Synthesis, Structure and Reactions of the Homoleptic Alkyne Nickel(0) Complex (Alkyne)$_4$Ni$_3$ (Alkyne: 2-Methyl-4-trimethylsilyl-3-butyn-2-ol)☆

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Received June 24, 1996

Key Words: Nickel(0) / Alkyne complexes / Hydrogen bonds

Treatment of (cdt)Ni (cdt: cyclododeca-1,5,9-triene) with 2 equivalents of 2-methyl-4-trimethylsilyl-3-butyn-2-ol leads to the selective formation of the homoleptic complex (alkyne)$_4$Ni$_3$ (compound **3**), which can be isolated in excellent yields. The solid-state structure of **3** exhibits three Ni centers, forming a bent Ni$_3$ chain connected by two bridging alkynes. The other two alkynes are terminally coordinated. Additionally, the trimeric units are stabilized by three intramolecular hydrogen bonds. Two intermolecular hydrogen bonds connect the trimeric units to form a polymer rope. According to the ^{13}C- and ^{1}H-NMR spectra in THF the structure of the complex **3** in solution is very similar to that in the solid state. The reaction of **3** with some alkynediols and with 2,5,5-trimethylhex-3-yn-2-ol affords compounds of the type (alkyne)$_2$Ni. Cot (cot: 1,3,5,7-cyclooctatetraene) converts **3** into [(cot)Ni]$_2$, which in turn reacts with 2,5-dimethylhex-3-yne-2,5-diol to form the dimeric complex (alkyne)$_2$Ni$_2$(cot) **6**. X-ray analysis of **6** reveals a very symmetrical structure in which cot connects both Ni(0) centers at opposite sides of the ring system.

R. Hoffmann et al. calculated the stabilities of alternative structures of monomeric, oligomeric and polymeric alkyne metal(0) complexes. It was found that in the case of polymeric compounds the metal is tetrahedrally coordinated, forming a helical chain as the most stable structure. Oligomeric complexes should also be stable in both cyclic tetrameric and hexameric compounds[1]. Until very recently, only some homoleptic Pt(0) complexes of the type (alkyne)$_2$Pt and one compound of the type (alkyne)$_3$Pt$_2$ were known; these can be regarded as the first members of the hypothetical range (alkyne)$_{n+1}$Pt$_n$[2]. Higher derivatives as well as homoleptic Pd(0) or Ni(0) complexes with monoalkynes were unknown.

We showed that homoleptic compounds of the type (alkyne)$_2$Ni(0) can be isolated if sterically hindered alkynes bearing OH groups act as ligands[3,4]. Both (alkyne)$_2$Ni **1** and (alkyne)$_4$Ni$_3$ **2** could be synthesized by using (CH$_3$)$_3$CC≡CC(CH$_3$)$_2$OH[4,5].

The surprising crystallization of **2** at −78 °C from solutions which only contained the complex **1** prompted us to examine if the formation of the trimeric complex **2** is a unique reaction. In this paper we describe the highly selective synthesis of the new trimeric compound [(CH$_3$)$_3$SiC≡CC(CH$_3$)$_2$OH]$_4$Ni$_3$ **3** and its solid-state structure as well as its structure in solution. Reactions with both other alkynes and cot will give a deeper insight into the organometallic chemistry and relative stabilities of homoleptic alkyne nickel(0) complexes.

Synthesis and Structure of 3

According to the NMR and IR spectra, reaction of (CH$_3$)$_3$SiC≡CC(CH$_3$)$_2$OH with (cdt)Ni results in the almost quantitative formation of the trimeric complex (alkyne)$_4$Ni$_3$, **3**, even when the components are allowed to react in a molar of ratio 2:1.

$$\text{(cdt)Ni} + \text{(CH}_3)_3\text{Si-C}{\equiv}\text{C-C(CH}_3)_2\text{OH} \xrightarrow[\text{- cdt}]{} \underset{\mathbf{3}}{[\text{(CH}_3)_3\text{Si-C}{\equiv}\text{C-C(CH}_3)_2\text{OH}]_4\text{Ni}_3}$$

The ^{13}C-NMR spectrum (50.3 MHz) in [D$_8$]THF at 25 °C exhibits only resonances for free cdt, compound **3** and free alkyne. In the IR spectrum only the characteristic bands for the valence frequencies of terminally and bridging coordinated alkynes ($\tilde{\nu}_{C≡C}$ = 1861 and 1607 cm^{-1}) and for free alkyne ($\tilde{\nu}_{C≡C}$ = 2170 cm^{-1}) are found. This high selectivity is in contrast to all other reactions of alkynes with (cdt)Ni, in which under similar conditions only the formation of (alkyne)$_2$Ni complexes in solution is observed. Only in the case of the compound **1** does a spontaneous aggregation reaction occur, yielding the crystalline trimer **2**[4].

