939 (<i>R</i> _{int} = 0.0519)	2604 (<i>R</i> _{int} = 0.0727)	5389 (<i>R</i> _{int} = 0.0597)
transmission factors	1.000–0.787	0.8789–0.7709	0.8527–0.4384	1.000–0.600
data/restraints/param	2315/10/136	2939/1/123	2604/0/131	5389/0/248
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0285, <i>R</i> _w = 0.0727	<i>R</i> = 0.0377, <i>R</i> _w = 0.0924	<i>R</i> = 0.0520, <i>R</i> _w = 0.1132	<i>R</i> = 0.0485, <i>R</i> _w = 0.1222
<i>R</i> indices (all data)	<i>R</i> = 0.0307, <i>R</i> _w = 0.0738	<i>R</i> = 0.0480, <i>R</i> _w = 0.0971	<i>R</i> = 0.1025, <i>R</i> _w = 0.1286	<i>R</i> = 0.0594, <i>R</i> _w = 0.1274
goodness of fit on <i>F</i> ²	1.033	1.008	1.013	1.027
max/min peak in final diff map, e-/Å ³	0.463/−0.263	0.710/−0.269	0.769/−0.486	2.046/−0.447
absolute structure parameter				0.16(3)

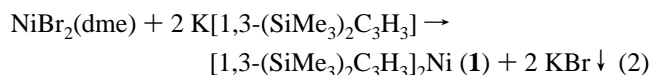
dimer is more thermodynamically stable by 3.7 kcal mol^{−1} (Δ*H*°; 5.3 kcal mol^{−1} for Δ*G*°). Steric congestion from the

**Figure 1.** Proposed diastereomeric forms of the trimethylsilylated hexadiene, with *C_i* (meso) (left) and *C₂* (rac) (right) symmetry.

adjacent SiMe₃ groups (closest Me···Me' contact = 3.89 Å) possibly raises the energy of the *C₂* form. As the diastereomer ratio reflects kinetic factors during coupling rather than thermodynamic effects (the two forms are not in equilibrium), it cannot automatically be assumed that the more abundant form is the one with *C_i* symmetry. Attempts using NOESY experiments to assign the resonances to their diastereomeric forms were not conclusive. Although the compound is crystalline, a single crystal X-ray structure was severely disordered,⁴⁸ multiple forms appear to be incorporated in the unit cell.

In an attempt to avoid the coupling reactions, the more soluble nickel halide NiBr₂(dme) was used as a reagent. Reaction of 2 equiv of K[1,3-(SiMe₃)₂C₃H₃] with NiBr₂(dme) in THF at −78

°C affords the bis(allyl)nickel complex (**1**) in 72% yield (eq 2):



The complex is initially isolated as an oil that crystallizes to an orange solid after several days at room temperature. It is soluble in a wide range of solvents, from THF to hexanes, and readily sublimates under vacuum. It melts at 64 °C and decomposes only above 100 °C. In the solid state, finely divided, sublimed **1** will survive for several hours in the air before noticeable decomposition begins, but larger, oily crystals can last several days in air. A hexanes solution of **1** can be layered on top of water, where no change is observed for several hours. The increase in oxidative and thermal stability compared to the pyrophoric, thermally sensitive (dec above 20 °C) parent compound (C₃H₅)₂Ni is striking.¹ The electrochemistry of **1** was briefly investigated with voltammetry and electrolysis in a nitrogen-filled drybox. Irreversible, one-electron oxidation was observed in both THF and dichloromethane; there was no evidence for electroactive oxidation products.⁴⁹

Like the parent complex (C₃H₅)₂Ni, **1** is diamagnetic, and both ¹H and ¹³C NMR spectra of the substituted compound display two forms in solution, identified as eclipsed (cis) (**1a**) and staggered (trans) (**1b**). Each form exhibits two resonances for their trimethylsilyl groups, which is consistent with the syn,

(48) Crystals of C₁₈H₄₂Si₄ are monoclinic, space group C2, with *a* = 18.400(10) Å, *b* = 6.521(4) Å, *c* = 13.294(9) Å, β = 125.879(11)°, *V* = 1292.4(14) Å³, *Z* = 2, and ρ_{calc} = 0.953 g cm^{−3} for fw = 370.88. Refinement of 1516 reflections (900 with *I* > 2.0σ(*I*)) collected at the University of Minnesota at 173(2) K led to residuals of *R*(*F*²) = 0.116 and *R*_w(*F*²) = 0.260 (for *I* > 2.0σ(*I*)).

anti arrangement of SiMe₃ groups observed in their solid-state structures (below). This SiMe₃ arrangement is different from the syn, syn arrangement found for the potassium salt.⁵⁰

The relative amounts of the eclipsed and staggered conformers change with temperature for both (C₃H₅)₂Ni and **1**, although not in the same way. For (C₃H₅)₂Ni, the staggered form is always predominant, and a 1:7.8 ratio of eclipsed to staggered isomers is observed at −75 °C (¹H NMR). At higher temperatures, more of the eclipsed form is present, and once room temperature is reached, for example, the eclipsed-to-staggered ratio is 1:3.¹⁴ Higher temperatures produce even more of the eclipsed form, but the two conformers remain interconvertible, and the eclipsed/staggered ratio reverts to 1:3 on cooling to room temperature.⁵¹

In contrast, the reaction represented in eq 2 generates a mixture of **1a** and **1b** in varying proportions, but the eclipsed **1a** is in excess (up to a **1a:1b** ratio of approximately 9:1) when the reaction is conducted at −78 °C. Excess **1a** is only observed when the reaction is performed at low temperature; if the reaction to form **1** is conducted at room temperature, **1b** is found to be predominant, with a **1a:1b** ratio of 2:3. A sample of **1** in solution will display essentially the same **1a:1b** ratio for weeks if room temperature is maintained, but the proportion of **1b** in the sample irreversibly increases if the temperature is raised. In a variable temperature ¹H NMR experiment, conversion of the eclipsed-to-staggered form was first noticeable at 358 K, and essentially complete conversion of **1a** to **1b** occurred by the time the sample was heated to 380 K (approximately 50 min total time). Conversion back to **1a** did not occur on cooling.

Reactions of 1 with Phosphines. The reactivity of **1** was explored with several phosphines and halogens. As a point of reference, tertiary phosphines PR₃ (R = Me, Et, Ph, C₆H₁₁) form adducts with (C₃H₅)₂Ni at low temperature, but they are unstable at room temperature. With PMe₃, an air- and moisture-sensitive 1:1 adduct has been isolated and crystallized at −78 °C.⁵ The X-ray crystal structure reveals eclipsed allyl ligands with a Ni–P distance of 2.218(1) Å. In solution, coupling is observed between the phosphorus and hydrogen atoms of the allyl ligands, but the coupling is lost above −40 °C; this has been taken as an indication that PMe₃ dissociation is occurring.

