



SYNTHESIS AND CRYSTAL STRUCTURE OF UNSYMMETRICAL TRINUCLEAR NICKEL(0) COMPLEXES WITH THE 1,3-BUTADIYNES IN THE MONODENTATE AND $\mu_2\text{-}\eta^2,\eta^2$ -BRIDGING MODE $[\text{Ni}_3(\text{L})(\text{cod})_3]$ (L = tmsb AND dpbd)

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Abstract—Novel trinuclear nickel(0) complexes $[\text{Ni}_3(\text{L})(\text{cod})_3]$ (cod = 1,5-cyclooctadiene) with L = 1,4-bis(trimethylsilyl)-1,3-butadiyne (**1**) and 1,4-diphenyl-1,3-butadiyne (**2**) have been prepared and their structures have been crystallographically determined. These trinuclear nickel(0) complexes are the first unsymmetrical trinuclear complexes with the 1,3-butadiynes in the monodentate and $\mu_2\text{-}\eta^2,\eta^2$ -coordination mode. The acetylenic C—C distance of 1.343(7) and 1.33(2) Å for **1** and **2** in the $\mu_2\text{-}\eta^2,\eta^2$ -bridging mode is rather larger than that of 1.267(7) and 1.26(2) Å for **1** and **2** in the monodentate mode, indicative of a larger contribution of π back donation. The weak $\nu_{\text{C}\equiv\text{C}}$ frequency was given at 1784 and 1782 cm^{-1} for **1** and **2**, respectively.

We have been interested in the polynuclear nickel(0) complexes with 1,3-butadiynes and their preparation and crystal structures have been reported.^{1–3} The 1,3-butadiynes have two $\text{C}\equiv\text{C}$ bonds which can be bound to soft metal atoms to provide alkyne complexes in the various coordination modes. Two types of coordination mode of the 1,3-butadiynes, monodentate and bridging modes are shown in Fig. 1. In particular, the 1,3-butadiyne complexes in the bridging mode (c and d)^{1,4–6} are quite unique, in addition to those in the monodentate mode (a and b).^{7–12} The dinuclear nickel(0) complexes with the alkynes in the bridging mode effectively generate catalytic reactions to give alkenes owing to hydrogenation.^{13,14} Reaction of

the cobalt carbonyl complex with alkynes produce the polyacetylene–poly(cobalt carbonyl) complexes⁵ having the coordination mode (d). A few examples of the cleavage of the central C—C bond of 1,3-butadiynes have been recently reported on Os,¹⁵ Ti^{16,17} and Zr¹⁸ complexes. We have also prepared the tetranuclear nickel(0) complex $[\text{Ni}_4(\text{dpbd})(\text{cod})_4]$ ¹ with 1,4-diphenyl-1,3-butadiyne (dpbd) in the η^2,η^2 -coordination mode (d), and furthermore have found that the cleavage of the central C—C bond of dpbd was caused by the reaction of $[\text{Ni}_4(\text{dpbd})(\text{cod})_4]$ with 1,1'-bis-(diphenylphosphino)methane (dppm) to provide the mixed-valence trinickel complex $[\text{Ni}_3(\mu\text{-dppm})_3(\mu\text{-C}\equiv\text{CPh})_2]$.² Thus, the bridging coordination modes on the alkyne and 1,3-butadiyne complexes are important to the activation and bond order reduction, in addition to the structural and theor-

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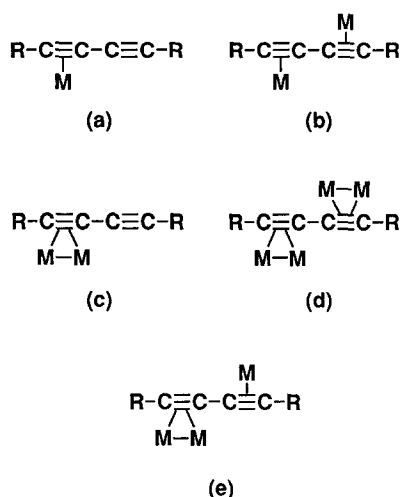