One reason for this significant difference may be seen in the higher electron deficiency of the silyl-substituted alkyne compared with the other alkynes used [for comparison: $\tilde{\nu}_{C\equiv C}$ = 2170 cm^{-1} for $(CH_3)_3SiC\equiv CC(CH_3)_2OH$ and $\tilde{\nu}_{C\equiv C}$ = 2230 cm^{-1} for $(CH_3)_3CC\equiv CC(CH_3)_2OH$)].

The result of the crystal structure determination of **3** is displayed in Figure 1. Figure 2 shows the network of hydrogen bonds stabilizing the supramolecular solid-state structure.

Figure 1. Molecular structure of **3**: Ni1–C10 1.889(3), Ni1–C2 1.898(3), Ni1–C1 1.910(3), Ni1–C9 1.973(3), Ni1–Ni2 2.5689(6), Ni2–C9 1.917(3), Ni2–C17 1.930(3), Ni2–C18 1.950(3), Ni2–C10 1.977(3), Ni2–Ni3 2.6628(6), Ni3–C18 1.883(3), Ni3–C26 1.892(3), NI3–C25 1.918(3), Ni3–C17 1.955(3), Si1–C1 1.845(3), Si2–C9 1.867(3), Si3–C17 1.854(3), Si4–C25 1.847(4), O1–C3 1.432(4), O2–C11 1.431(4), O3–C19 1.433(4), O4–C27 1.429(4), C1–C2 1.266(4), C2–C3 1.507(4), C9–C10 1.324(5), C10–C11 1.524(4), C17–C18 1.326, C18–C19 1.521(4), C25–C26 1.262(5), C26–C27 1.507(4), Ni1–Ni2–Ni3 122.80(2), C2–C1–Si1 161.0(3), C1–C2–C3 149.8(3), C10–C9–Si2 149.6(3), C9–C10–C11 145.0(3), C18–C17–Si3 149.0(3), C17–C18–C19 142.7(3), C26–C25–Si4 155.5(3), C25–C26–C27 153.9(3)

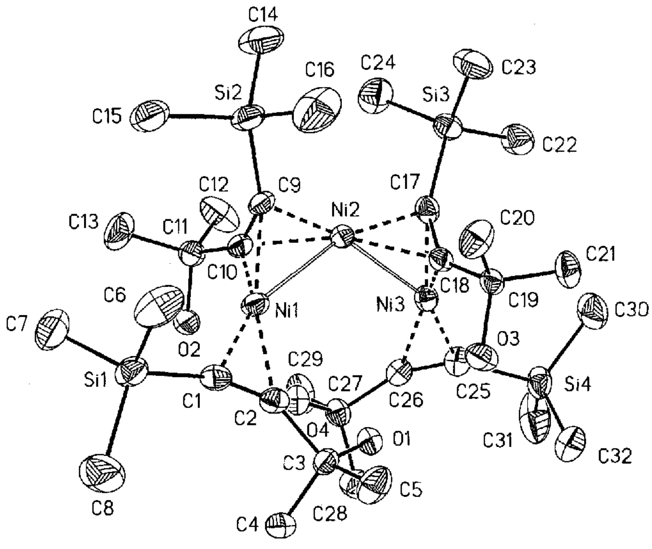
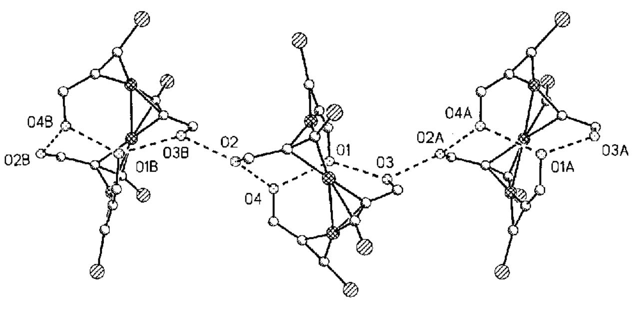


