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Pyridine-Based Mono(ligand)nickel(0) Complexes of 1,6-Heptadiene, 1-Phenyl-2-trimethylsilyl-acetylene, and 1,4-Bis(trimethylsilyl)-1,3-butadiyne

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Abstract: The reaction of *rac/meso*-(μ-η^2,η^2-C_7H_{12}){Ni(η^2,η^2-C_7H_{12})}$_2$ with 2,6-dimethylpyridine (Me_2py) affords (Me_2py)Ni(η^2,η^2-C_7H_{12}) (1). Complex 1 serves as precursor for the preparation of the Ni(0)-bis(alkyne) complexes (Me_2py)Ni(η^2-PhC≡CSiMe_3)$_2$ (2) and {(Me_2py)Ni}$_2$(μ-η^2,η^2-Me_3SiC≡C-C≡CSiMe_3)$_2$ (3). The latter is the first complex in which two metal centers are bridged by two butadiyne ligands. For 1–3 the molecular structures have been determined by X-ray crystallography.

Introduction

Nickel(0)-bis- or -tris(alkyne) complexes are of interest because they can provide insight into the mechanism of Ni-catalyzed coupling reactions of alkynes. Information about them is, however, scant. Complexes of the type (R_3P)Ni(PhC≡CPh)$_n$ (R = Ph, *c*-Hex; n = 2, 3) have, for example, not been characterized in detail,[1] and the parent ethyne complexes (R_3P)Ni(HC≡CH)$_2$ (R = Me, Et, Ph) are difficult to study because they decompose at 0 °C or below.[2] The problem of instability has been overcome in the case of the (R_3P)Ni(η^2,η^2-C_7H_8) (R = Me, Ph) by using the 1,6-heptadiyne ligand as a chelating ligand.[3] There are also several complexes known in which sterically rigid metal-bis(alkynyl) ligands chelate a L–Ni(0) moiety in scissor fashion.[4] MO calculations have shown that the existence of a homoleptic complex Ni(HC≡CH)$_3$ is sterically unfavorable,[5] but a related complex containing a cyclotriyne does exist.[6] Various Ni(0)-bis(alkyne) complexes without additional ligands have also recently been reported.[7]

The reasons for doing the work described in this paper are twofold. We were intrigued to know whether it is possible to prepare stable L–Ni(0)-bis(alkyne) complexes using the 2,6-dimethylpyridine (Me_2py) ligand and we were interested in how the Me_3Si-substituted alkynes PhC≡CSiMe_3 and Me_3SiC≡C-C≡CSiMe_3 might act as ligands to L–Ni(0). The present study complements previous work on L_2Ni(0)-butadiyne complexes, as well as the coupling reactions of alkynes and substituted butadiynes at [Cp_2M] (M = Ti, Zr) centers.

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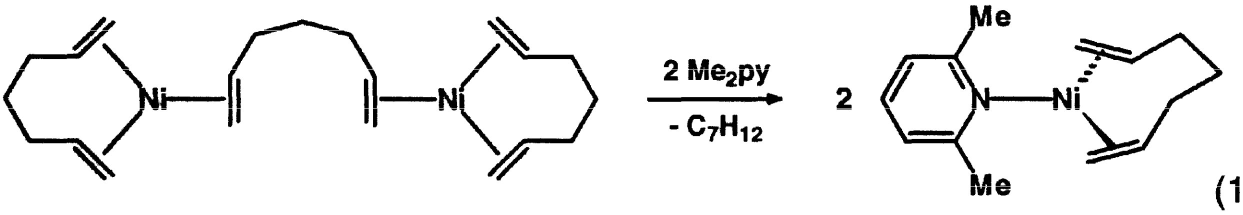
Results

$(2,6\text{-}Me_2C_5H_3N)Ni(\eta^2,\eta^2\text{-}C_7H_{12})$ (1)

When 2,6-dimethylpyridine is added to the colorless pentane solution of *rac/meso*-$(\mu\text{-}\eta^2,\eta^2\text{-}C_7H_{12})\{Ni(\eta^2,\eta^2\text{-}C_7H_{12})\}_2$[8] at –30 °C, the color turns intensive yellow. After standing at –30 °C yellow cubes of **1** crystallize in 80% yield (eq 1). Complex **1** melts at 73 °C. The IR spectrum (KBr) reveals a ν(C=C) vibrational band of the 1,6-heptadiene ligand at 1482 cm^{-1}. The mass spectrum of **1** exhibits the molecular ion at *m/e* = 261 (35%), which fragments by extruding either the diolefin to give $[(Me_2py)Ni]^+$ (165, 43%) or dimethyl-pyridine to afford $[(C_7H_{12})Ni]^+$ (154, 40%).