Reaction of **1** (a mixture of **1a** and **1b**) with PMe₃ in hexanes at room temperature yields two products: the staggered bis(allyl)nickel complex **1b** and an organophosphorus compound characterized with multinuclear NMR spectroscopy. Regardless of the starting **1a:1b** ratio, almost no **1a** (<5%) is identifiable in NMR spectra of the products, and X-ray crystallography was used to confirm that several crystals obtained from the concentrated reaction mixtures had unit cells matching only **1b**. The organophosphorus compound was not free PMe₃, as a broadened singlet (δ 1.15) in the ¹H NMR spectrum and a singlet (δ −21.6) in the ³¹P NMR spectrum do not match that of PMe₃ in C₆D₆

(for it, we have measured ¹H = 0.814 (d, *J* = 1.6 Hz); ³¹P NMR = −62.4 ppm). This was substantiated by the ¹³C{¹H} NMR spectrum, which contains an apparent quintet at δ 25.1 (*J* ≈ 10.1 Hz; cf. δ 16.43 (*J* = 10.7 Hz) for PMe₃).

Two-dimensional ¹H–¹³C HSQC^{52,53} coupled and phosphorus-decoupled data were used to confirm that carbon–phosphorus splitting was responsible for the multiplet in the ¹³C spectrum. The HSQC experiment {¹H, ³¹P} demonstrates that the apparent quintet (arising from virtual coupling) collapses to a singlet upon ³¹P decoupling (see Supporting Information for spectra). Such an A₄X spin system restricts the possible P₄-containing products, the most reasonable of which is the cyclic tetramethyltetraphosphane, (MeP)₄. The singlets in the ¹H and ³¹P spectra reflect the likely *D*_{2d} symmetry of the compound, as exists in structurally characterized analogues such as (PhP)₄⁵⁴ and [(*i*-Pr)P]₄.^{55,56} Attempts to separate the product from the accompanying **1b** have not been successful.

Tetramethyltetraphosphane has been described as a product in equilibrium with molten (MeP)₅, which served as the solvent.⁵⁷ The sole characterization for (MeP)₄ was a singlet in the ³¹P NMR spectrum at −67.7 ppm, a value recorded at 160 °C; no ¹H or ¹³C NMR data were reported. Although the ³¹P chemical shift is reasonable (a variety of cyclotetraphosphanes have ³¹P NMR chemical shifts in the range from −50 to −80 ppm^{58,59}), it is not definitive for (RP)₄ rings, as evidenced by the considerably more deshielded values displayed by [(C₅Me₅)P]₄ (−39.0 ppm)⁶⁰ and {[(SiMe₃)₂CH]P}₄ (−14.6 ppm).⁶¹

The energetics of the transformation of PMe₃ to (MeP)₄ are reasonable,⁵⁶ but in order for the latter to be the product of the reaction of **1** with PMe₃, multiple steps involving demethylation and P–P formation must be involved. Why such a transformation should occur with **1** but has not been reported with the unsubstituted (C₃H₅)₂Ni may be related to the relatively unencumbered coordination environment of the latter. In the PMe₃ adduct of (C₃H₅)₂Ni, the allyl ligation to the metal is unchanged (*η*³), and the reaction (*η*³-C₃H₅)₂Ni + PMe₃ → (*η*³-C₃H₅)₂Ni–PMe₃ is predicted to be to be exothermic by −4.4 kcal mol^{−1} (*ΔH*^o) (+6.0 kcal mol^{−1} for *ΔG*^o) (B3LYP/DGDZVP2 level).

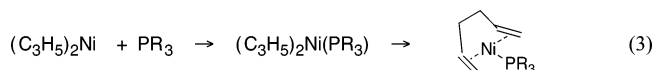
Preliminary computational studies suggest that the reaction **1a** + PMe₃ → (*η*³-allyl')₂Ni–PMe₃ would not be favorable (*ΔH*^o = +10.3 kcal mol^{−1}; *ΔG*^o = +24.1 kcal mol^{−1}), and the resulting complex is only a transition structure (*N*_{imag} = 1). For steric reasons, slippage of an allyl ligand from *η*³ to *η*¹ would probably be required for phosphine binding. Subsequent addi-

- (49) In THF containing 0.1 M [NBu₄][PF₆] and dichloromethane containing 0.05 M [NBu₄][B(C₆F₅)₄], a single chemically irreversible process was observed (0.81 V in THF, 0.92 V in dichloromethane, potentials vs ferrocene/ferrocenium) in cyclic voltammetry scans at scan rates of 0.1 V/s to 0.5 V/s (Pt or glassy carbon electrodes). Exhaustive bulk electrolysis in dichloromethane was consistent with one-electron coulometry and resulted in a very dark insoluble product that was not identified.
- (50) Simpson, C. K.; White, R. E.; Carlson, C. N.; Wroblewski, D. A.; Kuehl, C. J.; Croce, T. A.; Steele, I. M.; Scott, B. L.; Young, V. G., Jr.; Hanusa, T. P.; Sattelberger, A. P.; John, K. D. submitted for publication.
- (51) Curiously, in the substituted (2-MeC₃H₄)₂Ni, the eclipsed form predominates 2:1 at low (−75 °C) temperatures, but the staggered form is preferred over the eclipsed by 2.3:1 at room temperature (ref 13).

- (52) The HSQC (heteronuclear single quantum correlation) experiment correlates the chemical shift of a nucleus (e.g., ¹H) with the chemical shift of a directly bonded nucleus (e.g., ¹³C).
- (53) Davis, A. L.; Keeler, J.; Laue, E. D.; Moskau, D. *J. Magn. Reson.* **1992**, *98*, 207–216.
- (54) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365–369.
- (55) Steinicke, A.; Thiele, K. H.; Haaland, A.; Sokolov, V. I.; Volden, H. V. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1925–1930.
- (56) The reaction 4 PMe₃ → (MeP)₄ + 4 CH₃CH₃ is exothermic by −2.7 kcal mol^{−1} (*ΔH*^o; −10.3 kcal mol^{−1} in *ΔG*^o) (B3LYP/DGDZVP2 level). With the larger 6-311+G(2d,p) basis set, *ΔH*^o = −7.9 kcal mol^{−1} and *ΔG*^o = −16.1 kcal mol^{−1}. For both functional/basis set combinations, (MeP)₄ was optimized under *D*_{2d} symmetry, and it was a minimum on the potential energy surface (*N*_{imag} = 0).
- (57) Baudler, M.; Hahn, J.; Clef, E. Z. *Naturforsch., B: Chem. Sci.* **1984**, *39B*, 438–444.
- (58) Albrand, J. P.; Cogne, A.; Robert, J. B. *J. Am. Chem. Soc.* **1978**, *100*, 2600–2604.
- (59) Smith, L. R.; Mills, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3852–3857.
- (60) Jutzi, P.; Meyer, U. *J. Organomet. Chem.* **1987**, *333*, C18–C20.
- (61) Schmitz, M.; Leininger, S.; Bergstrasser, U.; Regitz, M. *Heteroatom Chem.* **1998**, *9*, 453–460.

tions of PMe_3 might then occur as the phosphine begins to demethylate, and P–P bond formation ensues. The final release of the cyclotetraphosphane would be accompanied by the rearrangement of the allyl ligands to the thermodynamically preferred staggered form.