Figure 2. System of hydrogen bridges of **3**. Selected intra- and intermolecular distances [Å]: O1–O3 2.753(4), O1–O4 2.707(4), O2–O4 2.709(4), O2–O3B 2.772(4); methyl groups have been omitted for clarity



Each of the three nickel(0) centers is surrounded by four carbon atoms of two coordinating alkynes, forming three distorted tetraedra. Two of the alkynes act as bridging ligands; the other two alkynes are both terminally coordinated. The metal atoms form a bent three-membered chain with an average Ni–Ni distance of 2.62 Å and a Ni–Ni–Ni angle of 122.8°.

As expected the average C≡C bond lengths of the terminally bound alkynes (1.26 Å) are significantly shorter than those of the bridging alkyne (1.32 Å). The Ni–C bonds display normal bond lengths between 1.88 and 1.95 Å. The higher value for the bend-back angle of the coordinated $C\equiv C{-}Si(CH_3)_3$ group in comparison with the corresponding angle of the $C\equiv C{-}C(CH_3)_2OH$ group may be explained by the $d_\pi p_\pi$ interaction of the silicon atom with the alkyne triple bond[2(c),6]. In addition to the twelve Ni–C bonds with typical values for the bond length (1.88–1.95 Å) and the two Ni–Ni interactions, sets of three intramolecular and two intermolecular hydrogen bonds per trimeric unit are built up, forming a polymeric "rope". The same type of hydrogen-bonded network was also found in the nickel(0) compound **2** and may be considered as a more general means of stabilization of such types of trimeric compounds containing alkynols as ligands.

Pure **3** is stable under argon in the solid state but unstable in solution at room temperature. However, it can be investigated by NMR spectroscopy at −15 °C. In solution **3** shows C_2 symmetry. In the 100.6-MHz ^{13}C-NMR spectrum ([D$_8$]THF, −15 °C) the four signals for the coordinated bridging and terminal alkyne carbon atoms are observed at δ = 126.1, 129.9, 157.7, and 165.4. The signals for $C(CH_3)_2OH$ appear at δ = 69.6 and 70.4 and those of its methyl groups $C(CH_3)_2OH$ at δ = 31.1, 32.8, 33.9, 34.6. The methyl carbon atoms of the $(CH_3)_3Si$ groups show only two resonances at δ = 0.4 and 1.7, indicating that the terminally coordinated alkynes as well as the bridging alkynes are bound highly symmetrically. On the other hand, the presence of only one set of signals indicates the absence of other diastereomeric complexes. So the solution contains only both enantiomers, which are also found in the X-ray structure analysis. Consistent with this spectrum the 400-MHz ^{1}H-NMR spectrum ([D$_8$]THF, −15 °C) exhibits only two signals, at δ = 0.19 and 0.27, each representing nine hydrogen atoms for the methyl groups of the trimethylsilyl groups and four resonances, each with an intensity of three hydrogen atoms, at δ = 1.33, 1.46, 1.48, 1.66 for $C(CH_3)_2OH$. The C–H-correlated spectrum (400 MHz, [D$_8$]THF, −15 °C, HMQC) shows the resonances at δ = 1.46 and 1.48 corresponding to the resonances at δ = 31.1 and 32.8 in the ^{13}C-NMR spectrum and the resonances at δ = 1.33, 1.66 corresponding to those at δ = 33.9, 34.6, respectively. Two signals for the protons of the OH groups are observed at δ = 5.63 and 6.53. In order to observe long-range couplings, an HMBC spectrum (400 MHz, [D$_8$]THF, −15 °C) was also recorded. It clearly shows that the lowest-field signal in the ^{13}C-NMR spectrum at δ = 165.4 relates to the protons of the methyl groups of the $C(CH_3)_2OH$ moieties at δ = 1.33 and 1.66, and the signal at δ = 157.7 relates to those at δ = 1.46 and 1.48. Consistent with this, the resonance at δ = 129.9 relates to that at δ = 0.27 of the methyl groups of the $Si(CH_3)_3$ group, and the resonance at δ = 126.1 relates to that at δ = 0.19.