(1)

1

The ^1H (200 MHz) and ^{13}C (75.5 MHz) NMR signals of the 1,6-heptadiene ligand of **1** are as expected for $L\text{–}Ni(\eta^2,\eta^2\text{-}C_7H_{12})$ complexes,[8,9] i.e., seven ^1H and four ^{13}C resonances are observed. The chemical shifts correspond to those of $(C_5H_5N)Ni(\eta^2,\eta^2\text{-}C_7H_{12})$. Thus, the *ortho* methyl substituents of the pyridine ligand in **1** apparently have little electronic effect. Interestingly, the Me_2py ligand gives rise to two methyl resonances (δ_H = 2.53, 2.51; δ_C = 25.4, 25.1) up to 40 °C, indicating that no rotation of the pyridine ligand about the N–Ni(0) bond axis occurs. The spectra are consistent with a *TP*–3 Ni(0) coordination, with Me_2py and a chelating 1,6-heptadiene occupying the three sites. The symmetry of the complex in solution is C_S, with the mirror plane passing through Ni, the central C atom of 1,6-heptadiene, and the Me_2py ring plane.

The molecular structure of **1** has been determined by a single-crystal X-ray structure analysis[10] and is depicted in Figure 1. The 1,6-heptadiene ligand displays the known chair conformation, with the olefinic C atoms C1, C2, C6, and C7 situated in the *TP*–3 Ni(0) coordination plane (± 0.02 Å). The pyridine ring plane lies almost perpendicular (89°) to this plane, in spite of the asymmetric crystal environment (space group $P2_12_12_1$). This arrangement, together with the rigid structure of **1** in solution, suggest significant π-donation from the filled Ni(0) 3d orbitals in the trigonal plane into the pyridine π*-orbitals.

$(2,6\text{-}Me_2C_5H_3N)Ni(\eta^2\text{-}PhC{\equiv}CSiMe_3)_2$ (2)

In order to synthesize pyridine-based L–Ni(0)-bis(alkyne) complexes, we reacted $L\text{–}Ni(\eta^2,\eta^2\text{-}C_7H_{12})$ (L = py, Me_2py **1**) with various alkynes RC≡CR′ (R, R′ = H, Ph, Me_3Si). When yellow $(py)Ni(\eta^2,\eta^2\text{-}C_7H_{12})$[8] reacts with HC≡CH in diethyl ether at –78 °C the solution turns black immediately due to decomposition. Reactions with either $PhC{\equiv}CSiMe_3$ (–78 °C) or $Me_3SiC{\equiv}CSiMe_3$ (20 °C) in pentane afford red solutions, but no product has been isolated.

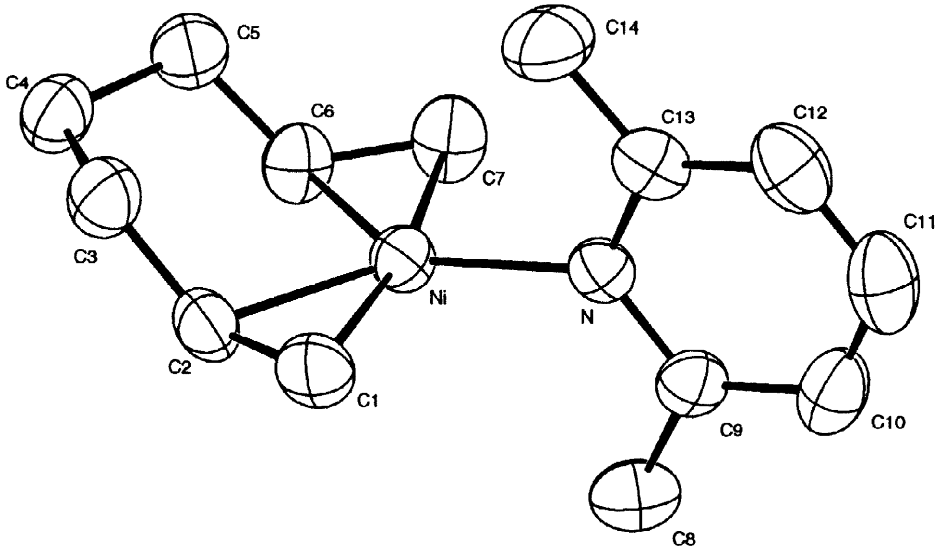
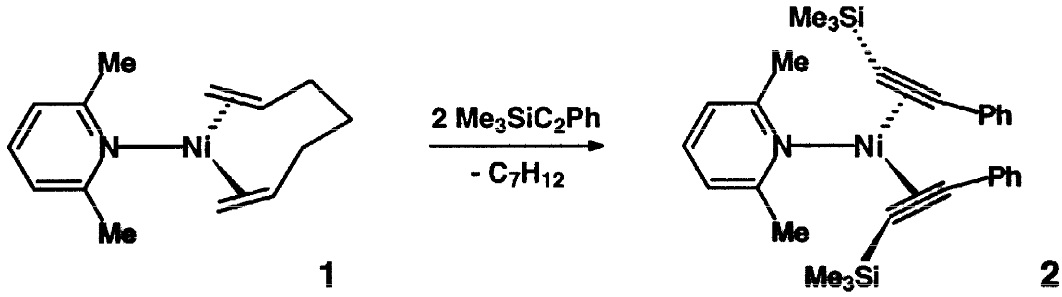


Figure 1. The molecular structure of **1**. Selected distances (Å) and angles (°) [D1 (D2) is the midpoint between the atoms C1 and C2 (C6 and C7)]: Ni–C1 1.984(4), Ni–C2 1.982(4), Ni–C6 1.989(4), Ni–C7 1.985(4), Ni–N 1.960(3), Ni–D1 1.857(4), Ni–D2 1.859(4), C1–C2 1.392(6), C2–C3 1.508(6), C3–C4 1.514(6), C4–C5 1.524(6), C5–C6 1.489(6), C6–C7 1.407(6), N–C9 1.351(5), N–C13 1.352(5), N–Ni–D1 114.7(2), N–Ni–D2 117.5(2), D1–Ni–D2 127.6(4), plane(Ni, N, C1, C2, C6, C7)/(Ni, N, C8 – C14) 89.

