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Diazadiene stabilized butadiene nickel(0) complexes: synthesis, characterization and reaction with acetylene and carbon monoxide.
Crystal structures of (dad)Ni-μ[$\sigma^{1,4}$; η^{1-4}-C_4H_4]Ni(dad) and (dad)Ni-μ[$\sigma^{1,4}$; η^{1-4}-C_4H_4]$Ni(CO)_2$

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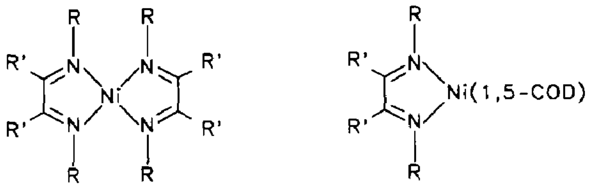
Abstract

Some new reactive diazadiene nickel butadiene compounds (dad)Ni(1,3-butadiene) (**4**) have been prepared by reduction of the appropriate (dad)Ni^{II} halides, (dad)NiX_2, (dad = RN = CR′CR′ = NR) with magnesium-1,3-butadiene · 2THF. The compounds are very reactive towards acetylene and CO. Reaction with acetylene leads to the binuclear complex **5** (R = 2,6-diisopropylphenyl). The structure of **5** can be described as a non-planar (dad)nickela-2,4-cyclopentadiene, with a (dad)Ni moiety *hapto*-4 bonded to the metallacyclodiene; the Ni–Ni distance is 2.677(1) Å. Further reaction of **5** with carbon monoxide gives **6**, in which the dad ligand at the *hapto*-4 bonded Ni atom has been replaced by two CO ligands, with the other dad ligand at the Ni^{II} center remaining unchanged. The crystal structure of **6** shows that replacement of one of the sterically demanding dad ligands gives a system with typical Ni^0/Ni^{II} geometries, although the Ni–Ni distance (2.561(2) Å) is shorter than that in **5**.

Introduction

The dad stabilized complexes such as **1** and **2** have proved to be excellent catalysts for the specific cyclotetramerization of monosubstituted alkynes [1]; in particular derivatives of **2** containing the non-conjugated diene 1,5-cyclooctadiene (COD), are especially reactive. Compounds of this type are prepared by replacement of one COD ligand in $(COD)_2Ni$ for one diazadiene (dad = RN=CR′CR′=NR, Scheme 1). When the substituents R on the dad are sterically demanding further substitution to give **1** does not take place.



(1) (2)

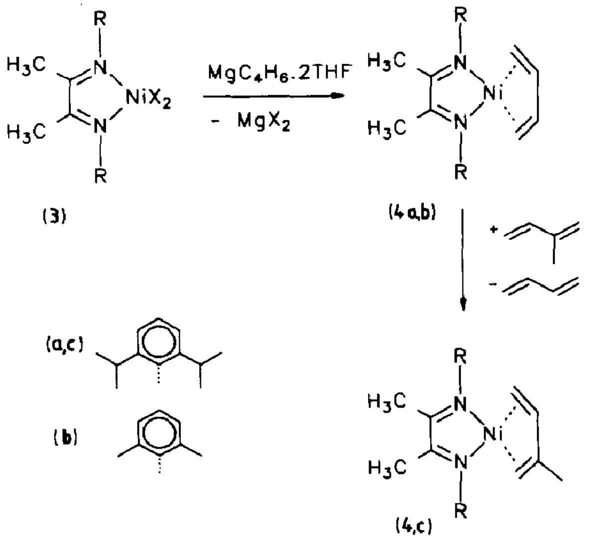
Scheme 1

Bis(1,3-diene) complexes of nickel are too reactive to be isolated [2], and (dad)Ni complexes containing non-chelating unactivated olefins are also unknown. However, dad-stabilized nickel dialkyls with very bulky dad ligands are known [3a,b]. Since compounds of type **2** are very good starting materials for catalytic as well as stoichiometric reactions, we decided to investigate the possibility of preparing dad-stabilized Ni^0 complexes containing small conjugated dienes (butadiene and isoprene) by direct reaction of the readily available $(dad)Ni^{II}$ halides **3** with the dianions of 1,3-dienes. Such complexes could show interesting features especially in reactions with acetylene and carbon monoxide.

Results

Preparation of the (dad)Ni(1,3-diene) complexes

Reaction of $(dad)Ni(II)X_2$ (**3**; X = Cl, Br) with $MgC_4H_6 \cdot 2THF$ [4] in pentane at room temperature gives intensely violet to red solutions from which $(dad)NiC_4H_6$ complexes can be isolated in moderate to good yields (Scheme 2). Reaction of **3b** with Mg(isoprene) · 2THF did not give the corresponding (dad)Ni-isoprene complex **4c**, but this was made by exchange of butadiene for isoprene in complex **4a**.