Compared with the free alkyne the coordinated alkyne carbon atoms carrying a $C(CH_3)_2OH$ moiety show shifts of $\Delta\delta$ = 42.2 and 45.9 downfield, and the alkyne carbon atoms carrying $Si(CH_3)_3$ groups show shifts of $\Delta\delta = 44.2$ and 51.9.

Correlations between the chemical shift $\Delta\delta$ of the alkyne carbon atoms and the coordination behaviour of the alkynes are described in refs.[7,8]. However, compared with our investigations it seems inappropriate to generalize these results for a variety of metal alkyne systems.

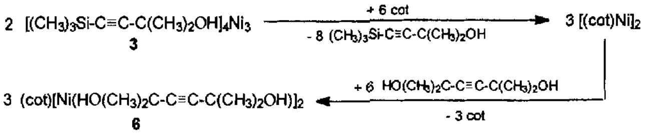
The IR spectrum of **3** shows the stretching vibrations of the coordinated C≡C bonds as strong bands at 1861 and 1607 cm^{-1}. So the IR spectrum is the more sensitive indicator for the differently bound alkynes. The use of the $\Delta\tilde{\nu}$ values for the determination of the strength of the alkyne coordination is described in refs.[9,10].

To confirm the presence of H−O···H interactions in solution, a NOESY spectrum (400 MHz, [D_8]THF, −15 °C) was recorded. It clearly shows an NOE interaction between the protons of the different OH groups at $\delta = 5.63$ and 6.53. Concentration variations of **3** have no influence on the position of these protons (200 MHz, [D_8]THF, −15 °C). Variation of the measuring temperature (200 MHz, [D_8]THF, 20, 0, −20, ..., −100 °C) only leads to the same shift for the protons of the OH groups ($\delta = 5.35$, 6.26 at 20 °C and 6.03, 6.94 at −100 °C). So it seems likely that there are also strong intramolecular hydrogen bonds in solution, which could have a more general influence on organometallic reaction pathways and catalytic processes.

Reactions of 3

Scheme 1 shows an overview of some ligand exchange reactions of **3** with other alkynes in THF at 25 °C. The alkynol $(CH_3)_3CC{\equiv}CC(CH_3)_2OH$ as well as some alkynediols form exclusively the $(alkyne)_2Ni$ complexes **4** and **5**. Complex **4** can also be prepared from the alkyne and (cdt)Ni whereas compound **5**, containing the bulky alkyne 3-ethyl-6-isopropyl-7-methyloct-4-yne-3,6-diol, was not accessible from (cdt)Ni. The NMR and IR data for **5** show that this complex has the same structure as other $(alkyne)_2Ni$ complexes[4].

Cot is able to displace all alkyne units from **3** to yield the dimeric compound $[(cot)Ni]_2$. On the other hand, $[(cot)Ni]_2$ reacts with 2,5-dimethylhex-3-yne-2,5-diol with formation of the mixed ligand complex $(alkyne)_2Ni_2(cot)$ **6**, indicating the very variable organometallic chemistry of alkyne−nickel(0) combinations. To our knowledge **6** is the first alkyne complex of nickel(0) to contain only alkyne units and cot.