The corresponding reaction of **1** with HC≡CH in THF at –60 °C leads to formation of polyacetylene. Between –60 and –20 °C complex **1** can be isolated unchanged from the reaction mixtures, but above –20 °C decomposition of **1** occurs. When **1** is reacted with $Me_3SiC{\equiv}CSiMe_3$ (pentane, 40 °C) or PhC≡CPh (diethyl ether, –78 °C), the solutions turn red, but here again no product has been isolated.

Complex **1** reacts, however, with $PhC{\equiv}CSiMe_3$ in pentane at 45 °C to produce a red solution, from which red prisms of **2** crystallize at –78 °C in 80% yield (eq 2). Complex **2** is thermally fairly stable (mp 49 °C dec). In the IR spectrum (KBr) the alkyne ligands give rise to a stretching band ν(C≡C) at 1810 cm^{-1}, which is at a significantly lower wavenumber than for the free alkyne (2160 cm^{-1}). In the mass spectrometer (75 °C) the complex eliminates the Me_2py ligand, and the largest observable ion is $[Ni(PhC_2SiMe_3)_2]^+$ (*m/e* = 406, 3%), which fragments further by cleaving an alkyne ligand to afford $[Ni(PhC_2SiMe_3)]^+$ (232, 3%). In solution up to 100 °C, no coupling of the alkyne ligands and the Ni center in **2** to give a nickelacyclopentadiene complex takes place (this holds also in the presence of additional alkyne).[11] This result is in sharp contrast to the observed coupling of two $PhC{\equiv}CSiMe_3$ ligands by the titanocene[12] or zirconocene core.[13]



(2)

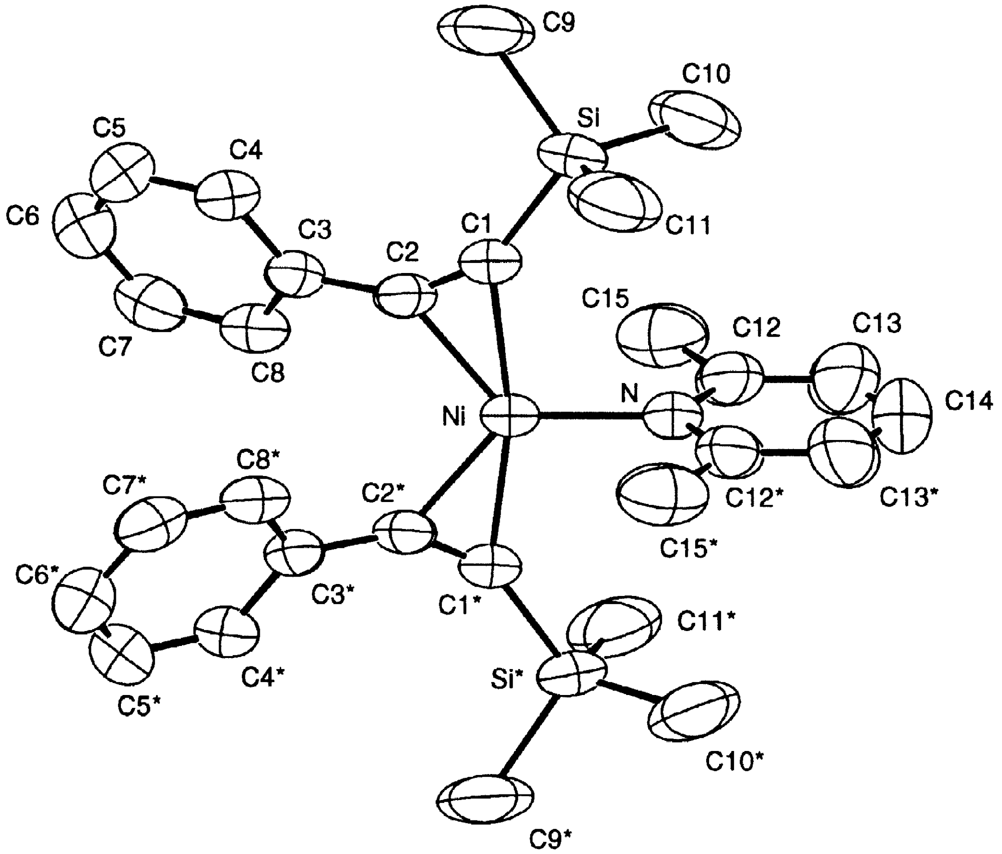


Figure 2. Molecular structure of **2**. Selected distances (Å) and angles (°) (D1 is the midpoint between the atoms C1 and C2): Ni–C1 1.984(2), Ni–C2 1.920(2), Ni–N 1.978(3), Ni–D1 1.847(2), C1–C2 1.263(3), C2–C3 1.451(3), C1–Si 1.834(2), N–Ni–D1 114.1(1), D1–Ni–D1* 131.8(2), Si–C1–C2 152.9(2), C1–C2–C3 149.4(2), plane(Ni,N,D1)/(Ni,Si,C1,C2,C3) 23, plane(Ni,N,D1)/(Ni,N,C12–C15) 80, plane(Ni, Si,C1,C2,C3)/(C2 - C8) 28.