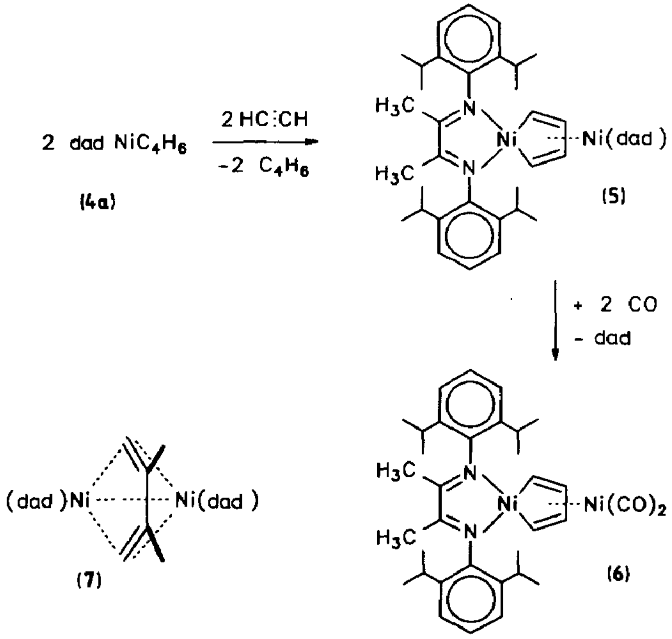


Scheme 2

The solvent in which the reaction is performed is of great importance; in a strongly coordinating solvent such as THF **3b** gives a mixture of (dad)NiC_4H_6, $(dad)_2Ni$ (approximately 40/60) and metallic nickel, whereas in pentane it gives 78% of **4b** (with about 7% of $(dad)_2Ni$). We have so far been unable to isolate (dad)Ni-butadiene complexes containing a dad ligand derived from glyoxal (R′ = H) and we think that this may be due to the difference in basicity between glyoxal- and biacetyl-based dads. Compounds **4** are very soluble in all the common solvents, and very air- and moisture-sensitive. **4a** seems to be more thermally stable than **4b**. (In contrast, Ni butadiene complexes stabilized by bipy or tmeda [5,6], are quite thermally labile.) The butadiene ligand is *hapto*-4 bonded to the metal. At ambient temperature three ^1H NMR signals are observed for 6 protons and two ^{13}C-NMR signals for the four carbon atoms. (This behaviour is also different from that of the bipy- and tmeda-stabilized Ni-butadiene complexes, in which the butadiene ligands are reported to be *hapto*-2 bonded.) Attempts to determine the crystal structure of **4a** were unsuccessful owing to a disorder involving two butadiene orientations and the C_4-backbone of the biacetyl fragment.

*Reaction of **4a** with acetylene followed by reaction with CO*

Reaction of (dad)NiC_4H_6 (**4a**) in pentane at room temperature with acetylene (Scheme 3) results in an immediate colour change from reddish-violet to deep blue. When the solution of **4a** is kept overnight under an atmosphere of acetylene, without stirring, blue crystals of **5** are obtained in moderate yield (49%). The crystals are slightly air and moisture sensitive. The solubility of the compound in common solvents is low and this prevents the recording of NMR spectra. When the reaction is carried out in THF only polyacetylene is isolated, probably because acetylene is much more soluble in polar solvents. Because of its low solubility



Scheme 3

characterisation of **5** is difficult. Elemental analysis shows an alkyne/Ni ratio of 1/1. Numerous mononuclear 1/1 nickel alkyne complexes are known [7], but these exhibit an infrared active C≡C vibration whereas there is no band from a coordinated triple bond in the 1700–1850 cm^{-1} region in the infrared spectrum of **5**. This fact and the correct elemental analysis lead us to conclude that we are dealing with an oligomeric structure. Evidence for the nature of the acetylene-bonding in **5** came from an X-ray analysis (vide infra), but some conclusions could already be drawn from the reaction of **5** with carbon monoxide. Stirring of **5** in pentane under an atmosphere of CO resulted in a change from a blue suspension to a green solution, from which dark green crystals of **6** were obtained (Scheme 3). Compound **6** is very stable and soluble in all common organic solvents, and so could be investigated by NMR spectroscopy. From NMR data, the elemental analysis and IR data it was concluded that **6** is a bimetallic complex with one dad and two carbonyl ligands, in which two acetylene molecules are coupled to a C_4H_4 moiety. No bridging carbonyl groups were present (IR), and no insertion of CO into the C_4H_4 species had taken place. From these results a nickelacyclopentadiene structure, containing a dicarbonylnickel fragment, was proposed for **6**, and a corresponding structure for the precursor **5**. Since the precise nature of the bridging C_4H_4 ligand could not be deduced from the available data, an X-ray diffraction study was also carried out for **6**.