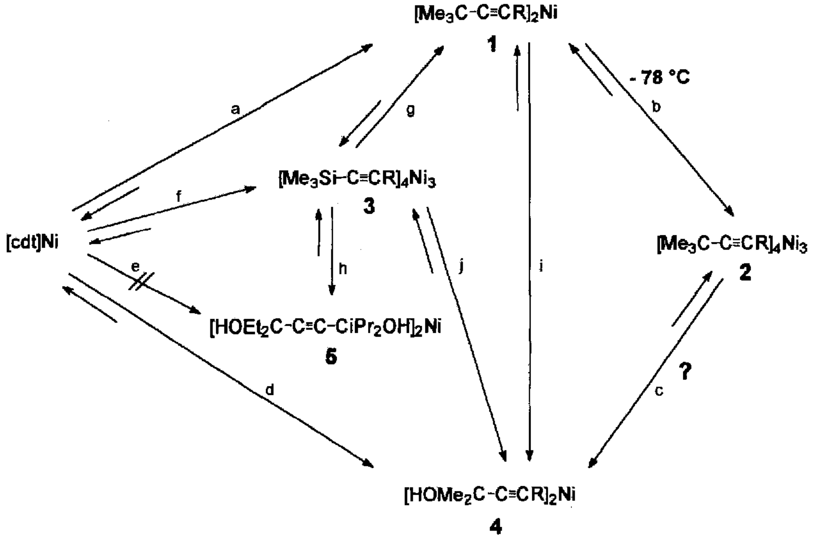


Due to the principal importance of alkyne-cot nickel complexes for modeling catalytic cyclotetramerization reactions of alkynes at the ligand-free nickel(0) center[11], an X-ray determination of **6** was carried out.

The compound crystallizes from THF as orange-red crystals. Figure 3 shows the molecular structure and selected bond lengths and angles. The Ni atom is situated on a crystallographic twofold axis. Therefore, the center of the cot ligand occupies a position at the crystallographic fourfold axis perpendicular to the twofold axis on which the Ni atom is found. Two (alkyne)Ni(0) fragments are coordinated symmetrically to the cot ring, which acts as a four-dendate bridging ligand. The Ni−C bonds between the coordinated alkyne and the central atom (average distance 1.88 Å) are significantly shorter than the distances between Ni and the coordinated cot (average length 2.09 Å). As expected the C=C and C≡C bond distances in the coordinated unsaturated systems are elongated compared with those in the free ligands.

In contrast to the postulated structure of binuclear cot nickel complexes that possibly play a role in the catalytic cyclotetramerization of acetylenes[11], in compound **6** the cot ring is not planar and both metal centers coordinate at opposite sides of the cot ring system.

Scheme 1



R = CMe2OH

a: + Me3C -C≡CR, - cdt[4]

b: - Me3C -C≡CR[4]

c: + HOMe2C -C≡CR, - Me3C -C≡CR

d: + HOMe2C -C≡CR, - cdt

e: + HOEt2C -C≡C-CiPr2OH

f: + Me3Si -C≡CR, - cdt

g: + Me3C -C≡CR, - Me3Si -C≡CR

h: + HOEt2C -C≡C-CiPr2OH, - Me3Si -C≡CR

i: + HOMe2C -C≡CR, - Me3C -C≡CR

j: + HOMe2C -C≡CR, - Me3Si -C≡CR

Figure 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Ni−C1 1.884(7), Ni−C5 2.102(7), Ni−C6 2.077(8), C1−C1a 1.26(1), C5−C6 1.46(1), C1−Ni−C1a 39.1(4), C1−Ni−C5 148.2(3), C1−Ni−C6 146.3(3), C1a−C1−C2 151.5(4)

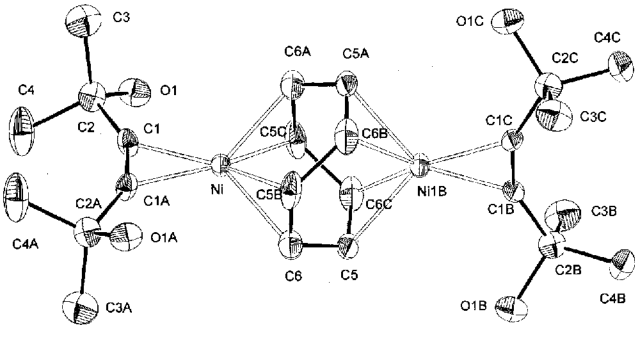
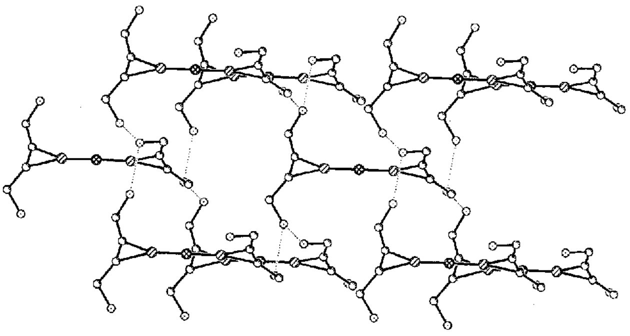


Figure 4. System of hydrogen bridges of **6**. Selected intermolecular distances (Å): O1aa−O1 2.73(1); methyl groups have been omitted for clarity; cot ligands indicated as ⊗



A very complex hydrogen-bonded network is built up, containing exclusively intermolecular hydrogen bonds. Figure 4 shows a part of the supramolecular structure. Each molecule of complex **6** shows eight intermolecular hydrogen bonds to its eight surrounding molecules. Each of the alkyne ligands forms two hydrogen bonds, with the two molecules in the layer above and below its own. Hydrogen bonds only occur between alkyne ligands whose Ni−alkyne planes are perpendicular to each other.