Fig. 1. The coordination mode of the 1,3-butadiynes.

etical interests in coordination chemistry. In this study we have prepared trinuclear nickel(0) complexes $[\text{Ni}_3(\text{L})(\text{cod})_3]$ [$\text{L} = \text{tmsb}$ (1) and dpbd (2)] with the 1,3-butadiynes in the unsymmetrical coordination mode (e) using 1,4-bis(trimethylsilyl)-1,3-butadiyne (tmsb) and 1,4-diphenyl-1,3-butadiyne (dpbd), and their structures have been crystallographically determined. The preparation and crystal structure of **1** have been already reported in a preliminary report.³

EXPERIMENTAL

General

All operations were performed using the usual Schlenk techniques. $[\text{Ni}(\text{cod})_2]$ (cod = 1,5-cyclooctadiene), 1,4-bis(trimethylsilyl)-1,3-butadiyne (tmsb) and 1,4-diphenyl-1,3-butadiyne (dpbd) were commercially purchased from Strem Chemicals and Tokyo Kasei Kogyo Co. Ltd. All organic solvents were dried and distilled by the standard method before use. IR spectra as KBr discs were measured in the range 4300 to 400 cm^{-1} with a JASCO FT IR 8000 spectrometer.

Preparation of $[\text{Ni}_3(\text{tmsb})(\text{cod})_3]$ (1)

$[\text{Ni}(\text{cod})_2]$ (49.5 mg, 1.8×10^{-4} mol) and tmsb (8.7 mg, 4.5×10^{-5} mol) were stirred in *n*-pentane (10 cm^3) for 4 h under Ar. The resultant red solution was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The glass tube was allowed to stand for 1 week at -20°C and the red crystals were collected. Yield 26 mg, 89%. IR (KBr, cm^{-1}) 1784 ($\nu_{\text{C}=\text{C}}$).

Preparation of $[\text{Ni}_3(\text{dpbd})(\text{cod})_3]$ (2)

$[\text{Ni}(\text{cod})_2]$ (27.5 mg, 1.0×10^{-4} mol) and dpbd (10.1 mg, 5.0×10^{-5} mol) were stirred in *n*-pentane (10 cm^3) for 2 h under Ar. The resultant reddish brown solution was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The glass tube was allowed to stand for 2 weeks at -15°C and the black crystals were collected. Yield 14 mg, 51%. IR (KBr, cm^{-1}) 1782 ($\nu_{\text{C}=\text{C}}$).

X-ray crystallography of $[\text{Ni}_3(\text{L})(\text{cod})_3]$ [$\text{L} = \text{tmsb}$ (1) and dpbd (2)].