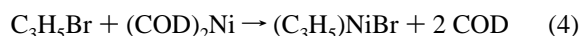
The bulkier phosphines PPh_3 and $\text{P}(\text{C}_6\text{H}_{11})_3$ form adducts with $(\text{C}_3\text{H}_5)_2\text{Ni}$ at low temperature, but coupling of the allyl ligands occurs on warming (at 0°C with PPh_3 ; at -20°C with $\text{P}(\text{C}_6\text{H}_{11})_3$) (eq 3):⁵



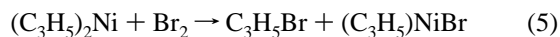
In contrast, after being stirred with triphenylphosphine in hexanes overnight, **1** is recovered with no change in the **1a:1b** ratio, and NMR data (^1H , ^{13}C , ^{31}P) indicate that free triphenylphosphine is in solution. The lack of reactivity likely indicates that the steric bulk of the trimethylsilyl groups prevents the phosphine from gaining access to the metal center. In this regard, **1** is like $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{M}$ ($\text{M} = \text{Cr}, \text{Fe}$), neither of which displays reactivity with PPh_3 .^{24,25}

Synthesis of Trimethylsilyl-Substituted (Allyl)nickel Halides. To gain more insight into the similarities and differences between complexes of the parent allyl C_3H_5^- and the substituted $\text{C}_3(\text{SiMe}_3)_2\text{H}_3^-$, mono(allyl)nickel bromide and iodide derivatives were synthesized and characterized.

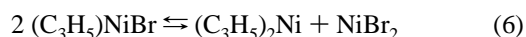
(Allyl)nickel bromides are red to red-purple, air- and moisture-sensitive compounds that can be prepared in several ways. One is by an oxidative addition reaction between an allyl bromide and a source of $\text{Ni}(0)$, such as $\text{Ni}(\text{CO})_4$ or bis(cyclooctadiene)-nickel (e.g., eq 4).⁶²



The reaction between bis(allyl)nickel and elemental bromine in an aromatic solvent also generates (allyl)nickel bromide (eq 5).¹¹

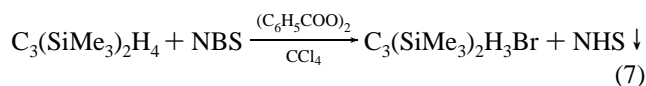


The allyl halide complex is a dimer in aromatic hydrocarbons (i.e., $[(\text{C}_3\text{H}_5)\text{NiBr}]_2$), but a Schlenk equilibrium is established if the compound is dissolved in a coordinating donor solvent such as DMF or HMPA (i.e., eq 6).⁹



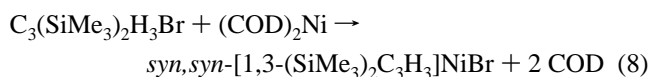
In aromatic solvents, (allyl)nickel bromide does not react with organic halides, but it does react in polar solvents by a radical chain mechanism that is initiated by heat, light, or reducing agents (e.g., sodium naphthalenide).^{7,9}

The oxidative addition method of (allyl)nickel halide preparation was investigated with trimethylsilylated ligands by preparing the previously unknown 3-bromo-1,3-(trimethylsilyl)propene (eq 7).⁶³



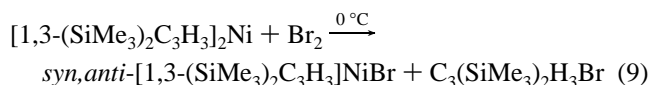
The reaction is refluxed under nitrogen for 3 h, after which the solution is filtered, the solvent is removed under vacuum, and the product is vacuum distilled as a colorless liquid in 70% yield.

The bis(trimethylsilyl)allyl bromide reacts with $(\text{COD})_2\text{Ni}$ in toluene to afford the substituted (allyl)nickel bromide (**2a**) (eq 8).



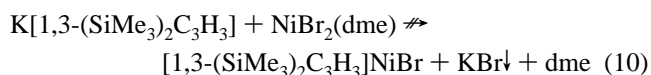
Compound **2a** is an air- and moisture-sensitive red-purple solid. Its ^1H NMR spectrum indicates that the trimethylsilyl groups are equivalent, and hence in a syn, syn arrangement. This is also the arrangement found in the solid state (see below).

The direct reaction of **1** with elemental bromine in benzene at 0°C can be used to form **2b** (eq 9).

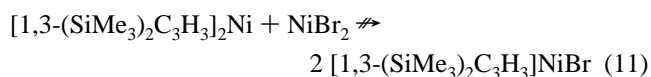


The ^1H NMR spectrum of **2b** indicates the presence of two diastereomers with inequivalent trimethylsilyl groups; thus the SiMe_3 arrangement is syn, anti for both conformers. Interestingly, the mono(allyl) derivative has preserved the syn, anti configuration of the starting material **1**.

An attempted alternative synthetic route for the preparation of the trimethylsilyl-substituted (allyl)nickel bromide involved the 1:1 reaction of $\text{K}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ with $\text{NiBr}_2(\text{dme})$ in THF at low temperature (eq 10).

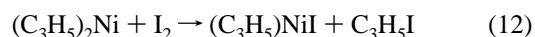


However, the only organometallic product isolated from the reaction was **1**, which was also the case when the reactions were attempted in toluene with one equivalent of $\text{Li}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$. After its formation, **1** evidently does not react further with the nickel bromide that is still present in solution; i.e., as in eq 11.



As is obvious from eq 9, no reaction is observed between **2** and $\text{C}_3(\text{SiMe}_3)_2\text{H}_3\text{Br}$ in an aromatic solvent. This is also true when **2** and $\text{C}_3(\text{SiMe}_3)_2\text{H}_3\text{Br}$ were mixed in the donor solvent THF. In addition, **2** is stable to rearrangement in THF; i.e., there is no NMR evidence for the formation of $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{-Ni}$.

Bis(allyl)nickel reacts with I_2 in diethyl ether to yield the synthetically useful $(\text{C}_3\text{H}_5)\text{NiI}$ (eq 12).¹¹



In a parallel fashion, iodine reacts smoothly with **1** in hexanes

(62) Stransky, N.; Herzsuh, R.; Gehrke, J. P.; Taube, R. *J. Organomet. Chem.* **1984**, 270, 353–356.

