Synthesis, Properties, and Solid-State Structures of Bis(alkyne)metal(0) Complexes (Metal = Ni, Pt) with Substituted Alkynediols and Alkynols

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Received November 20, 1995[⊗]

A variety of tetrasubstituted alkynediols react with (cdt)Ni (cdt = 1.5.9-cyclododecatriene) to give the homoleptic (alkyne)nickel complexes $(HOR^1R^2CC{\equiv}CCR^1R^2OH)_2Ni$ as yellow crystals that are stable in the solid state at room temperature ($R^1 = R^2 = Et$, **1**; $R^1 = Me$, $R^2 = Et$, **2**; $R^1 = Me$, $R^2 = Pr$, **3**; $R^1 = R^2 = -(CH_2)_5-$, **4**; $R^1 = Me$, $R^2 = i$-Bu, **5**). The ^{13}C-NMR spectra show resonances for the coordinated alkyne carbon nuclei in the 133.5−135.2 ppm region. Only one resonance was found for **1**−**4** indicating a symmetrical structure. More than one resonance was found for **5** as well as for its platinum analog, compound **8**, indicating the presence of different isomeric bis(alkyne)metal complexes. The structure of **1** has been established by single-crystal X-ray diffraction. The central atom is tetrahedrally coordinated to the four carbon atoms of two terminal alkynes. The network of hydrogen bonding between the four OH groups of neighboring molecules, which consists exclusively of intermolecular hydrogen bonds, stabilizes the crystal structure yielding a polymer-like chain. The platinum complex **9** ($R^1 = R^2 = Me$) shows similar structural properties. The reaction of (cdt)Ni or $(cod)_2Pt$ (cod = 1.5-cyclooctadiene) with the substituted alkynols $R_3CC{\equiv}CCR^1{}_2OH$ yields the new bis(alkyne)metal(0) compounds **10** (M = Ni, R = Me, R^1 = Me), **11** (M = Pt, R = Me, R^1 = Me), and **12** (M = Ni, R = Me, R^1 = Et). Single-crystal X-ray structure determinations of **10**−**12** reveal that the central metal atoms are tetrahedrally coordinated by the four carbon atoms of the alkyne ligands. Two $(alkyne)_2M$ units are connected via hydrogen bonds between the four OH groups to form a dimer in the solid state. Complex **10** reacts in solution below −15 °C to yield the trimeric complex $(alkyne)_4Ni_3$.

Introduction

The simplest stable homoleptic (alkyne)metal compounds of the type $(alkyne)_2M(0)$ are of interest not only as starting materials for organometallic reactions, in particular for catalytic processes, but also as model compounds for understanding the interaction of alkynes with metal surfaces. Until 1994, only platinum complexes of this type were known,[1−4] partly because attempts to isolate bis(alkyne)nickel(0) complexes had been unsuccessful.[5,6] However, some cyclotriynes have been shown to react with $(cod)_2Ni$ (cod = 1.5-cyclooctadiene) to give nickel(0) complexes in which the central atom is coordinated to the three alkyne moieties of the macrocycles.[7−9]

Very recently we were able to synthesize the first crystalline bis(alkyne)nickel(0) complex, $(2,5\text{-dimethylhex-3-yne-2,5-diol})_2Ni$, which was structurally characterized by single-crystal X-ray diffraction.[10]

By using 2-methyl-5,5-dimethylhex-3-yn-2-ol as the ligand, we also were able to isolate the trimeric homoleptic alkyne complex $(alkyne)_4Ni_3$, which contains two bridging alkyne ligands.[11] In both complexes the OH groups are tolerated by the low-valent nickel atom and appear to be very important in stabilizing the structure in the solid state.

In this paper we will show that homoleptic bis(alkyne)Ni compounds can be isolated with a wide variety of different alkynes although one requirement is that they possess OH groups. In order to determine whether one central metal atom was unique in determining the structure of these novel materials, two new platinum complexes also were prepared. One goal of this investigation was to study the molecular assembly

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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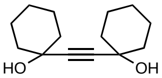
S0276-7333(95)00896-X CCC: $12.00

Table 1. Selected IR- and ^{13}C-NMR Values and Decomposition Temperatures for $(HOR^1R^2CC{\equiv}CCR^1R^2OH)_2Ni$ (1−5)

compd	alkyne	$\nu_{C\equiv C}$ (cm^{-1})	$\delta_{C\equiv}$ (ppm)	decomposn pt (°C)
1	$HOEt_2CC{\equiv}CCEt_2OH$	1904	134.3	173
2	$HOMe(Et)CC{\equiv}CC(Et)MeOH$	1889	133.5	132
3	$HOMe(Pr)CC{\equiv}CC(Pr)MeOH$	1887	134.5	119
4		1882	135.0	141
5	HOMe(*i*-Bu)CC≡CC(*i*-Bu)MeOH	1885	134.8−135.2[a]	88

[a] 6 signals.

and intermolecular interactions present in the crystals in order to understand the role of the OH groups in stabilizing the crystalline structure.

Results and Discussions

The reaction of (cdt)Ni with many substituted alkynediols in THF at −40 °C leads to the formation of the homoleptic (alkyne)$_2$Ni complexes according to eq 1. The

$$(cdt)Ni + 2HOR^1R^2CC{\equiv}CCR^1R^2OH \rightarrow (HOR^1R^2CC{\equiv}CCR^1R^2OH)_2Ni + cdt$$

compounds **1**−**5** (see Table 1) could be isolated as pure crystalline compounds. At low temperatures there is no evidence for C−C linkage of the alkynes at the low-valent nickel center.