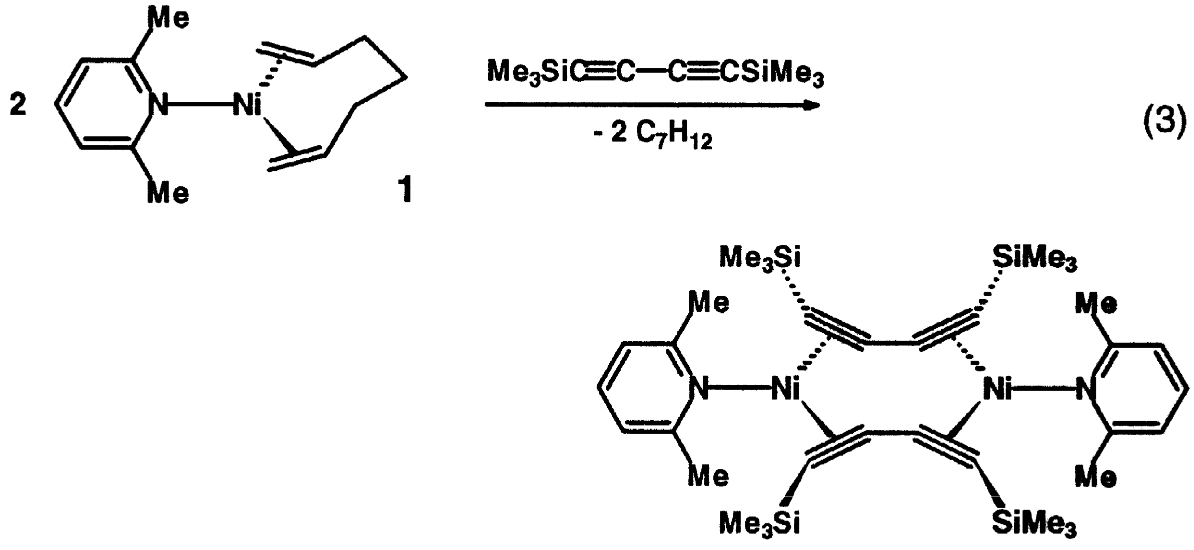
The 300 MHz ^{1}H NMR spectrum of **2** (30 °C) is poorly resolved. Broad signals at δ_H = 7.9–6.7 (13H) can be assigned to the phenyl and pyridine ring protons. A broad pyridine methyl signal is found at δ_H = 2.67 (6H) and (partly broad) $SiMe_3$ signals are observed in the range δ_H = 0.5 to –0.2 (18H). At –30 °C resolution is somewhat better, and, e.g., for the pyridine methyl groups five signals are observed. A similar picture arises from the ^{13}C NMR spectra (30/–30 °C). The spectra nevertheless confirm the composition of the complex, and indicate, moreover, the presence of various conformers (alkyne ligand rotamers) in solution, which start to equilibrate when the temperature is raised from –30 to 30 °C.

In order to clarify the bonding situation, the crystal structure of **2** was determined.[10] Figure 2 shows a projection of the molecule onto the mean plane passing through Ni, N, and the midpoint D1 of the bond C1–C2. The molecule contains an exact (crystallographic) 2-fold axis of symmetry, which passes though Ni, N, and C14. The nickel atom is *TP*–3 coordinated by the nitrogen atom of the Me_2py ligand and the C≡C bonds of two alkyne ligands. The C atoms of the C≡C bonds do not lie in the trigonal plane of the metal, but are twisted out of the plane such that the torsion angle N–Ni–D1–C1 is 23°. The mean plane of the pyridine ring makes an angle of 80° to the trigonal coordination plane of the Ni atom. It does, however, lie perpendicular to the plane through Ni, C1, and C2, possibly as a result of steric repulsion between two methyl groups of a $SiMe_3$ group and the pyridine ring. The mean planes through the phenyl rings intersect at an angle of 23°. The substituents on the alkyne groups are bent away from the C≡C bond by 30° [C1–C2–C3(Ph)] and 27° (C2-C1-Si), and similar values are observed for (dipy)Ni(η^2-PhC≡$CSiMe_3$) (35° and 31°).[14] The angle D1–Ni–D1* of 131.8° is larger than the analogous angle in $(Ph_3P)Ni(\eta^2,\eta^2-C_7H_8)$ (125°),[3] and the Ni–N distance of 1.98 Å in **2** is similar to that found in **1** (1.96 Å). The bond distances between Ni and the substituted alkyne carbon atoms Ni–C2(Ph) 1.92 Å and Ni–C1(Si) 1.98 Å differ, as expected,[15] and are longer than in (dipy)Ni(η^2–PhC≡$CSiMe_3$) (1.85, 1.89 Å). The C≡C bond length of 1.26 Å is close to the comparable distance in (dipy)Ni(η^2-PhC≡$CSiMe_3$) (1.28 Å).