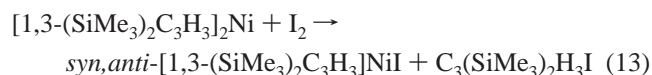
(63) Greenwood, F. L.; Kellert, M. D. *Org. Synth. Coll. Vol.* **1963**, 4, 108–110.

Table 2. Observed and Calculated Structural Parameters for Bis(π -allyl)nickel Complexes^a

	(C ₃ H ₅) ₂ Ni			[1,3-(SiH ₃) ₂ C ₃ H ₃] ₂ Ni		[1,3-(SiMe ₃) ₂ C ₃ H ₃] ₂ Ni			
	staggered	eclipsed	experimental (staggered)	staggered	eclipsed	staggered	experimental (1b)	eclipsed	experimental (1a)
Ni–C _{mid} , Å	1.986	1.985	1.980(1)	1.994	1.990	1.994	1.972(2)	1.985	1.944(3)
Ni–C _{syn} , ^b Å	2.028	2.029	2.029 (av)	2.076	2.038	2.105	2.070(2)	2.069	2.037(3)
Ni–C _{anti} , Å	2.028	2.029	2.029 (av)	2.028	2.054	2.026	2.016(2)	2.050	2.029(3)
C _{syn} –C _{mid} , Å	1.417	1.416	1.416 (av)	1.419	1.424	1.416	1.404(3)	1.420	1.416(4)
C _{mid} –C _{anti} , Å	1.417	1.416	1.416 (av)	1.424	1.420	1.425	1.414(3)	1.423	1.418(4)
C _{syn} –Ni–C _{anti} , deg	74.8	74.7	74.6(1)	74.7	75.0	74.5	74.86(8)	74.6	75.6(1)
C _{syn} –C _{mid} –C _{anti} , deg	120.7	120.8	120.5(1)	122.4	122.2	123.3	123.7(2)	122.8	123.1(2)
angle between allyl planes, deg	0.0	59.8	0.0	4.4	56.7	2.9	4.6	47.5	49.1
displacement of anti-substituent, Å	0.57	0.57	0.54 (av)	0.96	1.01	1.07	0.97	1.14	1.11
displacement of syn-substituent, Å	0.18	0.18	0.17 (av)	0.20	0.32	0.06	0.13	0.21	0.10 Å
relative energy (ΔH°)	0.0	+1.5		0.0	+0.6	0.0		+1.5	

^a B3LYP/DGDZVP2. Relative energy is in ΔH° , kcal mol^{−1}. ^b C_{syn} is the carbon adjacent to the syn-substituent (either SiH₃ or SiMe₃).

to yield a red-purple solid that can be recrystallized from hexanes as dark red blocks (eq 13).



The complex was characterized as [1,3-(SiMe₃)₂C₃H₃]₂NiI (**3**) with elemental analysis, NMR spectral data, and X-ray crystallography. The NMR data are complex, as not only inequivalent trimethylsilyl groups are evident, indicative of a syn, anti arrangement of trimethylsilyl groups, but also two diastereomers are present. These correspond to the staggered and eclipsed conformers found in the solid state (see below). In THF, **3** is stable to rearrangement in donor solvents, and as with **2**, no reaction is observed between **3** and C₃(SiMe₃)₂H₃Br in THF.

Crystallographic Results

Solid-State Structure of 1a. The structure determination of **1a** was obtained from orange crystals grown in hexanes solution over several days. The Ni atom lies on a crystallographic 2-fold axis, so that only half of the molecule is unique. One of the SiMe₃ groups is modeled as disordered over two positions (66:34). An ORTEP view of the complex is displayed as Figure 2. Selected bond distances and angles for the structure are listed in Table 2.

The complex has an eclipsed (cis) (η^3 -allyl')₂M geometry, with Ni–C bonds varying from 1.944(3) to 2.037(3) Å. The SiMe₃ groups in **1a** are arranged in a syn, anti configuration; the syn Si atoms, Si(2) and Si(2A), are near to the C₃ plane (their 0.10 Å displacement is reflected in the nearly linear C1–C2–C3–Si2 torsion angle of 176.5(7)°, whereas the anti Si atoms, Si(1) and Si(1A), are considerably shifted out of the allyl plane (by 1.11 Å, with a Si1–C1–C2–C3 angle of 47.8(4)°). Complex **1a** is the first structurally authenticated (η^3 -allyl')₂Ni complex with an eclipsed conformation and only the second example reported for any metal. Like the eclipsed [1,3-(SiMe₃)₂C₃H₃]₂Fe,²⁵ the C₃ planes are sharply canted to each other (49.1°; cf. 52.7° in the iron complex). As with other first-row trimethylsilyl substituted bis(allyl)metal complexes ([1,3-(SiMe₃)_nC₃H_{5–n}]₂Cr (*n* = 1–3),²⁴ [1,3-(SiMe₃)₂C₃H₃]₂Fe²⁵), there is no evidence for agostic bonding involving H atoms of the ligand.

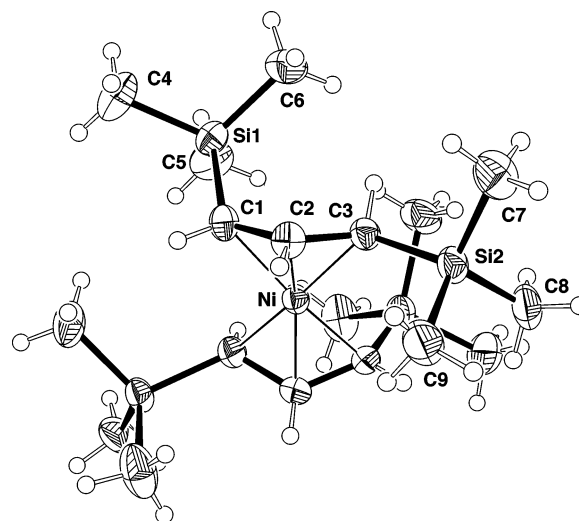


Figure 2. ORTEP of **1a**, giving the numbering scheme used in the text. Displacement ellipsoids are shown at the 50% level.

Solid-State Structure of 1b. Two polymorphs of **1b** with different spacegroups (*P*₂/*1*/*c* and *C*₂/*c*) were identified in separate crystallographic studies at 173 K. The unit cell volume is 3% larger for the *P*₂/*1*/*c* polymorph, and the symmetry of the molecule is approximately *C*₂. In the *C*₂/*c* polymorph, exact crystallographic *C*₂ symmetry is imposed on the molecule. It is not certain what conditions produce the different forms, as the crystals of both polymorphs were grown from hexanes at room temperature; it is possible that the rate of growth was slower in one case. The molecules are closely similar, and only the more symmetric structure is discussed here. Details for the *P*₂/*1*/*c* polymorph can be found in the Supporting Information. An ORTEP view of the complex is displayed as Figure 3. Selected bond distances and angles for the structure are listed in Table 2.