In contrast, the reaction of (cod)$_2$Ni with 2,4,7,9-tetramethyldec-5-yne-4,7-diol and the reaction of (cod)$_2$Ni with 3,6-diethyloct-4-yne-3,6-diol results in the formation of the mixed-ligand complexes (cod)Ni(alkyne), **6** and **7**, while 2,5-dimethylhex-3-yne-2,5-diol yields the corresponding (alkyne)$_2$Ni compound.[10] There are two possible routes for the formation of **6** and **7** from (cod)$_2$Ni: on one hand a substitution of a cyclooctadiene ligand against an alkyne and on the other hand the intermediate formation of the bis(alkyne)nickel complex and a subsequent syn-proportionation reaction with (cod)$_2$Ni.

The solid yellow compounds **1**−**5** (Table 1) are stable at room temperature and extremely sensitive toward air and moisture. They are insoluble in pentane but can be dissolved in polar solvents such as THF or DMF. However, their solubility and stability in these solutions is quite poor at room temperature and depends on the size of the R groups. The larger the R group the more soluble and stable in solution is the alkyne complex. The ^{13}C-NMR spectra (see Experimental Section) show that the signals of **1**−**5** for coordinated alkyne carbon atoms are located in the 133.5−135.2 ppm region, a shift of about 47 ppm downfield compared to the corresponding free alkynes. The tertiary carbon signals for the coordinated alkynes shift about 3 ppm downfield as opposed to the free alkyne. The spectra of **1**−**4**, which contain alkynes with unbranched alkyl groups, clearly show that the alkynes are symmetrically coordinated around the central metal atom. Only one resonance for the alkyne carbon nuclei and one resonance for the tertiary carbon atoms are observed. The ^{13}C-NMR spectrum of the (alkyne)$_2$Ni complex **5** (R^1 = Me, R^2 = *i*-Bu) is more complicated. In the region of the signals for the carbons of the C≡C triple bond a series of resonances is observed between 134.8 and 135.2 ppm (see Table 1) indicating the existence of structurally similar isomers in solution. These signals do not split at lower temperatures ([D$_8$]-THF, −60 °C, 50.3 MHz) and do not collapse at higher temperatures ([D$_8$]THF, +40 °C, 50.3 MHz). The corresponding platinum complex, **8**, exhibits the same type of ^{13}C-NMR spectrum.

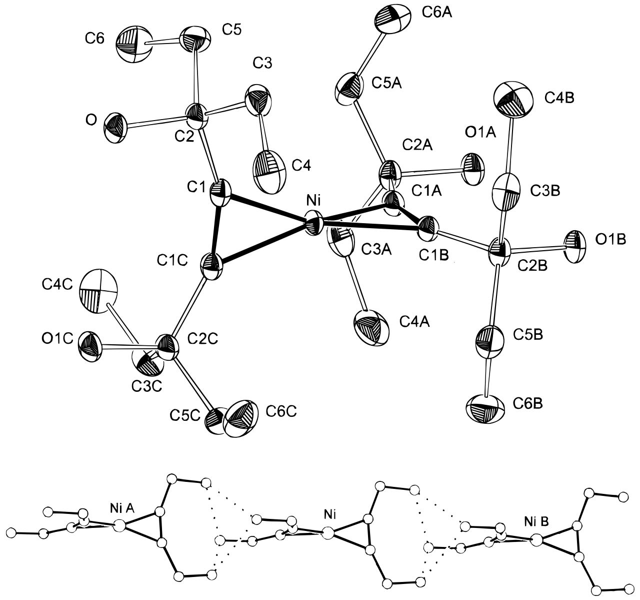


Figure 1. (a) Top: Solid-state structure of $(Et_2(OH)CC{\equiv}CC(OH)Et_2)_2Ni$, **1**. (b) Bottom: Supramolecular structure of $(Et_2(OH)CC{\equiv}CC(OH)Et_2)_2Ni$, **1**. O−O = 2.889, 2.937 Å; ethyl groups have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $(Et_2(OH)CC{\equiv}CC(OH)Et_2)_2Ni$, 1[a]

Ni−C(1)	1.875(1)	C(1)−C(1C)	1.259(3)
C(1)−C(2)	1.494(2)		
C(1)−Ni−C(1A)	153.08(8)	C(1)−Ni−C(1B)	152.01(8)
C(1)−Ni−C(1C)	39.23(8)	C(2)−C(1)−C(1C)	155.34(6)
C(1C)−C(1)−Ni	70.39(4)	C(2)−C(1)−Ni	134.25(9)

[a] Angle between planes (deg): [Ni−C(1)−C(1C)]−[Ni−C(1A)−C(1B)] = 87.81.