The deviation of the alkyne C atoms from the *TP*–3 Ni coordination plane presumably results from the spatial requirements of the phenyl substituents. The stabilizing effect of the C≡C bond substituents is clearly large enough to overcome the steric repulsion. The planarity of the pyridine ligand seems to leave enough space to accommodate the alkyne $SiMe_3$ substituents. In contrast to the formation of **2**, no reaction occurs between $(Ph_3P)Ni(\eta^2,\eta^2-C_7H_{12})$[8] and PhC≡$CSiMe_3$ (only starting complex is isolated up to 35 °C, even though the color of the solution changes to red). This is presumably due to the bulk of the Ph_3P ligand.

$\{(2,6-Me_2C_5H_3N)Ni\}_2(\mu-\eta^2,\eta^2-Me_3SiC{\equiv}C-C{\equiv}CSiMe_3)_2$ (3)

When complex **1** is reacted with PhC≡C-C≡CPh or $^tBuC{\equiv}C-C{\equiv}C^tBu$, the yellow solution turns black. No product has been isolated. However, **1** reacts with $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ in diethyl ether at –78 °C to yield red prisms (51%) of the dinuclear complex **3** (eq 3). While $L_2Ni(0)$-butadiyne complexes have already been known,[16,17] in complex **3** a (disubstituted) butadiyne ligand is coordinated to a L–Ni(0) fragment for the first time.



3

(3)

Complex **3** melts at 124 °C (dec). In the IR spectrum (KBr) stretching bands ν(C≡C) are observed at 1890 and 1850 cm^{-1} (free diyne: 2068 cm^{-1}). The 400 MHz ^1H NMR spectrum (THF-d_8, –30 °C) exhibits signals for the pyridine *para* and *ortho* protons (δ_H = 7.64, 7.19), the pyridine methyl groups (δ_H = 2.72), and the alkyne $SiMe_3$ groups (δ_H = 0.17). In the ^{13}C NMR spectrum the signals of the butadiyne ligand are at δ_C = 128.4 (≡C–) and 123.9 (≡CSi). The spectra confirm the 1 : 1 stoichiometry of Me_2py and diyne ligands, and the IR and ^{13}C NMR data indicate that the $Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3$ complexation in **3** is weaker than in $L_2Ni(0)$ complexes.[17] However, they give no further clues as to the structure of the complex. After much effort small crystals suitable for an X-ray analysis were obtained, and the crystal structure was determined.

The results of the analysis are summarized in Figure 3,[10] which reveals that **3** is a dimer with an unusual coordination of two diynes to two nickel atoms. Each Ni(0) atom is *TP*–3 coordinated to one Me_2py ligand and one of each of the C≡C bonds of two different butadiyne ligands. The diyne ligands thus take up bridging positions between the two Ni(0) centers. Unfortunately, the small crystal size and disorder in the trimethyl group attached to Si4 results in relatively high errors associated with the bond lengths and angles and precludes a detailed comparison of **3** with other structures. Several features of the structure are, however, significant. The central part of the molecule is not planar, as one would expect, but twisted along the Ni···Ni vector such that the local coordination plane of one Ni atom makes an angle of 20(2)° to that of the other.