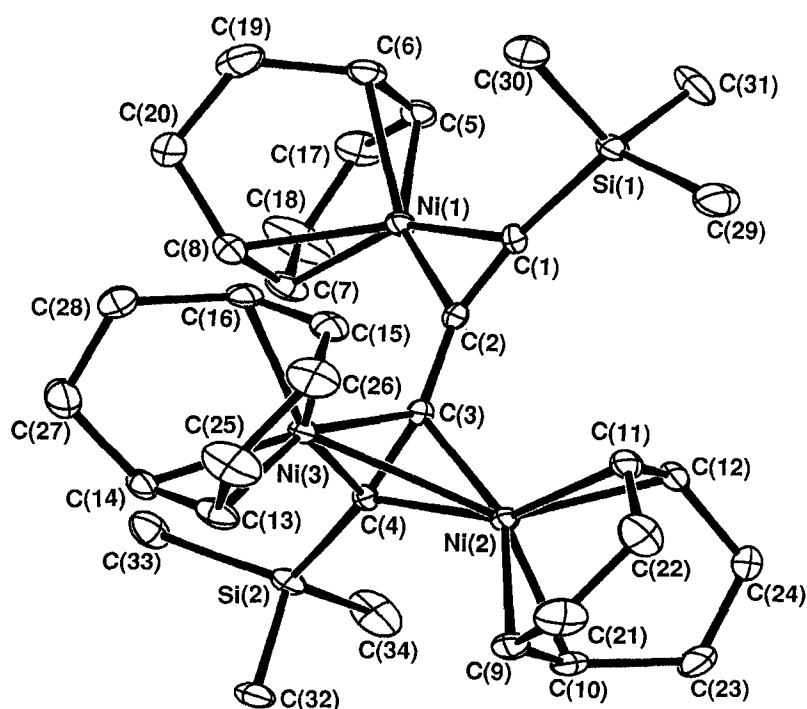
The crystals of **1** and **2** were extremely unstable against air and moisture. After the crystals were taken out from the sealed sample tube under Ar, they were quickly covered with liquid paraffin to protect from O_2 and moisture. A red crystal of **1** or a black crystal of **2** was respectively sealed in the capillary for the X-ray measurement together with liquid paraffin and was mounted on a Rigaku AFC-5R automated diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71069 \text{ \AA}$). The crystal data and measurement conditions for **1** and **2** are listed in Table 1. Intensity data were measured by ω - 2θ scans at 23°C and were corrected for Lorentz and polarization effects. A total of 4367 or 1799 independent reflections having $I = 3\sigma(I)$ for **1** or **2** respectively was used. The structures of both **1** and **2** were solved by a direct method (MITHRIL)¹⁹ and refined by full-matrix least squares with anisotropic thermal parameters. Isotropic hydrogen atoms were located by Fourier difference synthesis. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2\}^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)$. Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-ray Crystallography*, Vol. IV.²⁰ All calculations were performed using the TEXSAN²¹ crystallographic software package. The final R and R_w values were 0.046 and 0.052 for **1**, and 0.064 and 0.065 for **2**, respectively. Details of the structure determinations, crystal data, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for complex **1** and **2** are available from the Cambridge Crystallographic Data Centre and the author, Professor M. Munakata on request.

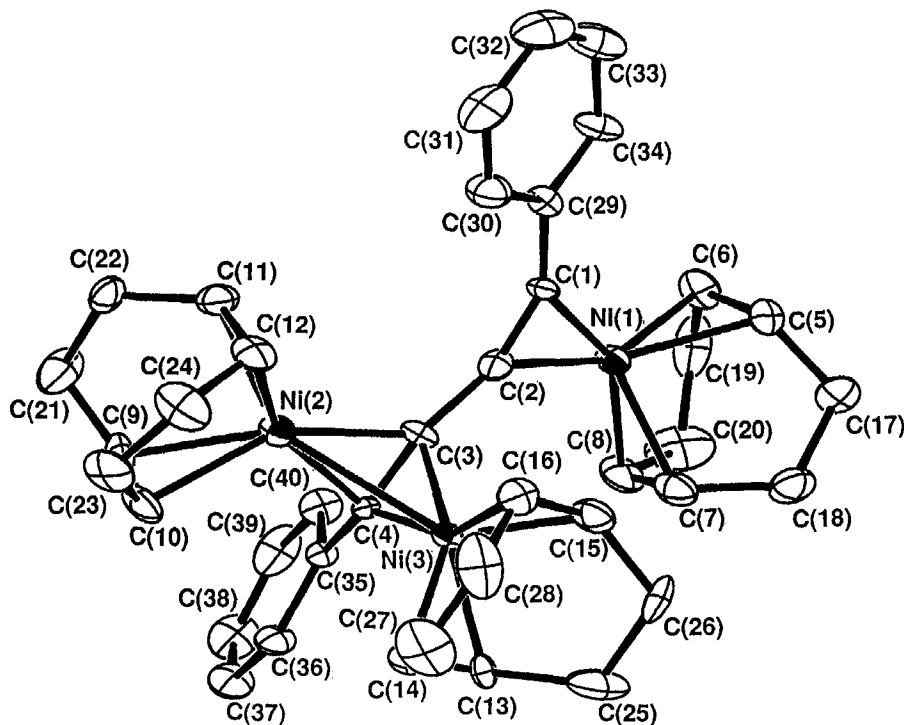
RESULTS AND DISCUSSION

The molecular structures of **1** and **2** are shown in Figs 2 and 3, respectively. On these nickel(0) 1,3-butadiyne complexes, the most remarkable feature