The infrared specta of **1**−**5** show the bands assigned to the stretching vibrations of coordinated C≡C bonds in the 1882−1904 cm^{-1} region (Table 1). The IR- and ^{13}C-NMR spectroscopic data correspond well with those of the described bis(alkyne)platinum compounds.[3]

The single-crystal X-ray structure determination of **1** (Table 5) confirms the expected tetrahedral geometry around the nickel(0) center (Figure 1a). Selected bond lengths and angles are tabulated (Table 2). The nickel atom is situated on the intersection of three crystallographic 2-fold axes. Therefore, only the nickel atom itself and half of one of the alkyne ligands are located by X-ray structure analysis, whereas the rest of the molecule is generated by symmetry operations. The Ni−C and C≡C bond lengths show values typical of the known (alkyne)Ni complex with 2,5-dimethylhex-3-yne-2,5-diol as the alkyne ligand.[10] Figure 1b shows the view of the supramolecular structure of **1**. Polymeric chains that are independent of each other exist. In these chains O_4-tetrahedrons are built up via four intermolecular hydrogen bonds which link adjacent molecules. This kind of supramolecular structure was also found in the analogous platinum compound[2] and in the complexes $(HOMe_2CC{\equiv}CMe_2OH)_2M$ (M = Ni, **10**;[10] M = Pt, **9**; see Table 5) and seems to be a general stabilizing principle in the solid-state structures of (alkynediol)$_2$M complexes. In bis(alkyne)metal complexes containing alkynols only two OH groups are present. The questions then arise whether low-valent metal complexes of such acetylenes can be synthesized and would these have a similar type of supramolecular structure.

The reaction of 1 molar equiv of (cdt)Ni with 2 equiv of 2-methyl-5,5-dimethylhex-3-yn-2-ol in pentane yields at room temperature quantitatively the complex (alkyne)$_2$Ni, **10**, in solution, which was identified by its IR spectrum (ν(C≡C) = 1892 cm^{-1}), ^{1}H-NMR spectrum, and ^{13}C-NMR spectrum (133.2 and 136.5 ppm for coordinated alkyne-carbon atoms). No signals were observed for bridging alkynes or coordinated cdt at room temperature. These results show that at room temperature no detectable quantities of other (alkyne)Ni complexes are present in solution, because only one set of signals indicative of only one kind of coordinated alkyne is observed. Surprisingly at −78 °C the trimeric complex (alkyne)$_4$Ni$_3$ crystallizes from the solution[11] as a result of an aggregation process at low temperature according to eq 2. Small quantities of **10** can be isolated

$$3(\text{alkyne})_2\text{Ni} \rightleftharpoons (\text{alkyne})_4\text{Ni}_3 + 2\text{alkyne}$$

from a pentane/THF solution (100/1) at −78 °C as yellow crystals. These are stable under argon at low temperature. The existence of different homoleptic (alkyne)-nickel complexes with the same alkyne leads us to conclude that only small energy differences exist between the different alkyne nickel species and that the ligand and the crystallization conditions have a decisive influence on the composition of the (alkyne)nickel(0) complexes that can be isolated.

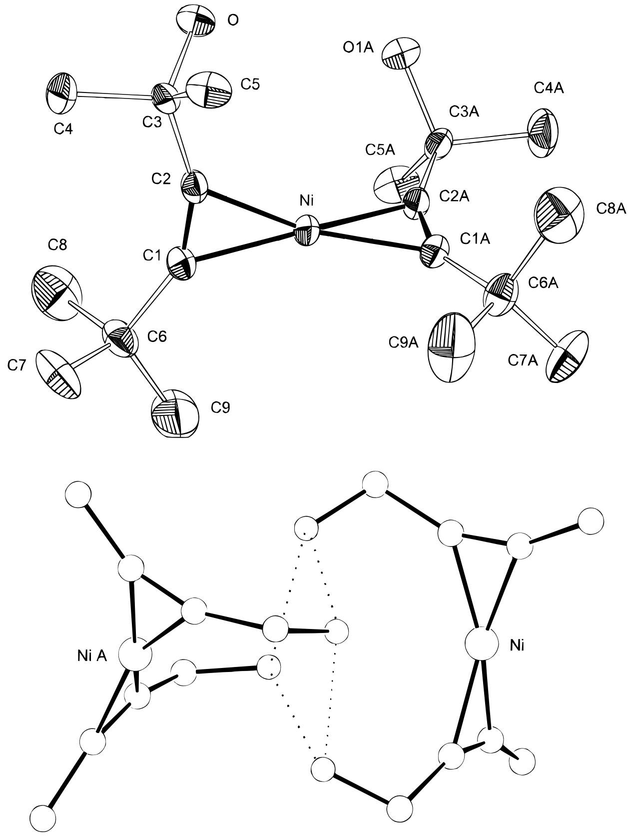


Figure 2. (a) Top: Solid-state structure of $(Me_3CC{\equiv}CC(OH)Me_2)_2Ni$, **10**. (b) Bottom: Supramolecular structure of $(Me_3CC{\equiv}CC(OH)Me_2)_2Ni$, **10**. O−O = 2.816, 2.775 Å; methyl groups have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $(Me_3CC{\equiv}CC(OH)Me_2)_2Ni$, 10[a]

Ni−C(1)	1.888(2)	Ni−C(2)	1.881(2)
C(1)-C(2)	1.260(4)	C(1)−C(6)	1.498(4)
C(2)−C(3)	1.499(4)		
C(1)−Ni−C(2)	39.0(1)	Ni−C(1)−C(2)	70.2(2)
C(1)−Ni−C(1A)	155.6(2)	C(2)−Ni−C(2A)	147.7(2)
C(1)−Ni−C(2A)	153.4(1)	C(2)−Ni−C(1A)	153.4(1)
C(1)−C(2)−Ni	70.8(2)	Ni−C(1)−C(6)	136.9(2)
Ni−C(2)−C(3)	133.9(2)	C(1)−C(2)−C(3)	154.9(2)
C(2)−C(1)−C(6)	152.5(3)		

[a] Angle between plane (deg): [Ni−C(1)−C(2)]−[Ni−C(1A)−C(2A)] = 94.33.