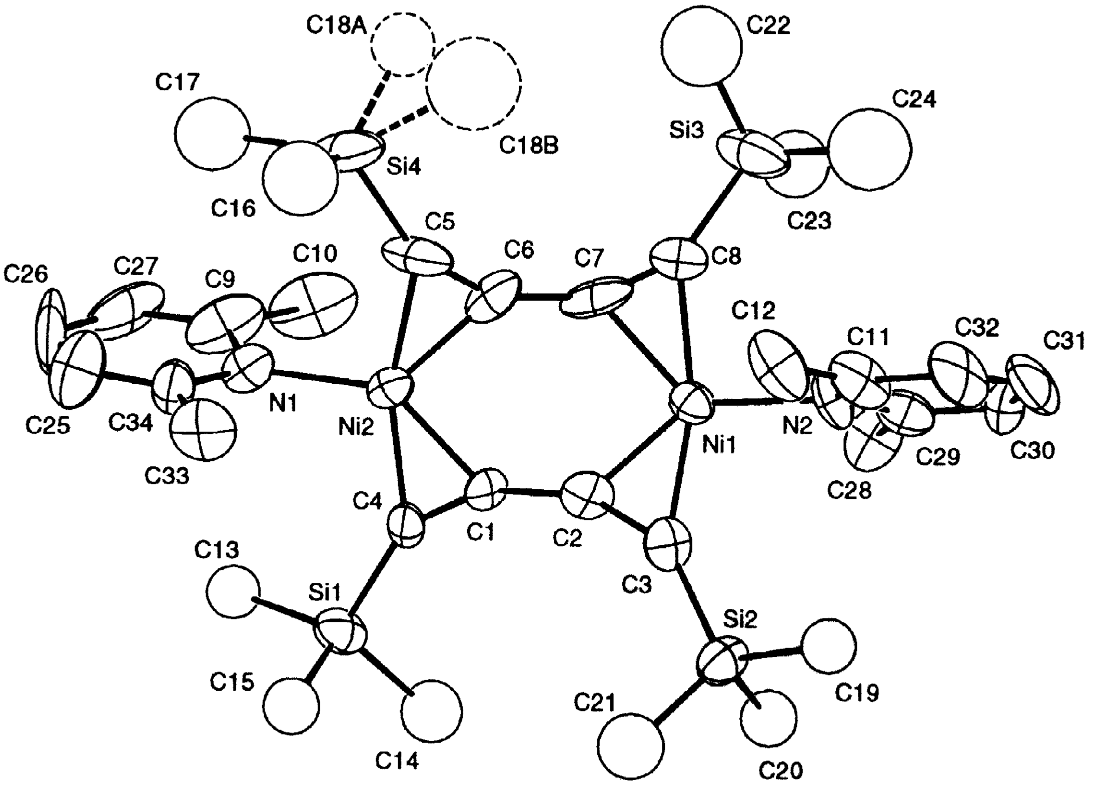


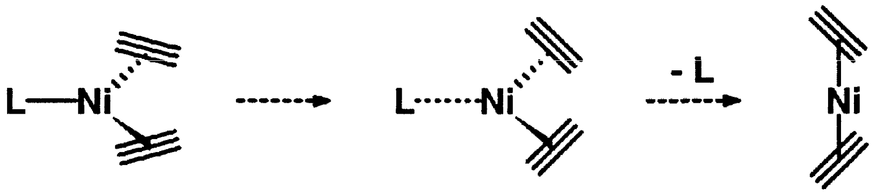
Figure 3. Molecular structure of **3** in the crystal. Selected distances (Å) and angles (°): Ni1···Ni2 4.189(5), Ni1–C2 1.94(2), Ni1–C3 2.00(2), Ni1–C7 1.95(2), Ni1–C8 2.01(2), Ni1–N2 1.99(2), Ni2–C1 1.94(2), Ni2–C4 1.98(2), Ni2–C5 1.98(2), Ni2–C6 1.93(2), C4–C1–C2 153(2), C1–C2–C3 153(2), C5–C6–C7 151.2(3), C6–C7–C8 155(2), C4–C1–C2–C3 -20(4), C5–C6–C7–C8 -34(4), Ni1–C2–C1–Ni2 -22(3), Ni1–C7–C6–Ni2 -41(3).

As a result the complex is chiral, at least in the crystal. The difference in the torsion angles of the bridging diyne entities [C4–C1–C2–C3 –20(4)°, C5–C6–C7–C8 –34(4)°] suggests that the distortion is far from symmetrical. Indeed, the asymmetry is reflected in the Ni2–C1–C2–Ni1 [–22(3)°] and Ni2–C6–C7–Ni1 [–41(3)°] torsion angles, which are also significantly different. In spite of this distortion, the Ni coordination planes defined by Ni, N, and the midpoints of the two C≡C bonds remain almost planar [average r.m.s. deviation 0.009 Å] and the Me_2py ligands almost perpendicular to their respective metal atom coordination planes [for Ni1 84(3)°, and for Ni2 83(3)°]. The Ni···Ni distance at 4.189(5) Å is too long for an interaction between the two metal centers.

Discussion

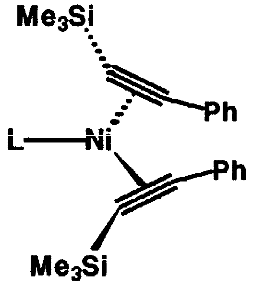
Whereas coupling of ethyne ligands with Ni(0) to form nickelacyclopentadienes has previously been observed when phosphine[18] or 1,4-diazabutadienes[19] were used as ligands, it has been recognized that mere coordination of two alkyne ligands at the *TP*–3 [L–Ni(0)] fragment does not suffice to induce a coupling reaction.[2a] It is suggested here that the "naked nickel atom" bears the largest coupling activity[20] and that the activity is reduced by *any* N- or P-donor ligand. Furthermore, Ni(0) coupling reactions with alkynes are unlikely to occur as far as disubstituted alkynes are concerned. It is thus of no surprise that for neither **2** nor **3** coupling of the alkyne ligands proceeds.

Nevertheless, the structure of **2** displays the interesting feature of a C_2 symmetrical distortion of the C≡C bonds about the coordination axis to Ni(0), placing the carbon atoms out of the *TP*–3 Ni(0) coordination plane. The structure can be considered to be model for an intermediate in the reaction coordinate when in a *TP*–3 L–Ni(alkyne)$_2$ complex the L–Ni bond is gradually weakened to the extent that the ligand L is finally cleaved and an *L*–2 Ni(alkyne)$_2$ complex[7] is formed.



Complex **3** as a dinuclear entity is presumably formed because of steric reasons. Reaction of **1** with alkynes leads to complete displacement of the 1,6-heptadiene ligand. The $SiMe_3$ disubstituted butadiyne ligand cannot satisfy the demands of mononuclear *TP*–3 Ni(0), neither in a L–Ni(butadiyne)$_2$ complex with singly coordinated butadiyne, nor in a L–Ni(butadiyne) complex (cumulene-like structural moieties have been observed for early transition metals[21,22]).

Finally, the stability of the $(Me_2py)Ni(alkyne)_2$ complexes **2** and **3** is opposed to the reactivity of [Cp_2Ti] and [Cp_2Zr] centers for which coupling of the alkynes to form metallacyclopentadienes[12,13,23] or cleavage of the butadiyne central C–C bond[24] is favored.