The complex has a classic staggered (trans) (η^3 -allyl')₂M geometry, and as with **1a**, the SiMe₃ groups are arranged in a syn, anti configuration. The syn Si atoms, Si1 and Si1', lie close to the C₃ plane (0.13 Å displacement, with a C1–C2–C3–Si1 torsion angle of 175.2(1)°, whereas the anti Si atoms, Si2 and Si2', are substantially displaced out of the allyl plane (by 0.97 Å; the Si2–C1–C2–C3 torsion angle is 42.5(3)°). As is typical with π -bound allyls, the shortest Ni–C distance (1.972(2) Å)

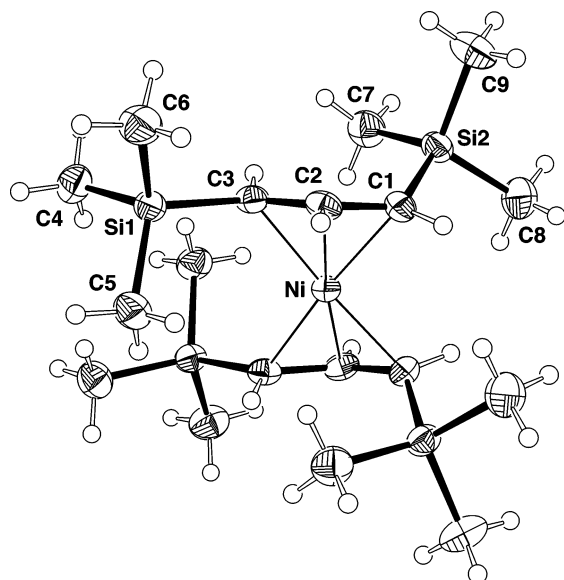


Figure 3. ORTEP drawing of **1b**, giving the numbering scheme used in the text. Displacement ellipsoids are shown at the 50% level.

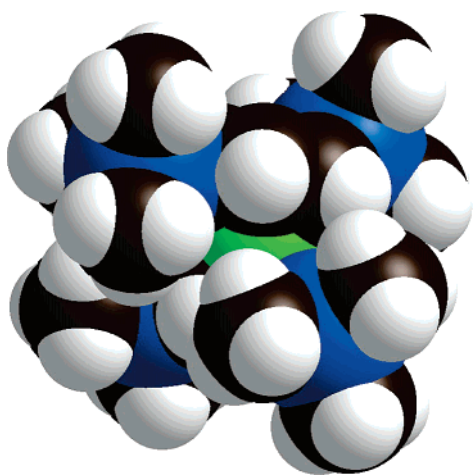


Figure 4. Space-filling drawing of **1b**; the nickel is the green atom in the center.

is to the central carbon of the allyl ligand. The carbon bearing the anti SiMe₃ group (C1) is slightly closer to the nickel (2.016(2) Å) than that with the syn SiMe₃ group (C3, at 2.070(2) Å). This lateral displacement ($\Delta = 0.054$ Å) is somewhat more than that displayed by **1a**, for which $\Delta = 0.008$ Å. A space-filling drawing of **1b** suggests the extent to which the metal center is encapsulated by the bulky allyl ligands (Figure 4).

The Ni–C bond lengths in **1b** are similar to the Ni–C bond lengths in the parent (C₃H₅)₂Ni (1.980(1) to 2.031(1) Å),¹⁹ as are the interplanar C₃ angles (4.6° in **1b**, 0.0° in (C₃H₅)₂Ni). The positions of the SiMe₃ groups on the ligands mimic the out-of-plane distortions present in the hydrogen atoms in (C₃H₅)₂Ni (e.g., the displacements of the anti hydrogens away from the nickel).

Solid-State Structure of 2a. The complex crystallizes from hexanes as a bromide-bridged dimer. The molecule lies on a crystallographic 2-fold axis; thus, only one-half of the molecule is unique. Whereas Br2 lies on the 2-fold axis, Br1 lies slightly off the axis and was modeled as disordered over it (50:50). Selected bond distances and angles for the structure are listed

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2a**

atoms	distance, Å	atoms	angle, deg
Ni–Br1	2.362(10)	Br1–Ni1–Br2	89.6(2)
Ni–Br2	2.365(1)	Ni1–Br1–Ni1	90.35(8)
Ni–C1	2.062(7)	Ni1–Br2–Ni1	90.32(6)
Ni–C2	1.978(6)	C1–C2–C3	120.0(7)
Ni–C3	2.039(6)		
C1–C2	1.385(9)		
C2–C3	1.457(9)		

in Table 3. An ORTEP view of the complex is displayed as Figure 5.

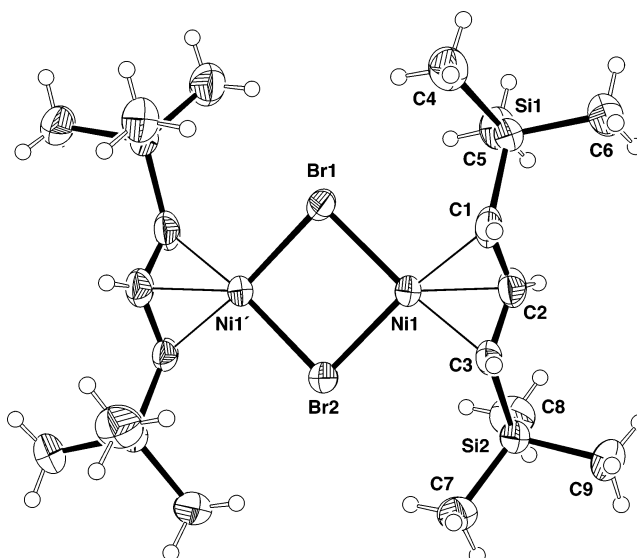


Figure 5. ORTEP drawing of **2a**, giving the numbering scheme used in the text. Displacement ellipsoids are shown at the 50% level.

The Ni–C bond lengths range from 1.978(6) to 2.062(7) Å, which are within 0.08 Å of those in **1b**. Although not required to be so by symmetry, the Ni–Br1 and Ni–Br2 bond lengths are identical within error (2.362(10) and 2.365(1) Å). The Ni···Ni' separation is 3.35 Å, too long to represent any significant interaction (cf. the 2.49 Å distance in nickel metal⁶⁴). The angle between the C₃ plane and (NiBr)₂ plane is 117.7°. The dimeric structure of **2a** joins a family of bridged π -allyl nickel species (Table 4), but the most directly comparable structure is the dimeric (2-carboxyethylallyl)nickel bromide, {[2-(CO₂C₂H₅)-C₃H₄]NiBr}₂, which has Ni–C bond lengths ranging from 1.90(2) to 2.06(2) Å and Ni–Br bonds of 2.334(5) and 2.378(5) Å.⁶⁵ Despite the differences in the substitution on the allyl ligands, these metrics are quite similar to those in **2a**.