Support of this research by the *Deutsche Forschungsgemeinschaft* (Sonderforschungsbereich 247) and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

General: All operations were carried out under argon using standard Schlenk and vacuum techniques. THF, ether and hydrocarbon solvents were dried and distilled from sodium diphenyl ketyl. The NMR solvents were dried in the same way. (cdt)Ni and $[(cot)Ni]_2$ were prepared as described in the literature[12]. 2-Methyl-4-trimethylsilyl-3-butyn-2-ol and 2,5-dimethyl-hex-3-yne-2,5-diol were obtained from Lancaster; 2,5,5-trimethylhex-3-yn-2-ol was prepared from 3,3-dimethylbut-1-yne (Aldrich) by reaction with butyllithium and acetone. 3-Ethyl-6-isopropyl-7-methyloct-4-yne-3,6-diol was prepared from the monosubstituted alkyne 3-ethylpent-1-yn-3-ol (Lancaster) in a similar way[13]. Compound **4** was prepared from (cdt)Ni and 2,5-dimethyl-hex-3-yne-2,5-diol in a similar way to that previously described[4].

100-MHz ^1H- and 50.3-MHz ^{13}C-NMR spectra: Bruker AC 200 spectrometer. 400-MHz ^1H- and 100.6-MHz ^{13}C-NMR spectra: Bruker DRX 400 spectrometer. – Infrared spectra: Perkin-Elmer FT-IR system, KBr plates. – Mass spectra: Finnigan MAT SSQ 710 mass spectrometer.

Preparation of **3**: (cdt)Ni (0.21 g, 0.95 mmol) and 0.30 g (1.90 mmol) of 2-methyl-4-trimethylsilyl-3-butyn-2-ol were mixed in 10 ml of pentane at −40 °C. After warming to room temperature the solution was filtered and the filtrate was allowed to stand for 2 h. The solution was concentrated to 5 ml. Compound **3** precipitated at −25 °C. Twofold recrystallization from pentane afforded pure **3**. Yield: 0.17 g (68%). dec. 108 °C. – ^1H NMR (400 MHz, $[D_8]$THF, −15 °C): δ = 0.19, 0.27 (each s, 9H, CH_3Si), 1.33, 1.46, 1.48, 1.66 (each s, 3H, CH_3C), 5.63, 6.53 (each s, 1H, OH). – ^{13}C NMR (100.6 MHz, $[D_8]$THF, −15 °C): δ = 0.4, 1.7 (CH_3Si), 31.1, 32.8, 33.9, 34.6 (CH_3C), 69.6, 70.4 [$C(CH_3)_2OH$], 126.1, 129.9 (≡CSi), 157.7, 165.4 (≡CC). – IR (Nujol): $\tilde{\nu}$ = 1861 (s, C≡C), 1607 (s, C≡C), 3183 (s, OH), 3255 (s, OH) cm^{-1}. $C_{32}H_{64}O_4Si_4Ni_3$ (801.3): calcd. C 47.97, H 8.05, Ni 21.97; found C 48.36, H 8.25, Ni 21.85.

Investigation of the Reaction Solution for the Transformation (cdt)Ni → **3**: (cdt)Ni (0.17 g, 0.77 mmol) and 0.24 g (1.54 mmol) of 2-methyl-4-trimethylsilyl-3-butyn-2-ol were dissolved at −40 °C in 7 ml of THF. After warming the solution was filtered and the filtrate allowed to stand at room temperature for 2 h. The solvent was evaporated in vacuo and the oily residue was investigated. **3**: ^{13}C NMR (50.3 MHz, $[D_8]$THF, 25 °C): δ = 0.4, 1.6 (CH_3Si), 31.3, 32.7, 33.9, 34.6 (CH_3C), 69.6, 70.3 [$C(CH_3)_2OH$], 126.2, 130.3 (≡CSi), 158.0, 165.3 (≡CC). – IR: $\tilde{\nu}$ = 1861 (s, C≡C), 1607 (s, C≡C) cm^{-1}.