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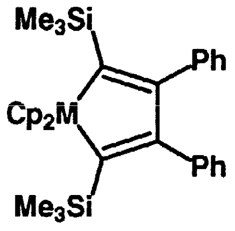
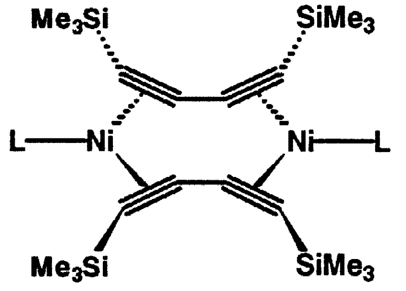


M = Ti [12]
Zr [13]



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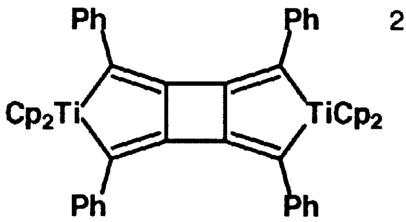

[23]

Experimental

All reactions have been carried out under argon as a protective gas. Elemental analyses were performed at the Microanalytisches Labor Kolbe, Mülheim/Ruhr. Uncorrected melting points were measured under argon in sealed glass capillaries by the melting-point apparatus Büchi SMP-20. ^{1}H NMR spectra were obtained with Bruker WH 400 (400 MHz), AM 200 (200 MHz), and WP 80 (80 MHz) spectrometers (5 mm tubes). ^{13}C NMR spectra were measured with Bruker WH 400, AM 200 (100.6, 50.3 MHz, 5 mm tubes), and WM 300 (75.5 MHz, 10 mm tubes) instruments. Solvent was THF-d_8, internal standard was TMS. The samples were prepared under argon at the temperature the spectra were recorded. IR spectra were recorded on a 7199 FT-IR spectrometer (Nicolet) using KBr pellets or Nujol mulls. EI mass spectra were obtained with a Finnigan MAT 311A spectrometer and refer to ^{58}Ni. Ni(CDT) was synthesized according to the literature.[25] Due to cocrystallization with CDT the purity of the Ni(CDT) employed was 95% (arithmetical molecular mass: 233 g/mol).

$(2,6\text{-Me}_2C_5H_3N)Ni(\eta^2,\eta^2\text{-}C_7H_{12})$ (1). To the colorless solution of *rac/meso*-$(\mu\text{-}\eta^2,\eta^2\text{-}C_7H_{12})\{Ni(\eta^2,\eta^2\text{-}C_7H_{12})\}_2$,[8] prepared from 2.33 g (10.0 mmol) Ni(CDT) and 2 mL 1,6-heptadiene in 20 mL of pentane, is added 1.07 g (10.0 mmol) of 2,6-dimethylpyridine in 20 mL of pentane at –30 °C. The reaction mixture turns intensive yellow. At –30 °C and after inoculation yellow cubes of 1 crystallize, which are separated from the mother liquor using a capillary frit, washed twice with pentane (–78 °C), and dried in vacuo; yield 2.10 g (80%); mp 73 °C. Anal. Calcd for $C_{14}H_{21}NNi$: C, 64.18; H, 8.08; N, 5.35; Ni, 22.40. Found: C, 64.09; H, 8.11; N, 5.31; Ni, 22.46. IR (KBr): 1482 cm^{-1} (ν, C=C). MS (55 °C): *m/e* (%) = 261 (35) M$^+$, 165 (43) $[Me_2C_5H_3NNi]^+$, 154 (40) $[C_7H_{12}Ni]^+$, 107 (100) $[Me_2C_5H_3N]^+$. ^{1}H NMR (200 MHz, THF-d_8, -80 °C):

δ = 2.98 (2H, –CH=), 2.30 (2H, $–CH_aHCH=$), 2.07 (2H, $=CH_EH$), 1.84 (2H, $=CHH_Z$), 1.77 (1H, $–CH_aH–$), 1.63 (1H, $–CHH_b–$), 0.83 (2H, $–CHH_bCH=$); 7.57 (1H, py_{para}), 7.15 (2H, py_{meta}), 2.53, 2.51 (each 3H, py-CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, –80 °C): δ = 68.3 (2C, –CH=), 47.8 (2C, $=CH_2$), 34.4 (2C, $–CH_2CH=$), 31.6 (1C, $–CH_2–$); 159.2, 158.8 (each 1C, py_{ortho}), 135.8 (1C, py_{para}), 122.0 (2C, py_{meta}), 25.4, 25.1 (each 1C, py-CH_3).

Crystal data for **1**: $C_{14}H_{21}NNi$, M_r = 262.0 g·mol^{-1}, crystal color green-yellow, crystal size 0.25 × 0.42 × 0.56 mm, space group $P2_12_12_1$ [No.19], a = 7.717(1), b = 13.069(2), c = 13.376(2) Å, V = 1348.9(3) Å^3, D_{calcd} = 1.29 g·cm^{-3}, μ = 14.13 cm^{-1}, F(000) = 560 e, Z = 4, orthorhombic, Enraf-Nonius CAD-4 diffractometer, scan mode ω–2θ, $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}, no absorption correction, 1791 measured reflections (+h,+k,+l), 1769 independent reflections, 1518 observed reflections [$I \geq 2\sigma(I)$]. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares[27] on F^2 for all data with Chebyshev weights, R = 0.036 (obs. data), wR^2 = 0.081 for 147 refined parameters, H atoms riding, residual electron density +0.47 eÅ^{-3}.