Crystal structure determination *

Crystallographic data for **5** and **6** were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, and details are given in Table 1. Fractional atomic coordinates are listed in tables 2 and 3, and selected bond lengths and angles in tables 4 and 5.

Figures 1 and 2 show the structures of **5** and **6** with the numbering scheme. In both cases the structures clearly contain a (dad)nickelacyclopentadiene ring, with a π-bonded (dad)Ni (**5**) or $Ni(CO)_2$ (**6**) moiety. In **6** the nickelacyclopentadiene ring is flat, whereas in **5** the four C-atoms of the ring lie in a plane, and the Ni atom is 0.32(1) Å out of that plane. In **6** one of the Ni atoms is coordinated in strictly square planar geometry by the chelating dad ligand and the carbon atoms C(4) and C(7) of the metallacycle (C(4)–C(5)–C(6)–C(7)), whereas the other Ni center is tetrahedrally coordinated by the two carbonyl ligands and the two π-bonds of the cyclodiene ring. In view of this geometry, which defines the complex as a Ni^{II}/Ni^{0} species, and the observed diamagnetism of complex **6** (NMR), it is not necessary to assume a bonding interaction between the two nickel centers. The Ni^{II}–Ni^{0} distance of 2.561(2) Å is slightly greater than the average Ni–Ni distance of 2.492 Å in metallic Ni.

On the other hand, the coordination of both Ni centres in **5** deviates strongly from any ideal geometry. The angle between the best planes defined by the atoms Ni(2)–N(4)–C(4)–C(3)–N(3) and Ni(2)–C(5)–C(6)–C(7)–C(8) is 31.3(1)°. The coordination of the *hapto*-4 bonded Ni centre also deviates from the ideal tetrahedral

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* Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD54429, the names of the authors, and the journal citation.

Table 1

Crystal data for **5** and **6**

	5	**6**
Chemical formula	$C_{60}H_{84}N_4Ni_2$	$C_{34}H_{44}N_2Ni_2O_2$
Crystal system	monoclinic	monoclinic
Space group, No.	$P2_1/n$ (14)	$P2_1/n$ (14)
Z	4	4
a, Å	13.641(1)	10.771(4)
b, Å	23.892(2)	19.615(8)
c, Å	18.103(3)	15.955(9)
β, deg	108.92(1)	105.71(4)
V, Å^3	5581(1)	3245(3)
d_{calc}, g/cm^3	1.164	1.290
λ (Cu-K_α), Å	1.54056	1.54056
θ range, (°)	2.25–76.50	2.25–76.50
h range	0–30	−13–12
k range	17– −22	0–24
l range	0–22	0–20
F(000), electrons	1056	1043
μ, cm^{-1}	5.5	14.4
Crystal dimensions, mm^3	0.2×0.3×0.17	0.3×0.4×0.4
Temperature, K	298	220
No. of reflections	12717	6127
Independent reflections	11152	5586
Significant reflections	9571	5243
No. of refined parameters	322	366
Final R_f $\Sigma(\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0469	0.0632
Final R_w $[\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma\|wF_o^2\|]^{1/2}$	0.0469	0.0789

geometry. It seems likely that the molecule is distorted because of the steric interaction between the large *o,o'*-diisopropylphenyl groups on the dad ligands. There is a lengthening of the Ni–Ni distance by 0.12 Å compared with that in **6**. On the other hand, a (dad)Ni^0 species, which is much richer in electrons than a $(OC)_2Ni^0$ species, should be more prone to supply electrons to a neighbouring Ni^{II} centre. In such a case one would expect a shorthening of the Ni–Ni distance with respect to **6**, but steric and electronic influences evidently counteract this effect in this complex. It is remarkable that the C_4H_4 moiety in **5** does not adopt a totally symmetrical flyover position between the two formally identical (dad)Ni centers, such as was found earlier by Diercks et al. for an intermediate in the (dad)Ni-catalysed cyclotetramerization of a propargylic ether [8].