Preparation of **6**: $[(cot)_2Ni]_2$ (0.70 g, 2.15 mmol) and 0.48 g (3.38 mmol) of 2,5-dimethylhex-3-yne-2,5-diol were suspended in 25 ml of THF. The suspension was then refluxed for 72 h. After cooling to room temperature the precipitate was extracted with benzene and recrystallized from THF. Yield: 0.49 g (45%). dec. 118 °C. – ^1H NMR (200 MHz, $[D_4]$methanol/$[D_8]$dioxane = 1:1, 60 °C): δ = 1.30 (s, 3H, CH_3), 5.76 (s, 1H, CH=), OH not detected. – ^{13}C NMR (50.3 MHz, $[D_4]$methanol/$[D_8]$dioxane = 1:1, 60 °C): δ = 31.8 (CH_3), 70.1 [$C(CH_3)_2OH$], 102.7 (CH=), 132.8 (≡CC). – IR (Nujol): $\tilde{\nu}$ = 1851 (s, C≡C), 3292 (s, OH) cm^{-1}. – $C_{24}H_{36}O_4Ni_2$ (505.9): calcd. Ni 23.20; found Ni 22.86.

Reactions of the Alkyne Complexes:

3 → **1**: (cdt)Ni (0.24 g, 1.08 mmol) was mixed with 0.339 g (2.17 mmol) of 2-methyl-4-trimethylsilyl-3-butyn-2-ol in 10 ml of pentane at −40 °C. After warming the solution was filtered and left standing at room temperature for 2 h. Then 0.160 g (1.12 mmol) of 2,5,5-trimethylhex-3-yn-2-ol was added. The solution was allowed to stand at room temperature for 2 h, then the solvent was evaporated in vacuo to afford an oily residue. **1**: ^{13}C NMR (50.3 MHz, $[D_8]$THF, 25 °C): δ = 30.4 [$C(CH_3)_3$], 31.5−33.5 (m, CH_3), 67.7 [$C(CH_3)_2OH$], 133.0, 136.5 (≡C); no signals for other nickel species are obtained. – IR: $\tilde{\nu}$ = 1889 (s, C≡C) cm^{-1}.

3 → **4**: (cdt)Ni (0.25 g, 1.13 mmol) and 0.35 g (2.26 mmol) of 2-methyl-4-trimethylsilyl-3-butyn-2-ol were mixed in 13 ml of THF at −40 °C. The solution was filtered and the filtrate was allowed to stand at room temperature for 2 h. A solution of 0.16 g (1.13 mmol) of 2,5-dimethylhex-3-yne-2,5-diol in 10 ml of ether was added. The solution was left standing at room temperature for 2 h and then concentrated to 5 ml. The precipitated **4** was washed twice with ether. Yield: 0.17 g (85% based on the alkynediol). – IR (Nujol): $\tilde{\nu}$ = 1889 (s, C≡C), 3250 (s, OH) cm^{-1}. – $C_{16}H_{28}O_4Ni$ (343.1): calcd. Ni 17.11; found: Ni 17.03. – Hydrolytic decomposition and GC investigation of the organic products: only 2,5-dimethylhex-3-yne-2,5-diol was found as the alkyne.