The result of the solid-state study of **10** (Table 5) is shown in Figure 2a. Selected interatomic distances and angles are listed in Table 3. Yet again the metal atom is tetrahedrally coordinated by the four alkyne-carbon atoms. The observed values for the C≡C bond lengths correspond to those of **1**. **10** crystallizes as a dimer, via four hydrogen bonds in which the oxygen atoms each occupy a corner of a "square". The oxygen atoms of any one molecule lie diagonal with respect to each other so that no intramolecular hydrogen bond can be formed (Figure 2b). A very similar structure was found for the corresponding platinum complex **11** (Table 5), which results from the reaction of (cod)$_2$Pt with 2-methyl-5,5-dimethylhex-3-yn-2-ol. Its IR- and ^{13}C-NMR data are also very similar to those of **10**: ν(C≡C) = 1889 cm^{-1}; δ(C≡) 127.8 and 131.9 ppm. The reaction of 3-ethyl-6,6-dimethylhept-4-yn-3-ol with (cdt)Ni yields the complex (alkyne)$_2$Ni, **12**, as yellow crystals that are stable in the solid state under argon at low temperatures. In the IR spectrum of **12** the band for the C≡C stretching vibration appears at 1901 cm^{-1}. The ^{13}C-NMR signals for the carbon atoms of the coordinated alkynes are observed at 128.5 and 138.2 ppm. By using diethyl ether as the solvent, single crystals of **12** suitable for single-crystal X-ray structural analysis were obtained at −78 °C (Table 5). Complex **12** shows the anticipated structural features; namely, the nickel atom is tetrahedrally coordinated by the four alkyne-carbon atoms with typical bond distances and angles (Figure 3a; for selected values, see Table 4). The tertiary butyl group of one of the alkyne ligands is disordered. The supramolecular structure shows that dimers as described for **10** and **11** are formed (Figure 3b). The (cod)-Ni(alkynediol) complexes **6** and **7** are yellow-orange, air-sensitive compounds. Their X-ray structure investigations (Table 5) show the same type of hydrogen-

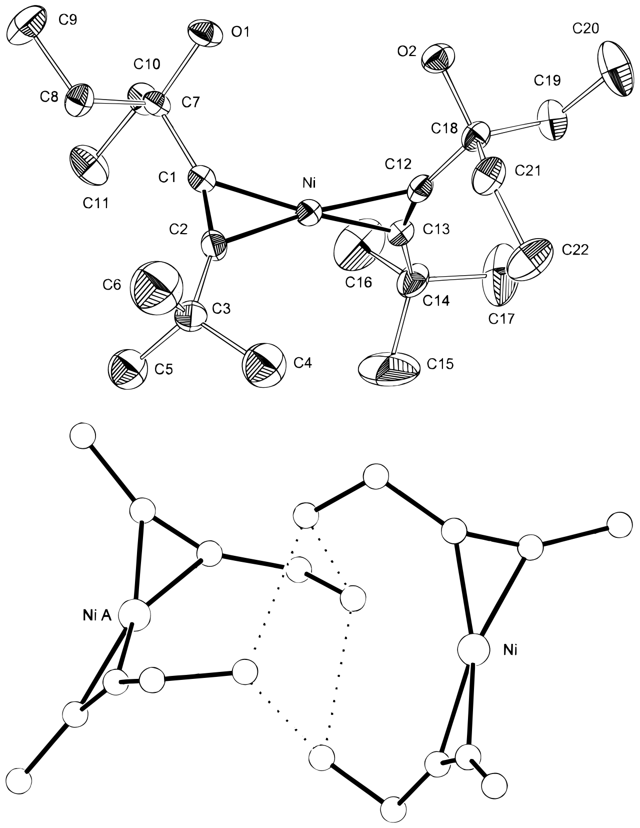


Figure 3. (a) Top: Solid-state structure of $(Me_3CC{\equiv}CC(OH)Et_2)_2Ni$, **12**. (b) Bottom: Supramolecular structure of $(Me_3CC{\equiv}CC(OH)Et_2)_2Ni$, **12**. O−O = 2.788, 2.807 Å; methyl and ethyl groups have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of $(Me_3CC{\equiv}CC(OH)Et_2)_2Ni$, 12

Ni−C(1)	1.874(4)	Ni−C(2)	1.875(4)
Ni−C(12)	1.882(4)	Ni−C(13)	1.880(4)
C(1)−C(2)	1.259(5)	C(12)−C(13)	1.250(5)
C(1)−C(7)	1.485(5)	C(2)−C(3)	1.510(5)
C(12)−C(18)	1.501(5)	C(13)−C(14)	1.493(5)
C(1)−Ni−C(2)	39.2(2)	Ni−C(1)−C(2)	70.5(2)
C(1)−Ni−C(12)	150.3(2)	C(2)−Ni−C(13)	152.8(2)
C(7)−C(1)−C(2)	155.5(4)	C(3)−C(2)−C(1)	154.6(4)
Ni−C(12)−C(13)	70.5(2)	C(18)−C(12)−C(13)	155.6(4)
C(14)−C(13)−C(12)	156.8(4)		