Unlike the arrangement found in **1a** or **1b**, the SiMe₃ groups in **2a** are in a syn, syn configuration; the Si atoms Si1 and Si2 lie close to the C₃ plane (0.13 and 0.10 Å, respectively; the Si1–C1–C2–C3 torsion angle is –175.1(5)°; the C1–C2–C3–Si2 torsion angle is 176.5(5)°. The syn, syn configuration has been observed before in other bridged allyl dimers of nickel, such as {(1,3-Me₂C₃H₃)Ni(μ -Me)}₂⁶⁶ and {[1-Me-3-(OSiMe₃)-C₃H₃]NiCl}₂⁶⁷ (Table 4). The arrangement in **2a** is the first time

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Table 4. Selected Structural Data for Bridged (π -Allyl)Nickel Dimers (Distances in Å)^a

compound	Ni–X, X'	Ni–Ni'	Ni–C (range)	allyl substituents	ref
{[1,3-(SiMe ₃) ₂ C ₃ H ₃]NiBr} ₂ (2)	2.362, 2.365	3.35	1.978–2.062	syn, syn	this work
{[1,3-(SiMe ₃) ₂ C ₃ H ₃]NiI} ₂ (3a , 3b)	2.513, 2.539; 2.521, 2.528	3.49	1.973–2.049; 1.979–2.041	syn, anti	this work
{[2-(CO ₂ C ₂ H ₅)C ₃ H ₄]NiBr} ₂	2.334, 2.378	3.24	1.90–2.06	N/A	65
{[2-PhC ₃ H ₄]Ni(O ₂ CCF ₃) ₂ }	1.924, 1.924	3.10	1.971–1.980	N/A	75
{[2-(SiMe ₃)C ₃ H ₄]Ni(O ₂ CCF ₃) ₂ }	1.918, 1.929	2.98	1.927–1.991	N/A	75
{[1-PhC ₃ H ₄]Ni(O ₂ CCF ₃) ₂ }	1.876, 1.973	2.93	1.890–2.052	syn	75
{[1-Me-3-(OSiMe ₃)C ₃ H ₃]NiCl} ₂	2.234, 2.263	3.04	1.957–2.043	syn, syn	67
{[C ₃ H ₅]Ni(OSi(O- <i>t</i> -Bu) ₃) ₂ }	1.917, 2.049	2.67	1.915–1.920	N/A	76
{[2-MeC ₃ H ₄]Ni(O ₂ CCF ₃) ₂ }	1.927, 1.934	3.04	1.973–1.987	N/A	77
{[1,3-Me ₂ C ₃ H ₃]Ni(CH ₃) ₂ }	2.044, 2.067	2.37	1.953–2.039	syn, syn	66
{[2-MeC ₃ H ₄]Ni(O ₂ CC ₆ H ₄ (- <i>o</i> -NPh ₂)) ₂ }	1.905–1.920	2.95	1.955–1.991	N/A	78

^a The average value is listed.**Table 5.** Selected Bond Distances (Å) and Angles (deg) for **3a** (top table) and **3b**

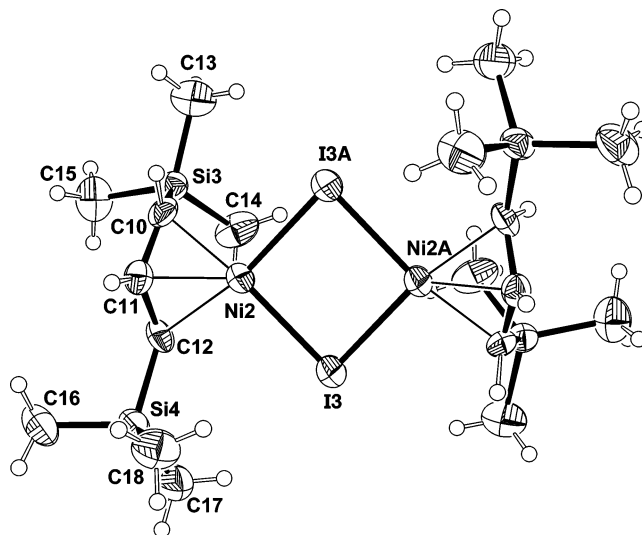
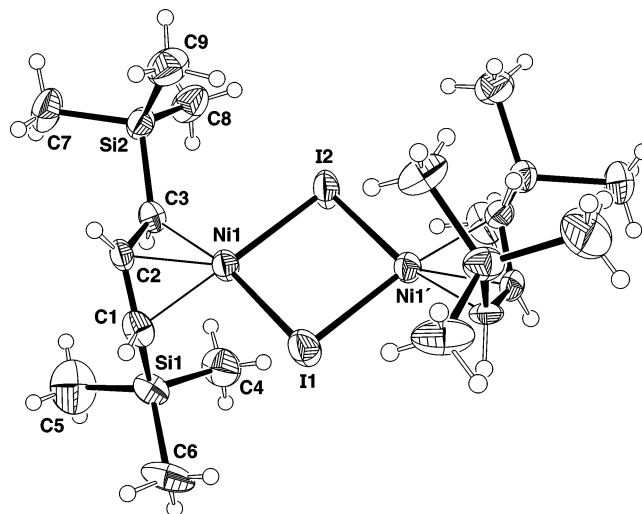
atoms	distance	atoms	angle
Ni2–I3	2.513(1)	I3–Ni2–I3'	92.61(4)
Ni2–I3'	2.539(1)	Ni2–I1–Ni2'	87.35(4)
Ni2–C10	2.020(8)	C10–C11–C12	120.3(7)
Ni2–C11	1.973(8)		
Ni2–C12	2.049(7)		
C10–C11	1.422(11)		
C11–C12	1.402(11)		

atoms	distance	atoms	angle
Ni1–I1	2.528(1)	I1–Ni1–I2	92.43(4)
Ni1–I2	2.521(1)	Ni1–I1–Ni1'	87.42(5)
Ni1–C1	2.041(7)	Ni1–I2–Ni1'	87.73(5)
Ni1–C2	1.979(7)	C1–C2–C3	119.1(7)
Ni1–C3	2.038(8)		
C1–C2	1.436(12)		
C2–C3	1.404(11)		

it has been observed in a neutral transition metal complex containing trimethylsilylated allyl ligands, however.

Solid-State Structure of 3. Like **2a**, complex **3** crystallizes as a halide-bridged dimer with crystallographically imposed symmetry. In the case of **3**, however, there are two independent half-molecules in the asymmetric unit. The molecule with atom Ni2 (**3a**) is fully generated by a 2-fold axis parallel to the *a*-axis and perpendicular to the diamond core; the molecule with atom Ni1 (**3b**) is completely generated by a 2-fold axis parallel to the *b*-axis that contains both bridging iodide atoms. Both structures are similar except for the orientation of the ligands; structure **3a** has an eclipsed orientation, while structure **3b** has a staggered orientation. Both are discussed together here. Selected bond distances and angles for the structures are listed in Table 5. An ORTEP view of **3a** is displayed as Figure 6; **3b** is shown in Figure 7.