Table 1. Crystal data and the measurement conditions of [Ni₃(L)(cod)₃] [L = tmsb (1) and dpbd (2)]

Complex	1	2
Molecular formula	Ni ₃ Si ₂ C ₃₄ H ₅₄	Ni ₃ C ₄₀ H ₄₆
Formula weight	695.07	702.90
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.947(2)	13.297(4)
<i>b</i> (Å)	15.407(3)	11.365(6)
<i>c</i> (Å)	10.213(2)	22.536(3)
α (°)	96.47(2)	90.0
β (°)	102.32(2)	102.54(1)
γ (°)	107.05(1)	90.0
<i>V</i> (Å ³)	1724.7(6)	3324(2)
<i>Z</i>	2	4
<i>D</i> _c (g cm ⁻³)	1.338	1.404
<i>F</i> (000)	740	1480
λ (Mo <i>K</i> _α) (Å)	0.71069	0.71069
μ (Mo <i>K</i> _α) (cm ⁻¹)	17.18	17.17
Scan type	ω -2 θ	ω -2 θ
Scan rate (° min ⁻¹)	8.0	8.0
Scan width (°)	0.73 + 0.30 tan θ	1.10 + 0.30 tan θ
No. of reflections measured	8303 (total), 7923 (unique)	6911 (total), 6575 (unique)
Reflections used in refinement	4367 [<i>I</i> = 3 σ (<i>I</i>)]	1799 [<i>I</i> = 3 σ (<i>I</i>)]
<i>R</i> ^a	0.046	0.064
<i>R</i> _w ^b	0.052	0.065

^a $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$.^b $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2\}^{1/2}$, where $w = 4F_o^2 / \sigma(F_o^2)$.Fig. 2. Molecular structure of [Ni₃(tmsb)(cod)₃](1).

Fig. 3. Molecular structure of $[\text{Ni}_3(\text{dpbd})(\text{cod})_3](\mathbf{2})$.

is that each coordination mode of two coordinating $\text{C}\equiv\text{C}$ bonds to the nickel atom is different: one $\text{C}\equiv\text{C}$ bond is coordinated to one nickel atom in the monodentate mode and another $\text{C}\equiv\text{C}$ bond is bridged to two nickel atoms in the $\mu_2\text{-}\eta^2,\eta^2$ -bridging mode. Complexes **1** and **2** are the first trinuclear complexes with 1,3-butadiynes in the unsymmetrical coordination mode (e). The three nickel atoms are also coordinated by two $\text{C}=\text{C}$ bonds of cod. The former nickel atom has a distorted trigonal geometry and the latter two nickel atoms have a distorted tetrahedral geometry. The $\text{Ni}(2)\text{—Ni}(3)$ bond is almost perpendicular to the plane defined by $\{\text{C}(2), \text{C}(3)$ and $\text{C}(4)\}$. The torsion angle between the planes defined by $\{\text{C}(1), \text{C}(2)$ and $\text{C}(3)\}$ and $\{\text{C}(2), \text{C}(3)$ and $\text{C}(4)\}$ is about 12° and 20° for **1** and **2**, respectively. The 1,3-butadiyne plane of **2** is considerably distorted. The orientation of $\text{Ni}(1)$ in monodentate mode on **1** is different from that on **2** when the orientation of the $\text{Ni}(2)\text{—Ni}(3)$ bond in the bridging mode is fixed against the plane defined by $\{\text{C}(2), \text{C}(3)$ and $\text{C}(4)\}$. Selected bond distances and bond angles of **1** and **2** are listed in Tables 2 and 3, respectively. The coordination modes, bond distances and bond angles on the reported 1,3-butadiyne complexes are summarized in Table 4.