[a] Angle between plane (deg): [Ni−C(1)−C(2)]−[Ni−C(12)−C(13)] = 94.78.

bonded network as described for the mixed-ligand complex (cod)Ni(2,5-dimethylhex-3-yn-2,5-diol).[10]

Summary

From this study we can conclude the following: (i) $(alkyne)_2Ni$ complexes are quite stable in the solid state because they are stabilized by hydrogen bonds between the OH groups of neighboring molecules. (ii) In each Ni or Pt complex that was investigated by single-crystal X-ray diffraction four OH groups from neighboring alkynes are responsible for the same type of hydrogen-bonded network. This network is set up by four intermolecular hydrogen bonds. When the ligands are alkynediols, this feature leads to the formation of polymeric chains, whereas when alkynols are used, dimeric complexes are formed. (iii) Only small energy differences exist between the complexes $(2\text{-methyl-5,5-dimethylhex-3-yn-2-ol})_4Ni_3$ and $(2\text{-methyl-5,5-dimethylhex-3-yn-2-ol})_2Ni$. Both complexes can be isolated.

Experimental Section

All operations were carried out in an argon atmosphere using standard Schlenk and vacuum techniques. THF, diethyl ether, and hydrocarbon solvents were dried and distilled from sodium diphenyl ketyl. The NMR solvents were dried in the same way. The alkynes were prepared according to the literature procedures from Li_2C_2 and the ketone or by the reaction of commercial monosubstituted acetylenes with butyllithium and the ketone.[12,13]

(cdt)Ni and $(cod)_2Pt$ were prepared as described.[14,15]

The 200 MHz ^{1}H- and 50.3 MHz ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer. The 400 MHz ^{1}H- and 100.6 MHz ^{13}C-NMR spectra were recorded on a Bruker DRX 400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer FT-IR system working quickly with a Nujol mull between KBr plates.

Single-crystal X-ray structure determinations were carried out at low temperature on an Enraf-Nonius CAD4 diffractometer; the structures were solved by direct (**1**, **6**, **7**, **10**, **12**) or Patterson methods (**9**, **11**), respectively, followed by least-squares refinement using the programs SHELX-86 and SHELXL-93.[16] Computation of the structures was done with the program XPMA, and the molecular illustrations were drawn using the program ZORTEP.[17] The crystal and intensity data of **1**, **6**, **7**, and **9**−**12** are given in Table 5.

Nickel Compounds. $(3,6\text{-Diethyloct-4-yne-3,6-diol})_2Ni$, 1. A 2.37 mmol (0.532 g) amount of (cdt)Ni and 4.73 mmol (0.937 g) of 3,6-diethyloct-4-yne-3,6-diol were mixed in 50 mL of THF at −40 °C. The solution was allowed to reach room temperature and was then filtered, whereupon 30 mL of hexane was added. At room temperature **1** precipitated as yellow needles. Single crystals were obtained from DMF. Yield: 2.09 mmol (0.95 g); 88.2%. Anal. Calc for $C_{24}H_{44}O_4Ni$: Ni, 12.89. Found: Ni, 12.76. IR (Nujol): 1904 (s, C≡C), 3400 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_7$]DMF, 35 °C, 50.3 MHz): δ 0.99 (m, CH_3, 24 H), 1.67 (m, CH_2, 16 H). ^{13}C-NMR ([D$_7$]DMF, 35 °C, 200 MHz): δ 9.1 (CH_3), 35.4 (CH_2), 74.3 (CEt_2OH), 133.3 (C≡). Decomposn pt = 173 °C.

$(3,6\text{-Dimethyloct-4-yne-3,6-diol})_2Ni$, 2. A 1.22 mmol (0.270 g) amount of (cdt)Ni and 2.44 mmol (0.410 g) of 3,6-dimethyloct-4-yne-3,6-diol were mixed at −40 °C in 40 mL of THF. After being warmed to room temperature, the mixture was filtered and 30 mL of hexane was added. At 25 °C **2** crystallized in the form of yellow needles. Yield: 0.72 mmol (0.281 g); 59.0%. Anal. Calc for $C_{20}H_{36}O_4Ni$: C, 60.27; H, 9.11; Ni, 14.55. Found: C, 60.36; H, 8.75; Ni, 14.62. IR: 1889 (s, C≡C), 3306 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_7$]DMF, 200 MHz, 25 °C): δ 0.98 (t, CH_3, 12 H), 1.54 (s, CH_3, 12 H), 1.68 (q, CH_2, 8 H), 4.74 (s, OH, 4 H). ^{13}C-NMR ([D$_7$]DMF, 25 °C, 50.3 MHz): δ 9.3 (CH_3), 30.4 (CH_3), 36.4 (CH_2), 70.6 (CMeEtOH), 133.5 (C≡). Decomposn pt = 132 °C.