The Ni–C bond lengths in **3a** range from 1.973(8) to 2.049(7) Å (1.979(9) to 2.041(7) Å in **3b**), which, like those in **2**, are similar to those in the bis(allyl) complexes **1a** and **1b**. The Ni–I bond lengths are only slightly different in **3a** (2.513(1) and 2.539(1) Å) and are nearly equal in **3b** (2.521(1) and 2.528(1) Å). The Ni···Ni' separation of 3.49 Å (the same in **3a** and **3b**) precludes any metal–metal interaction. This compound represents the first structurally authenticated LNi(μ -I)₂NiL dimer, and there are few other iodide-bridged nickel centers available for comparison. The nickel-iodide bond distances in **3a/3b** are somewhat shorter than the 2.62 Å (av) distance found in the carbamoyl cluster (μ -OCNEt₂)₄Ni₂(μ -I)₂Ni(NHET₂),⁶⁸ for example, but weak metal–metal bonding exists between the

**Figure 6.** ORTEP drawing of **3a**, giving the numbering scheme used in the text. Displacement ellipsoids are shown at the 50% level.**Figure 7.** ORTEP drawing of **3b**, giving the numbering scheme used in the text. Displacement ellipsoids are shown at the 50% level.

nickel centers in the latter (Ni···Ni' separation of 2.67 Å), which complicates a direct comparison.

In contrast to the arrangement found in **2a**, the SiMe₃ groups in **3a/3b** are in syn, anti relationships. As is typical for such

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configurations, the syn Si atoms (Si4 in **3a**; Si2 in **3b**) are close to the C₃ plane (0.14 and 0.10 Å, respectively), whereas the anti Si atoms (Si3 in **3a**; Si1 in **3b**) are considerably displaced from the allyl plane (1.02 and 0.90 Å, respectively); similar values are found in **2a**.

Computational Results

(C₃H₅)₂Ni. The electronic structure of bis(allyl)nickel has been investigated repeatedly at various levels of sophistication.^{15–17,69,70} For ease of comparison with the substituted derivatives, the staggered and eclipsed forms of (C₃H₅)₂Ni were reexamined at the B3LYP/DGDZVP2 level of theory under C₂ symmetry (nearly identical results were obtained with the crystallographically observed C_i symmetry). The agreement of the staggered geometry with the single-crystal neutron diffraction structure¹⁹ is quite good; the calculated Ni–C(1,3) and Ni–C2 distances of 2.028 and 1.986 Å can be compared with the average Ni–C(1,3) and Ni–C2 distances observed at 2.029(1) and 1.980(1) Å, and the calculated C–C–C angle (120.7°) in the ligand essentially matches the observed angle of 120.5(1)°. The bond distances and angles in the calculated structure of the eclipsed form (Ni–C(1,3) = 2.029 Å; Ni–C2 = 1.985 Å; C–C–C = 120.8°) are almost the same as those in the staggered conformation. The angle between the C₃ planes is markedly different in the two conformations, however, parallel (0.0°) in the staggered form, 59.8° in the eclipsed. The solid-state structure of (C₃H₅)₂Ni has parallel ligands.

Most calculations have identified the staggered form as slightly lower in energy than the eclipsed conformation, and that is found to be the case with the B3LYP/DGDZVP2 combination (1.5 kcal mol^{–1} for both Δ*H*° and Δ*G*°). Recently, Casarin found that quasi-relativistic DFT calculations indicated that the two forms were virtually identical in energy (0.1 kcal mol^{–1} in favor of the eclipsed conformation, although, with the use of a triple-ζ quality basis set on all atoms (instead of on nickel only), the preference shifted to 0.13 kcal mol^{–1} in favor of the staggered form).¹⁷ It should be noted that, in solution at room temperature, both conformers are present in an eclipsed-to-staggered ratio of 1:3,¹⁴ and only the staggered form has been identified in the solid state.¹⁹

As a more realistic model for **1a/1b**, the molecule [1,3-(SiH₃)₂C₃H₃]₂Ni was optimized using the B3LYP/DGDZVP2 method under C₂ symmetry, the highest possible with syn, anti silyl groups. Some asymmetry is now evident in the binding of the allyl ligand; in the staggered conformation, the distance from Ni to C1, which bears the syn SiH₃ group, is 2.076 Å, and Si1 is relatively close to the C₃ plane (0.20 Å). The corresponding Ni–C3 distance is 2.028 Å, and Si3 is displaced by 0.96 Å from the allyl plane. The Ni–C2 distance (1.994 Å) is only slightly longer than that calculated for unsubstituted (C₃H₅)₂Ni, and the calculated C–C–C angle has widened slightly to 122.4°; the C₃ allyl planes now form an angle of 4.4°. These values closely model features in **1b**, including the longer Ni–C(*syn*-TMS) vs Ni–C(*anti*-TMS) distance (2.070(2) and 2.016(2) Å, respectively), the difference in silyl group displacements (close to the allyl plane for the *syn*-groups, markedly displaced for the *anti*-groups), and the interplanar C₃ angle (4.4° in the model; 4.6° in **1b**).

Calculations on the eclipsed version of [1,3-(SiH₃)₂C₃H₃]₂Ni under C₂ symmetry were found to reproduce the structure of **1a** to a reasonable degree. The similarities include the slightly more symmetrical bonding of the allyl ligand (2.038 Å to the carbon with the anti SiMe₃ group and 2.054 Å to the carbon with the syn SiMe₃ group) and the tilting of the C₃ ligand planes (calculated at 56.7°; experimentally found in **1a** at 49.1°). It is apparent that the inclusion of SiH₃ groups is sufficient to reproduce the major features of both the staggered and eclipsed forms of [1,3-(SiMe₃)₂C₃H₃]₂Ni. The staggered conformer continues to be the more stable, although by even less than in the case of the unsubstituted complex (0.6 kcal mol^{–1} in Δ*H*°, 1.3 kcal mol^{–1} in Δ*G*°).

As an additional check on the possible steric influence of the trimethylsilyl groups, the structures of [1,3-(SiMe₃)₂C₃H₃]₂Ni were optimized with the B3LYP/DGDZVP2 combination using the crystal structures of **1a** and **1b** as starting geometries; C₂ symmetry was used throughout. As in the SiH₃ substituted model, the calculated values for the trimethylsilyl substituted models closely match those of the experimental [1,3-(SiMe₃)₂C₃H₃]₂Ni structures (see Table 2).