The acetylenic $\text{C}(3)\text{—C}(4)$ distance is 1.343(7) and 1.33(2) Å for **1** and **2**, whose distances are equal

within the standard deviation. The $\text{C}(1)\equiv\text{C}(2)$ distance is also 1.267(7) and 1.26(2) Å for **1** and **2**, respectively. It was found that the acetylenic C—C distance in the $\mu_2\text{-}\eta^2,\eta^2$ -bridging mode is much longer than the $\text{C}\equiv\text{C}$ distance in the monodentate mode, indicative of a larger contribution of π back donation. These four coordinating $\text{C}\equiv\text{C}$ distances are all longer than that (1.218 Å) of free 1,3-butadiyne. The acetylenic C—C distance in the $\mu_2\text{-}\eta^2,\eta^2$ -bridging mode is slightly shorter than that [1.36(1) Å] of $[\text{Ni}_4(\text{dpbd})(\text{cod})_4]^1$ and those [1.35, 1.375(4) Å] of the other Mo^4 and $\text{Co}^{5,6}$ diyne complexes. On the other hand, the $\text{C}\equiv\text{C}$ distance in the monodentate mode is close to those [1.272(4), 1.279(9) Å] of the other nickel(0) diyne complexes.⁷

The average Ni—C distance in the η^2,η^2 -bridging mode of 1.922(5) and 1.91(2) Å for **1** and **2** is slightly longer than those [1.901(5) and 1.87(2) Å for **1** and **2**] in the monodentate mode. Similarly to the coordinating $\text{C}\equiv\text{C}$ bond, it was revealed that the Ni—C distance in the η^2,η^2 -bridging mode is longer than that in the monodentate mode. The average Ni—C distance in the η^2,η^2 -bridging mode is shorter than that [1.947(8)] of $[\text{Ni}_4(\text{dpbd})(\text{cod})_4]^1$ and those [1.974(1) and 1.988 Å] of the other Mo and Co diyne complexes.^{4,5} On the other hand, the average Ni—C distance in the monodentate mode is longer than those [1.881(3), 1.882(6) Å] of other Ni^0 diyne complexes.⁷

Table 2. Selected bond distances (Å) and bond angles (°) of [Ni₃(tmsb)(cod)₃] (**1**)

Ni(2)—Ni(3)	2.687(1)	Ni(1)—C(1)	1.913(5)
Ni(1)—C(2)	1.889(5)	Ni(2)—C(3)	1.897(5)
Ni(2)—C(4)	1.925(5)	Ni(3)—C(3)	1.927(5)
Ni(3)—C(4)	1.938(5)	Ni(1)—C(cod) _{av.}	2.080(6)
Ni(2)—C(cod) _{av.}	2.093(6)	Ni(3)—C(cod) _{av.}	2.086(6)
C(1)—C(2)	1.267(7)	C(3)—C(4)	1.343(7)
C(2)—C(3)	1.446(7)	C(cod)=C(cod) _{av.} of Ni(1)	1.364
C(cod)=C(cod) _{av.} of Ni(2)	1.354	C(cod)=C(cod) _{av.} of Ni(3)	1.348
C(1)—Ni(1)—C(2)	38.9(2)	Ni(3)—Ni(2)—C(3)	45.8(2)
Ni(3)—Ni(2)—C(4)	46.1(2)	C(3)—Ni(2)—C(4)	41.1(2)
Ni(2)—Ni(3)—C(3)	44.9(2)	Ni(2)—Ni(3)—C(4)	45.7(1)
C(3)—Ni(3)—C(4)	40.7(2)	Ni(1)—C(1)—C(2)	69.5(3)
Ni(1)—C(2)—C(1)	71.6(4)	Ni(1)—C(2)—C(3)	135.5(4)
C(1)—C(2)—C(3)	152.4(5)	Ni(2)—C(3)—C(2)	131.5(4)
Ni(2)—C(3)—C(4)	70.6(3)	Ni(3)—C(3)—C(2)	122.9(4)
Ni(3)—C(3)—C(4)	70.1(3)	C(2)—C(3)—C(4)	149.5(5)
Ni(2)—C(4)—C(3)	68.3(3)	Ni(3)—C(4)—C(3)	69.2(3)

Table 3. Selected bond distances (Å) and bond angles (°) of [Ni₃(dpbd)(cod)₃] (**2**)