$(4,7\text{-Dimethyldec-5-yne-4,7diol})_2Ni$, 3. A 1.49 mmol (0.330 g) amount of (cdt) Ni and 2.99 mmol (0.598 g) of 4,7-dimethyldec-5-yne-4,7-diol were dissolved at −40 °C in a mixture of 15 mL of diethyl ether and 10 mL of THF. After being warmed to room temperature, the mixture was filtered. At room temperature **3** crystallized in the form of yellow needles. Yield: 0.68 mmol (0.375 g); 45.3%. Anal. Calc for $C_{24}H_{44}O_4Ni$: C, 63.40; H, 9.76; Ni, 12.75. Found: C, 63.19; H, 10.04; Ni, 12.70. IR: 1887 (s, C≡C), 3286 (s, OH) cm^{-1}.

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Table 5. Crystal and Intensity Data for the Compounds ($Et_2(OH)CC{\equiv}CC(OH)Et_2)_2Ni$, 1, ($^iBuMe(OH)CC{\equiv}CC(OH)Me^iBu)Ni(cod)$, 6, ($Et_2(OH)CC{\equiv}CC(OH)Et_2)Ni(cod)$, 7, ($Me_2(OH)CC{\equiv}CC(OH)Me_2)_2Pt$, 9, ($Me_3CC{\equiv}CC(OH)Me_2)_2Ni$, 10, ($Me_3CC{\equiv}CC(OH)Me_2)_2Pt$, 11, and ($Me_3CC{\equiv}CC(OH)Et_2)_2Ni$, 12

compd	**1**	**6**	**7**	**9**	**10**	**11**	**12**
formula	$C_{24}H_{44}O_4Ni$	$C_{22}H_{38}O_2Ni$	$C_{20}H_{34}O_2Ni$	$C_{16}H_{28}O_4Pt$	$C_{18}H_{32}O_2Ni$	$C_{18}H_{32}O_2Pt$	$C_{22}H_{40}O_2Ni$
M_r	455.3	393.2	365.2	479.4	339.2	475.5	395.2
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite
temp (K)	183	183	193	183	183	183	183
cryst color	yellow	yellow	yellow	colorless	yellow	colorless	yellow
cryst size (mm)	0.4 × 0.4 × 0.3	0.4 × 0.2 × 0.2	0.6 × 0.4 × 0.1	0.3 × 0.2 × 0.15	0.4 × 0.4 × 0.4	0.8 × 0.6 × 0.3	0.4 × 0.3 × 0.3
a (Å)	8.9050(1)	13.581(1)	10.729(2)	15.30(1)	13.610(1)	13.396(5)	25.166(5)
b (Å)	21.660(2)	15.002(2)	9.564(3)	8.830(4)	14.332(2)	14.124(8)	9.618(2)
c (Å)	26.002(5)	10.451(2)	20.102(4)	15.471(6)	40.972(4)	21.91(2)	22.851(5)
α (deg)	90	90	90	90	90	90	90
β (deg)	90	92.55(5)	102.18(2)	108.37(2)	90	107.67(2)	118.70(3)
γ (deg)	90	90	90	90	90	90	90
V ($Å^3$)	5015(1)	2127.2(5)	2016.3(8)	1984(2)	7991(1)	3950(5)	4851(1)
Z	8	4	4	4	16	8	8
F(000)	1984	856	792	936	2944	1872	1728
ρ_{calc} (g cm^{-3})	1.206	1.228	1.203	1.605	1.127	1.599	1.082
cryst system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*Fddd*	*C*2/*c*	*P*2$_1$/*c*	*Cc*	*Fddd*	*C*2/*c*	*C*2/*c*
abs coeff (mm^{-1})	0.798	0.924	0.997	7.083	0.973	7.107	0.810
abs corr				XABS2[18]		XABS2[18]	
min−max transm				0.831−1.245		0.846−1.152	
θ limit (deg)	2.45−27.41	2.02−25.04	1.94−23.96	2.70−23.56	2.55−27.42	1.95−25.00	2.70−27.44
scan mode	$\omega-2\theta$	$\omega-2\theta$	ω-2θ	ω-2θ	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan speed (deg min^{-1})	1−10	1−10	1−10	1−10	1−10	1−10	1−10
refl measd	1433	1954	3828	2304	4556	3571	5649
indepdt refl.	1433	1871 (R = 0.0680)	2834 (R = 0.0453)	1540 (R = 0.0570)	2286 (R = 0.0412)	3471 (R = 0.0903)	5525 (R = 0.0587)
obs refl $F_o^2 > 2\sigma(F_o^2)$	1286	1748	2390	1427	1632	2867	3376
no. of params	115	188	344	190	104	197	236
GOOF	1.120	1.153	0.876	1.157	1.157	1.153	1.281
R1	0.0230	0.0344	0.0294	0.0501	0.0366	0.0570	0.0578
wR2	0.0582	0.1023	0.0665	0.1286	0.0974	0.1573	0.1411
final diff map electron density (e $Å^{-3}$)	0.306	0.425	0.316	2.260	0.739	2.541	0.847

^{1}H-NMR ([D$_8$]THF, 25 °C, 400 MHz): δ 0.90 (s, CH_3, 6 H), 0.94 (s, CH_3, 6 H), 1.48 (s, CH_3, 12 H), 1.50−2.00 (m, CH_2, 16 H), 4.11 (s, OH, 4 H). ^{13}C-NMR ([D$_8$]THF, 25 °C, 100.6 MHz): δ 14.7 (CH_3), 18.8 (CH_2), 30.6 (CH_3), 47.3 (CH_2), 70.5 (CPr−MeOH), 134.5 (C$\equiv$). Decomposn pt = 119 °C.