Of particular interest is the C₃ interplanar angle calculated for the eclipsed structure; it has decreased from 56.7° in the SiH₃ substituted model to 47.5° with the inclusion of trimethylsilyl groups. The latter angle is close to the experimentally found value of 49.1°. This suggests that this structural feature is controlled by steric interactions among the SiMe₃ groups; with a smaller tilt angle, there are no Me⋯Me' contacts of less than 4.0 Å, the sum of the van der Waals' radii for two methyl groups.⁷¹

Although it has not been observed in the bis(allyl)nickel structures, the geometry of staggered [1,3-(SiMe₃)₂C₃H₃]₂Ni was calculated under C₂ symmetry with both trimethylsilyl substituents in syn, syn arrangements. The optimized structure was a minimum (*N*_{imag} = 0), with Ni–C distances ranging from 1.999 to 2.089 Å. It is distinctly higher in energy than the staggered form with syn, anti substituents (by 4.1 kcal mol^{–1} in Δ*H*°, 3.7 kcal mol^{–1} in Δ*G*°).

Conclusions

Trimethylsilyl substituents affect the properties of allyl nickel complexes in ways ranging from subtle to substantial. It is possible to identify several categories of similarities and differences, as summarized below.

(1) *Structure and thermodynamics.* The crystal structures of (C₃H₅)₂Ni and **1b** are remarkably similar in the core features of the metal–ligand geometry. The nickel–carbon bond lengths are within 0.04 Å of each other, and the angles between the C₃ planes differ by less than 5°, even though DFT calculations suggest that the potential energy surface for the interplanar angle is nearly flat and, hence, easily perturbable. Although the trimethylsilyl groups cause substantial changes in other attributes of the complexes, they exert little effect on the framework Ni–C distances.

Consistent with this finding, the DFT calculations on the eclipsed and staggered conformations of (C₃H₅)₂Ni, [1,3-(SiH₃)₂C₃H₃]₂Ni, and [1,3-(SiMe₃)₂C₃H₃]₂Ni indicate that successively greater substitution does not change the relative

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stability of the two forms (Table 2). The staggered form is always preferred but not by more than 1.5 kcal mol⁻¹. The consistency of the preference energy indicates that the trimethylsilyl groups do not exert a major effect on the relative thermodynamic stability of the molecules.

(2) *Kinetic stability.* Probably the most obvious difference between the properties of (C₃H₅)₂Ni and **1** is the considerably improved oxidative and thermal stability of the latter. Although (C₃H₅)₂Ni is pyrophoric, **1** can survive in air for hours (as a powder) to days (as large crystals). Steric shielding of the metal center is undoubtedly the source of this kinetic stability (Figure 4).

The enhanced thermal stability of **1** (dec over 100 °C) may also be a kinetic phenomenon. The decomposition of (C₃H₅)₂Ni is accompanied by the coupling of the allyl ligands,⁵ but a similar process may be more difficult with the sterically bulky trimethylsilylated analogue.

The kinetic influence of the substituted allyl ligands is also evident in the difference in the solution behavior of **1** and (C₃H₅)₂Ni. The eclipsed and staggered conformations of the latter are in dynamic equilibrium, and the ratio is adjustable by a variation in the temperature.¹⁴ Orbital symmetry arguments indicate that the interconversion of the two conformations cannot be accomplished by a simple rotation of the allyl ligands⁷² and likely involves a sequence of π - σ - π rearrangements of the binding modes. In contrast, the eclipsed (**1a**) and the staggered (**1b**) forms of **1** are not in detectable equilibrium. Their relative ratios in solution are constant until a temperature of 85 °C is reached, at which point *irreversible* conversion of **1a** to **1b** occurs. Although the enthalpic difference between the two forms is small (~1.5 kcal mol⁻¹), the set of ligand rearrangements that would be required to convert **1b** back to **1a** must be more difficult for the bulky trimethylsilylated ligands than for the parent anion.

(3) *Reactions with phosphines and halides.* Given the apparent thermodynamic similarities between (C₃H₅)₂Ni and **1**, their different reactions with nucleophiles, like their susceptibility to oxidation, probably stem largely from the kinetic differences arising from the bulky trimethylsilylated ligands. This is apparent in the reactions of the two compounds with phosphines. All phosphines do not react in the same way with (C₃H₅)₂Ni, and this is also true with **1**. With (C₃H₅)₂Ni, an unstable adduct is formed with PPh₃ (and other bulky phosphines such as (C₆H₁₁)₃P and (*i*-Pr)₃P), which decomposes with the formation of a nickel hexadiene complex. The lack of any detectable interaction between **1** and PPh₃ is probably a direct consequence of the shielding of the metal center by the bulky allyl groups. With the smaller PMe₃, however, the roles are partially reversed; i.e., (C₃H₅)₂Ni forms a thermally unstable 18-e⁻ adduct that can be characterized at low temperature, but which dissociates at room temperature without affecting the nickel complex. In contrast, on reaction with a mixture of **1a/1b**, trimethylphosphine is converted to tetramethyltetraphosphane, (MeP)₄, leaving

behind the thermodynamically more stable staggered **1b**. The full mechanism of this transformation is complex and is under investigation.

The reaction of **1** with halogens is similar to that of (C₃H₅)₂Ni in that both bis(allyl) complexes will lose an allyl ligand when treated with Br₂ or I₂ to form (allyl')NiX species. The extra kinetic stabilization imparted by the bulky allyl ligands results in some differences, however, such as the resistance to Schlenk rearrangements in donor solvents.

A subtle effect can be recognized in the derivatives of **1** that does not exist with (C₃H₅)₂Ni, namely, the variable occurrence of syn, syn and syn, anti ligand substituents. Syn, syn arrangements are uniformly observed in bis(trimethylsilyl)allyl complexes of the s- and f-block metals, i.e., in those cases in which a largely ionic allyl-metal interaction can be presumed.^{27–29,73,74} Syn, anti conformations to date have only been observed in d-block transition metal complexes, where they are the rule for the first row series [1,3-(SiMe₃)₂C₃H₃]₂M (M = Cr, Fe, Co, Ni). The observation of both syn, syn and syn, anti versions of the mono(allyl)nickel species **2** indicates that the SiMe₃ arrangement is a conserved feature of the bis(allyl) starting materials; i.e., the syn, anti version of **2** and **3** were both derived directly from **1**, which contains syn, anti groups. The syn, syn version of **2** was derived from 1,3-(SiMe₃)₂C₃H₄Br, to which the syn and anti distinction does not apply. The fact that the bis(allyl)metal species are derived from alkali metal salts (Li, K) with syn, syn substituents suggests that this arrangement is not conserved on transfer of the ligands to transition metal centers.

The chemistry of (C₃H₅)₂Ni and that of the trimethylsilylated derivatives described here differ in various ways, both in degree and kind. We anticipate that greater use of such substituted ligands will lead to new and unexpected elaborations in stoichiometric and catalytic nickel allyl chemistry.

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Supporting Information Available: The HSQC spectra of (MeP)₄ and additional structure refinement details and X-ray crystallographic files in CIF format for **1a**, **1b**, **2**, **3**, and the *P*_{21/c} polymorph of **1b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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