$(2,6\text{-}Me_2C_5H_3N)Ni(\eta^2\text{-}PhC{\equiv}CSiMe_3)_2$ (2). 810 mg (4.66 mmol) of $PhC{\equiv}CSiMe_3$ is added at 20 °C to the light yellow solution of 610 mg (2.33 mmol) **1** in 10 mL of pentane. Upon heating the mixture for a short period to 45 °C the color turns into intensive red. Cooling to –78 °C affords red cubes, which are separated from the mother liquor using a capillary frit, washed twice with cold pentane, and dried in vacuo at 20 °C; yield 960 mg (80%); mp 49 °C (dec.). Anal. Calcd for $C_{29}H_{37}NNiSi_2$: C, 67.70; H, 7.25; N, 2.72; Ni, 11.41; Si, 10.92. Found: C, 67.54; H, 7.46; N, 2.75; Ni, 11.36; Si, 10.83. IR (KBr): 1810 cm^{-1} (ν, C≡C). MS (75 °C): m/e (%) = 406 (3) $[M–C_7H_9N]^+$, 232 (3) $[(PhC{\equiv}CSiMe_3)Ni]^+$. ^1H NMR (300 MHz, THF-d_8, 30 °C): δ = 7.9–6.7 (13H, py, Ph), 2.67 (broad, 6H, CH_3-py), 0.5–(–0.2) (18H, $SiCH_3$).

Crystal data for **2**: $C_{29}H_{37}NNiSi_2$, M_r = 514.5 g·mol^{-1}, crystal color red brown, crystal size 0.35 × 0.39 × 0.39 mm, monoclinic, space group $C2/c$ [No. 15], a = 16.635(4), b = 17.039(1), c = 12.806(3) Å, V = 2965.4(9) Å^3, D_{calcd} = 1.15 g·cm^{-3}, μ = 7.51 cm^{-1}, F(000) = 1096 e, Z = 4, Enraf-Nonius CAD-4 diffractometer, scan mode ω–2θ, $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}, no absorption correction, 3533 measured reflections (±h,+k,+l), 3382 independent reflections, 2329 observed reflections [$I \geq 2\sigma(I)$]. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares[27] on F^2 for all data with Chebyshev weights, R = 0.041 (obs. data), wR^2 = 0.085 for 155 refined parameters, H atoms riding, residual electron density +0.25 eÅ^{-3}.

$\{(2,6\text{-}Me_2C_5H_3N)Ni\}_2(\mu\text{-}\eta^2,\eta^2\text{-}Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3)_2$ (3). A yellow solution of 1.0 g (3.82 mmol) **1** in 10 mL of diethyl ether is treated at 20 °C with 742 mg (3.82 mmol) $Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3$ in 5 mL diethyl ether. While the mixture is stirred at 40 °C for 15 min its color turns into deep red. Upon cooling to –78 °C red cubes (**3**) crystallize, which are separated from the mother liquor using a capillary frit, washed with cold pentane, and dried in vacuo at 20 °C; yield 702 mg (51%); mp 124 °C (dec.). Anal. Calcd for $C_{34}H_{54}NNi_2Si_4$: C, 56.67; H, 7.55; N, 3.89; Ni, 16.30; Si, 15.59. Found: C, 55.99; H, 7.58; N, 3.92; Ni, 16.70; Si, 15.77. IR (KBr): 1890, 1850 cm^{-1} (ν, C≡C). ^1H NMR (400 MHz, THF-d_8, –30 °C): δ = 7.64 (2H, py_{para}), 7.19 (2H, py_{meta}), 2.72 (12H, CH_3-py), –0.17 (36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, –30 °C): δ = 160.7 (4C, py_{ortho}), 136.6 (2C, py_{para}), 122.2 (4C, py_{meta}), 26.9 (4C, py-CH_3); 128.4 (4C, CC≡), 123.9 (4C, SiC≡), 0.3 (12C, $SiCH_3$).

Crystal data for **3**: $C_{34}H_{54}N_2Ni_2Si_4$, M_r = 720.6 g·mol^{-1}, crystal color red brown, crystal size 0.20 × 0.15 × 0.15 mm, trigonal, space group $P3_2$ [No. 145], a = 13.178(1), c = 21.043(2) Å, V = 3184.7(5) Å^3, D_{calc} = 1.143 g·cm^{-3}, μ = 10.28 cm^{-1}, $F(000)$ = 560, Z = 3, Enraf-Nonius CAD4 MACH3 diffractometer, scan mode ω–θ, $[(\sin\theta)/\lambda]$ = 0.55 Å^{-1}, no absorption correction, 3462 measured reflection (–h,+k,±l), 3461 independent reflections, 2257 observed reflections [$I \geq 2\sigma(I)$]. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares[27] on F^2 for all data, R = 0.079 (obs. data), wR^2 = 0.203, 323 parameters, H atoms riding, residual electron density +0.82 e·Å^{-3}.

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