(Bis(1-hydroxycyclohexyl)ethyne)$_2$Ni, 4. A 1.10 mmol (0.243 g) amount of (cdt)Ni and 2.20 mmol (0.488 g) of bis(1-hydroxycyclohexyl)ethyne were dissolved at −40 °C in a mixture of 75 mL of diethyl ether and 50 mL of THF. After being warmed to room temperature, the solution was filtered. At −30 °C the product crystallized. Afterward it was washed twice with pentane and dried in vacuum. Yield: 0.45 mmol (0.227 g); 41.2%. Anal. Calc for $C_{28}H_{44}O_4Ni$: C, 66.90; H, 8.83; Ni, 11.53. Found: C, 68.12; H, 8.73; Ni, 11.49. IR: 1882 (s, C$\equiv$C), 3237 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_8$]THF, 25 °C, 200 MHz): δ 1.73 (m, CH_2, 40 H); 4.11 (s, OH, 4 H). ^{13}C-NMR ([D$_8$]-THF, 25 °C, 50.3 MHz): δ 24.1 (CH_2); 26.5 (CH_2); 41.2 (CH_2); 69.8 (CH_2); 135.0 (C$\equiv$). Decomposn pt = 141 °C.

(2,4,7,9-Tetramethyldec-5-yne-4,7-diol)$_2$Ni, 5. A 2.16 mmol (0.447 g) amount of (cdt)Ni and 4.32 mmol (0.977 g) of 2,4,7,9-tetramethyldec-5-yne-4,7-diol were mixed at room temperature in 60 mL of pentane. At −30 °C **5** precipitated. The precipitate was isolated, washed twice with cold pentane (−20 °C), and dried in vacuum. Yield: 1.52 mmol (0.777 g); 70.4%. Anal. Calc for $C_{28}H_{52}O_4Ni$: C, 65.76; H, 10.25; Ni, 11.48. Found: C, 64.02; H, 9.86; Ni, 11.63. IR: 1885 (s, C$\equiv$C), 3304 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_8$]THF, 25 °C, 400 MHz): δ 0.96 (m, CH_3, 24 H), 1.47 (s, CH_3, 12 H), 1.62 (m, CH_2, 8 H), 2.00 (m, CH, 4 H), 3.85 (s, OH, 4 H). ^{13}C-NMR ([D$_8$]THF, 25 °C, 100.6 MHz): δ 24.8 (CH_3), 25.8 (CH), 31.9 (CH_3), 53.1 (CH_2), 70.0−71.1 (4 signals, C-*i*-BuMeOH), 134.8−135.2 (6 signals, C$\equiv$). Decomposn pt = 88 °C.

(cod)Ni(2,4,7,9-tetramethyldec-5-yne-4,7-diol), 6. A 1.02 mmol (0.280 g) amount of 2,4,7,9-tetramethyldec-5-yne-4,7-diol and 1.10 mmol (0.250 g) of (cod)$_2$Ni were refluxed in 10 mL of THF for 2 h. Then the solvent was removed in vacuum and the residue was dissolved in 10 mL of diethyl ether. At −20 °C **6** precipitated. Yield: 0.56 mmol (0.220 g); 54.8%. Anal. Calc for $C_{22}H_{38}O_2Ni$: Ni, 14.93. Found: Ni, 14.81. IR: 1815 (s, C$\equiv$C), 3381 (s, OH) cm^{-1}. ^{1}H-NMR (C_6D_6, 25 °C, 100 MHz): δ 1.02 (m, CH_3, 12 H), 1.34 (s, CH_3, 6 H), 1.53 (m, CH, 2 H), 1.85−2.00 (m, CH_2, 12 H), 2.84 (s, OH, 2 H), 5.28 (s, CH$=$, 4 H). ^{13}C-NMR (C_6D_6, 25 °C, 50.3 MHz): δ 25.0, 29.9, 30.2, 31.8 (CH_3, CH_2), 52.6 (CH_2); δ 73.4 (C-*i*-BuMeOH); δ 95.1 (CH$=$); δ 136.0 (C$\equiv$).

(cod)Ni(3,6-diethyloct-4-yne-3,6-diol), 7. The experimental procedure was carried out in a similar method to that used for **6**. Anal. Calc for $C_{20}H_{34}O_2Ni$: Ni, 16.07. Found: Ni, 16.12. IR: 1808 (s, C$\equiv$C), 3253 (s, OH) cm^{-1}.

(2-Methyl-5,5-dimethylhex-3-yn-2-ol)$_2$Ni, 10. A 1.14 mmol (0.251 g) amount of (cdt)Ni and 2.58 mmol (0.369 g) of 2-methyl-5,5-dimethylhex-3-yn-2-ol were dissolved at −60 °C in 10 mL of pentane. After being warmed to room temperature, the solution was filtered and left standing at room temperature for 4 h. The solvent was evaporated in vacuum. IR: 1892 (s, C$\equiv$C), 3331 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_8$]THF, 25 °C, 200 MHz): δ 1.27 (s, CH_3, 18 H), 1.45 (s, CH_3, 12 H), 3.72 (s, OH, 2 H). ^{13}C-NMR ([D$_8$]THF, 25 °C, 50.3 MHz): δ 30.3 (CMe_3), 31.3−32.5 (CH_3), 67.1 (CMe_2OH), 133.2 and 136.5 (C$\equiv$). Single crystals were obtained from pentane/THF (100/1) as a byproduct of (alkyne)$_4$Ni$_3$. Some crystals were separated. Anal. Calc for $C_{18}H_{32}O_2Ni$: C, 63.75; H, 9.51. Found: C, 63.52, H, 9.78. IR: 1892 (s, C$\equiv$C), 3227 (s, OH) cm^{-1}.