3 → **5**: Compound **3** (0.07 g, 0.09 mmol) and 0.14 g (0.52 mmol) of 3-ethyl-6-isopropyl-7-methyloct-4-yne-3,6-diol were dissolved in 30 ml of THF at room temperature. The solution was left standing at this temperature for 3 d. Compound **5** precipitated at −30°C. Yield: 0.04 g (30%). dec. 133°C. – ^1H NMR (200 MHz, [D_8]THF, 25°C): $\delta = 0.91-1.08$ (m, 18H, CH_3), 1.65−1.78 (m, 4H, CH_2), 2.03−2.06 (m, 2H, CH), 3.63 and 3.97 (each s, 1H, OH). – ^{13}C NMR (50.3 MHz, [D_8]THF, 25°C): $\delta = 9.1, 0.2$ (CH_3), 17.0, 17.4, 19.1 (CH_3), 34.9, 35.0 (CH), 35.4, 35.6 (CH_2), 74.7, 80.0 (*C*C≡). – ^{13}C MNR (50.3 MHz, [D_6]DMF, 25°C): $\delta = 9.0, 9.1, 9.2$ (CH_3), 16.7−19.1 (6 signals CH_3), 74.6, 79.8 (*C*C≡), 133.8, 137.0 (C≡). IR (Nujol): $\tilde{\nu} = 1882$ (s, C≡C), 3393 (s, OH) cm^{-1}. $C_{28}H_{52}O_4Ni$ (511.4): calcd. C 65.76, H 10.25; found: C 64.59, H 10.71. MS (EI): *m*/*e* 510 (M^{+} ^{58}Ni, 5%) the isotopic pattern corresponds well with the simulated one, 284 (M^+−alkyne, 10%), 266 (M^+−alkyne−H_2O, 6%) 248 (M^+−alkyne−2 H_2O, 63%), 183 (M^+−alkyne−C_3H_5, 19%), 165 (M^+−alkyne−C_3H_5−H_2O, 100%).

3 → *[(cot)Ni]$_2$*: Compound **3** (0.06 g, 0.07 mmol) and 0.02 g (0.22 mmol) of cot were dissolved in 7 ml of pentane at −40°C. The solution was allowed to warm to room temperature and left standing at this temperature for 4 d. The precipitate was washed with pentane.

Yield: 0.03 g (82%). – IR (Nujol): no bands for coordinated alkynes and OH groups. – $C_{16}H_{16}Ni_2$ (325.7): calcd. C 59.01, H 4.95; found C 58.67, H 5.15. – Hydrolytic decomposition and GC investigation of the organic products: only cot was found.

X-ray diffraction data: CAD4 diffractometer using graphite-monochromated Mo-K_α radiation. The crystals were mounted in a cold nitrogen stream. Data were corrected for Lorentz and polarization effects, but not for absorption[14]. The structures were solved by direct methods (SHELXS[15]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[16]). Hydrogen atoms were included at calculated positions with fixed thermal parameters; all non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **3**[17]: $C_{32}H_{64}O_4Si_4Ni_3$, $M_r = 801.32$ g mol^{-1}, dark red quadratic, size 0.40 × 0.38 × 0.38 mm, monoclinic, space group $P2_1/n$, $a = 11.833(1)$, $b = 16.692(2)$, $c = 23.224(2)$ Å, $\beta = 100.57(1)°$, $V = 4509.3(7)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.18$ cm^{-3}, μ (Mo-K_α) = 13.7 cm^{-1}, $F(000) = 1712$, 10221 reflections in $-h, +k, +l$, measured in the range $2.43° \leq \Theta \leq 27.35°$, 9778 independent reflections, $R_{int} = 0.029$, 6556 reflections with $F_o > 4\sigma(F_o)$, 406 parameters, $R = 0.040$, $wR^2 = 0.086$, GOOF = 1.055, largest difference peak: 0.51 e Å^{-3}.

Crystal Data for **6**[17]: $C_{24}H_{36}O_4Ni_2$, $M_r = 505.96$ g mol^{-1}, orange-red quadratic, size 0.15 × 0.1 × 0.07 mm, tetragonal, space group $I\bar{4}$ (No. 82), $a = 9.225(1)$, $b = 9.225(1)$, $c = 14.374(3)$ Å, $V = 1221.8(3)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.38$ g cm^{-3}, μ (Mo-K_α) = 15.7 cm^{-1}, $F(000) = 536$, 1506 reflections in $+h, +k, +l$, measured in the range $2.62° \leq \Theta$ 26.90°, 1340 independent reflections, $R_{int} = 0.040$, 1274 reflections with $F_o > 4\sigma(F_o)$, 74 parameters, $R = 0.0628$ $wR^2 = 0.1670$, GOOF = 1.157, largest difference peak: 1.067 e Å^{-3}.

☆ Dedicated to Professor Walter Siebert on the occasion of his 60th birthday.

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[17] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405337 (**3**) and CSD-405338 (**6**), the names of the authors, and the journal citation.

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