Ni(2)—Ni(3)	2.677(3)	Ni(1)—C(1)	1.84(2)
Ni(1)—C(2)	1.89(2)	Ni(2)—C(3)	1.94(2)
Ni(2)—C(4)	1.95(2)	Ni(3)—C(3)	1.87(2)
Ni(3)—C(4)	1.88(2)	Ni(1)—C(cod) _{av.}	2.07(2)
Ni(2)—C(cod) _{av.}	2.10(2)	Ni(3)—C(cod) _{av.}	2.07(2)
C(1)—C(2)	1.26(2)	C(3)—C(4)	1.33(2)
C(2)—C(3)	1.47(2)	C(cod)=C(cod) _{av.} of Ni(1)	1.34
C(cod)=C(cod) _{av.} of Ni(2)	1.39	C(cod)=C(cod) _{av.} of Ni(3)	1.31
C(1)—Ni(1)—C(2)	39.4(6)	Ni(3)—Ni(2)—C(3)	44.4(5)
Ni(3)—Ni(2)—C(4)	44.5(5)	C(3)—Ni(2)—C(4)	40.1(6)
Ni(2)—Ni(3)—C(3)	46.4(5)	Ni(2)—Ni(3)—C(4)	46.7(5)
C(3)—Ni(3)—C(4)	41.7(6)	Ni(1)—C(1)—C(2)	72(1)
Ni(1)—C(2)—C(1)	68(1)	Ni(1)—C(2)—C(3)	138(1)
C(1)—C(2)—C(3)	153(2)	Ni(2)—C(3)—C(2)	135(1)
Ni(2)—C(3)—C(4)	70(1)	Ni(3)—C(3)—C(2)	127(1)
Ni(3)—C(3)—C(4)	69(1)	C(2)—C(3)—C(4)	141(2)
Ni(2)—C(4)—C(3)	70(1)	Ni(3)—C(4)—C(3)	69(1)

On the monodentate nickel atom, the average C=C(cod) distance of 1.364 Å for **1** is slightly longer than that (1.34 Å) for **2**. The latter distance indicates no elongation of the C=C bond owing to the coordination of the Ni⁰ atom, although the former distance is longer than that (1.341 Å) of free cod. On the other hand, the average C=C distance on the η^2, η^2 -bridging nickel atoms is 1.351 and 1.35 Å for **1** and **2**, whose distances are similar within the standard deviation. These C=C distances are slightly longer than that (1.341 Å) of free cod and that (1.34 Å) of [Ni₄(dpbd)(cod)₄],¹ although the average C=C distance on the η^2, η^2 -bridging nickel

atoms is shorter than that (1.367 Å) of the dinickel(0) cod complex^{13,14} with alkyne in the bridging mode. The average Ni—C(cod) distance of 2.080(6) and 2.07(2) Å for **1** and **2** on the monodentate nickel atom, and those of 2.090(6) and 2.08(2) Å for **1** and **2** on the η^2, η^2 -bridging nickel atom are within those [2.052(2)–2.12(2) Å] of other nickel(0) cod complexes.^{13,14,22}

The Ni(1)—Ni(2) distance of 2.687(1) for **1** is slightly longer than [2.677(3) Å] for **2**. Both of these Ni—Ni distances are longer than that [2.655(2) Å] of [Ni₄(dpbd)(cod)₄],¹ those [2.329(4)–2.617(2) Å] of the other nickel(0) alkyne complexes in the bridg-

Table 4. Summary of the coordination mode, the bond distances and angles of the diyne complexes