(3-Ethyl-6,6-dimethylhept-4-yn-3-ol)$_2$Ni, 12. A 1.60 mmol (0.353 g) amount of (cdt)Ni and 3.57 mmol (0.60 g) of 3-ethyl-6,6-dimethylhept-4-yn-3-ol were mixed at −35 °C in 20 mL of pentane. After reaching room temperature, the mixture was filtered and left standing for 2 h at room temperature. The solution was concentrated to 5 mL. At −78 °C **12** precipitated. Single crystals were obtained from diethyl ether. Yield: 0.32

mmol (0.126 g); 20%. Anal. Calc for $C_{22}H_{40}O_2Ni$: C, 66.96; H, 10.23. Found: C, 64.96; H, 10.60. IR: 1901 (s, $C\equiv C$), 3441 (s, OH) cm^{-1}. ^{1}H-NMR (C_6D_6, 25°C, 200 MHz): δ 1.06 (t, CH_3, 12 H), 1.24 (s, CH_3, 18 H), 1.77 (q, CH_2, 8 H). ^{13}C-NMR (C_6D_6, 25 °C, 50.3 MHz): δ 9.1 (CH_3), 31.3 (CMe_3), 31.8 (CH_3), 35.5 (CH_2), 73.9 (CEt_2OH), 129.8 and 138.2 ($C\equiv$).

Platinum Compounds. (2,4,7,9-Tetramethyldec-5-yne-4,7-diol)$_2$Pt, 8. A 0.050 mmol (0.206 g) amount of Pt(cod)$_2$ and 1.00 mmol (0.227 g) of (2,4,7,9-tetramethyldec-5-yne-4,7-diol) were dissolved at room temperature in 20 mL of diethyl ether. The mixture was filtered and then concentrated to 8 mL. At −78 °C **8** precipitated. **8** was isolated, washed with pentane, and dried in vacuum. Yield: 0.44 mmol (0.293 g); 87.4%. Anal. Calc for $C_{28}H_{52}O_4Pt$: C, 51.90; H, 8.10. Found: C, 52.18; H, 8.30. IR: 1884 (s, $C\equiv C$), 3298 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_8$]THF, 20 °C, 200 MHz): δ 0.98 (m, CH_3, 24 H); δ 1.46 (s, CH_3, 12 H); δ 1.62 (m, CH_2, 8 H); δ 2.02 (m, CH, 4 H); δ 3.92, 3.95, 3.98 (s, OH, 4 H). ^{13}C-NMR ([D$_8$]THF, 25 °C, 50.3 MHz): δ 25.0 (CH_3), 25.2 (CH), 31.5−31.8 (6 signals, CH_3), 52.6 and 52.7 (CH_2), 69.1−69.2 (3 signals, C-*i*-BuCH_3OH), 130.5−131.0 (6 signals, $C\equiv$).

(2,5-Dimethylhex-3-yne-2,5-diol)$_2$Pt, 9. The experimental procedure was modified from that reported in the literature and was carried out in a similar method to that for **11**.[5] Single crystals are obtained from THF/hexane.

(2-Methyl-5,5-dimethylhex-3-yn-2-ol)$_2$Pt, 11. A 0.47 mmol (0.193 g) amount of (cod)$_2$Pt and 0.94 mmol (0.133 g) of 2-methyl-5,5-dimethylhex-3-yn-2-ol were mixed at −30 °C in 5 mL of diethyl ether. The solution was allowed to warm to room temperature and was then left standing for 3 h. Afterward it was concentrated to 2 mL. At −78 °C **11** precipitated as colorless crystals. Yield: 0.11 mmol (0.052 g), 23%. Anal. Calc for $C_{18}H_{32}O_2Pt$: C, 45.45; H, 6.79. Found: C, 45.88; H, 6.79. IR: 1889 (s, $C\equiv C$), 3325 (s, OH) cm^{-1}. ^{1}H-NMR ([D$_8$]THF, 25 °C, 200 MHz): δ 1.28 (s, CH_3, 18 H), 1.45 (s, CH_3, 6 H), 1.46 (s, CH_3, 6 H), 2.38 (s, OH, 2 H). ^{13}C-NMR (C_6D_6, 25 °C, 50.3 MHz): δ 29.6 (CMe_3), 31.5−32.6 (CH_3), 65.2 (CMe_2OH), 128.6 and 131.3 ($C\equiv$).

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

Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles (46 pages). Ordering information is given on any current masthead page. Additional material on the X-ray structure analyses is available from the Fachinformationszentrum Chemie, Physik, Mathematik GmbH, 76344 Eggenstein-Leopoldshafen 2, Germany, by mentioning the deposit numbers CSD-404129 (**1**), 404310 (**6**), 404309 (**7**), 404130 (**9**), 404311 (**10**), 404132 (**11**), and 404131 (**12**), the author, and the journal citation.

OM950896U