Complexes	Coordination mode	M—M (Å)	M—C(av.) (Å)	C≡C(av.) (Å)	C—C≡C (°) ^a	Refs
[Na-15-crown-5][WF ₅ (PhC≡C—C≡CSiMe ₃)]·CH ₃ CN	(a)		2.021(5) ^b	1.307(8) ^b 1.200(8) ^d	140.2(5)	8
[FeIr ₂ (μ ₃ -η ² -PhC≡C—C≡CPh)(CO) ₇ (PPh ₃) ₂]	(a)		2.18(5) ^b	1.40(2) ^b 1.22(7) ^d	132(5)	9
[Ni(Pr ₂ PCH ₂ CH ₂ CH ₂ PPr ₂)(HC≡C—C≡CH)]	(a)		1.882(6) ^b	1.279(9) ^b 1.19(1) ^d	146.2(6)	7
{[(C ₃ Me ₃) ₂ Sm] ₂ (PhC≡C—C≡CPh)}·2C ₆ H ₅ Me	(b)		2.62(1) ^b	1.33(2) ^b	154(1)	10, 11
{[(C ₃ Me ₃) ₂ Sm] ₂ (PhC≡C—C≡CPh)}·2C ₆ H ₅	(b)		2.656(9) ^b	1.363(1) ^b	146.9(10)	11
[W ₂ Cl ₈ (PhC≡C—C≡CSiMe ₃)(pv) ₂]	(b)		2.06(3) ^b	1.40(4) ^b 1.25(4) ^b	146(3) 137(3)	12
[Ni ₂ (Pr ₂ PCH ₂ CH ₂ CH ₂ PPr ₂)(HC≡C—C≡CH)]	(b)		1.881(3) ^b	1.272(4) ^b	149.4(3)	7
[η ¹ -C ₆ H ₅](CO) ₂ Mo ₂ (μ ^{1,2} -η ¹ -C ₆ H ₅ C≡C—C≡CC ₆ H ₅)]	(c)	2.9624(4)	2.185(3) ^c	1.375(4) ^c 1.208(5) ^d	136.5(3)	4
[Co ₄ (Me ₃ SiC≡C—C≡CSiMe ₃)(CO) ₁₂] ^e	(d)	2.474	1.988 ^c	1.35 ^c	146.7	5
[Co ₄ (CO) ₁₂ (PhC≡C—C≡CPh) ₁₂]	(d)	2.461(1)	1.974(1) ^c	1.334(3) ^c	141.8(1)	6
[Ni ₄ (PhC≡C—C≡CPh)(cod) ₄]	(d)	2.655(2)	1.947(8) ^c	1.36(1) ^c	146(1)	1
[Ni ₃ (Me ₃ SiC≡C—C≡CSiMe ₃)(cod) ₃]	(e)	2.687(1)	1.901(5) ^b 1.922(5) ^c	1.267(7) ^b 1.343(7) ^c	152.4(5) 149.5(5)	this work
[Ni ₃ (PhC≡C—C≡CPh)(cod) ₃]	(e)	2.677(3)	1.87(2) ^b 1.91(2) ^c	1.26(2) ^b 1.33(2) ^c	153(2) 141(2)	this work

^a The C—C≡C angle indicates the C(1)—C(2)—C(3) angle on the R—C≡C(1)—C(2)≡C(3)—R.^b The C≡C bond is coordinated to the Ni⁰ atom in the monodenate mode.^c The C≡C bond is coordinated to the Ni⁰ atom in the bridging mode.^d The C≡C bond is not coordinated to the metal atom.^e The bond distances and angles were calculated from crystal data and atomic coordinates in Ref. 5.

ing mode^{13,14,23,24} and that (2.492 Å) in the metallic nickel, suggesting the Ni⁰—Ni⁰ bond is relatively weak. These Ni—Ni distances are also rather longer than that (2.461–2.474 Å) of the cobalt diyne complex^{5,6} in the bridging mode (d).

The C≡C—C angle for the C(1)—C(2)—C(3) and C(2)—C(3)—C(4) angles is 152.4(5) and 149.5(5)° for **1**, and 153(2) and 141(2)° for **2**, respectively. These angles are rather more bent than that (180°) of free 1,3-butadiyne, suggesting that the C≡C bond leads to a C=C bond.¹ It is interesting that the C(2)—C(3)—C(4) angle of **2** is smaller than of **1**, although both of the C(1)—C(2)—C(3) angles are similar.

The weak $\nu_{C\equiv C}$ frequency of **1** and **2** was given at 1784 and 1782 cm⁻¹, respectively, whose values were close to that (1782 cm⁻¹) of [Ni₄(dpbd)(cod)₄],¹ although the frequency is larger than (1757 cm⁻¹) of the nickel(0) diyne complexes⁷ in the monodentate mode.

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