The bond distances in the metallacyclopentadiene rings of **5** and **6** show the same pattern: the two metal–C σ-bond lengths are comparable with those of alkyl-nickel bonds [9]; the two adjacent bonds are shorter than the central C–C bond, reflecting the diene character. However, compared to those in a normal diene the double bonds are lengthened, in keeping with their acting as ligands for the other nickel atom. The differences in the lengths of the bonds between the ring carbon atoms and these *hapto*-4 bonded Ni centres are of interest. In **5** these bonds (average 2.09 Å) are much shorter than there is in **6** (average 2.18 Å), and so the back-bonding

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms of **5** (esd's)

Atom	x	y	z	U_{eq}
Ni(1)	0.42975(3)	0.10323(2)	0.19842(2)	0.0358(4)
C(1)	0.3124(2)	0.01901(11)	0.2284(2)	0.052(3)
C(10)	0.2680(3)	−0.03749(13)	0.2363(3)	0.087(5)
N(1)	0.3833(2)	0.02739(8)	0.19330(12)	0.042(2)
C(11)	0.4134(2)	−0.02026(10)	0.1571(2)	0.045(2)
C(12)	0.4936(2)	−0.05556(11)	0.1985(2)	0.051(3)
C(121)	0.5632(3)	−0.04357(12)	0.2810(2)	0.060(3)
C(122)	0.5385(4)	−0.0811(2)	0.3414(2)	0.104(6)
C(123)	0.6779(3)	−0.0488(2)	0.2876(2)	0.085(5)
C(13)	0.5118(3)	−0.10366(13)	0.1617(2)	0.068(4)
C(14)	0.4556(3)	−0.1153(2)	0.0852(2)	0.082(4)
C(15)	0.3810(3)	−0.07863(14)	0.0434(2)	0.071(4)
C(16)	0.3579(2)	−0.03033(12)	0.0774(2)	0.055(3)
C(161)	0.2756(3)	0.0094(2)	0.0288(2)	0.069(4)
C(162)	0.2991(4)	0.0279(2)	−0.0454(2)	0.102(6)
C(163)	0.1680(3)	−0.0159(2)	0.0082(3)	0.116(7)
C(2)	0.2756(2)	0.06828(12)	0.2525(2)	0.054(3)
C(20)	0.1859(3)	0.0670(2)	0.2843(3)	0.098(5)
N(2)	0.3218(2)	0.11598(8)	0.24229(12)	0.042(2)
C(21)	0.2664(2)	0.16709(11)	0.2444(2)	0.047(3)
C(22)	0.2867(2)	0.19753(13)	0.3136(2)	0.058(3)
C(221)	0.3710(3)	0.1810(2)	0.3881(2)	0.069(4)
C(222)	0.4551(3)	0.2265(2)	0.4132(3)	0.093(5)
C(223)	0.3268(4)	0.1677(3)	0.4536(3)	0.141(8)
C(23)	0.2248(3)	0.2444(2)	0.3131(2)	0.079(4)
C(24)	0.1478(3)	0.2608(2)	0.2477(3)	0.084(5)
C(25)	0.1298(2)	0.2310(2)	0.1804(2)	0.072(4)
C(26)	0.1868(2)	0.18307(12)	0.1766(2)	0.055(3)
C(261)	0.1586(3)	0.1495(2)	0.1015(2)	0.066(4)
C(262)	0.1785(3)	0.1825(2)	0.0362(2)	0.103(6)
C(263)	0.0465(3)	0.194(2)	0.0763(3)	0.116(7)
Ni(2)	0.59112(3)	0.17231(2)	0.25607(2)	0.0355(4)
C(3)	0.7110(2)	0.25914(11)	0.3357(2)	0.042(2)
C(30)	0.7639(2)	0.31474(12)	0.3538(2)	0.057(3)
N(3)	0.6300(2)	0.24872(8)	0.27190(12)	0.039(2)
C(31)	0.6045(2)	0.29004(11)	0.2104(2)	0.046(3)
C(32)	0.6510(3)	0.28463(13)	0.1512(2)	0.061(3)
C(321)	0.7287(3)	0.2393(2)	0.1528(2)	0.079(4)
C(322)	0.7016(4)	0.2068(2)	0.0765(3)	0.125(7)
C(323)	0.8381(3)	0.2624(2)	0.1746(3)	0.108(6)
C(33)	0.6235(4)	0.3245(2)	0.0916(2)	0.087(5)
C(34)	0.5556(4)	0.3666(2)	0.0889(3)	0.091(5)
C(35)	0.5124(3)	0.3713(2)	0.1465(3)	0.078(4)
C(36)	0.5363(2)	0.33351(13)	0.2093(2)	0.059(3)
C(361)	0.4895(3)	0.3421(2)	0.2746(3)	0.084(5)
C(362)	0.5136(3)	0.4003(2)	0.3127(3)	0.115(7)
C(363)	0.3732(3)	0.3329(2)	0.2435(3)	0.118(7)
C(4)	0.7501(2)	0.21106(11)	0.3823(2)	0.041(2)
C(40)	0.8394(2)	0.21522(13)	0.4575(2)	0.057(3)
N(4)	0.70451(14)	0.16329(8)	0.35273(12)	0.039(2)
C(41)	0.7532(2)	0.11225(11)	0.3881(2)	0.042(2)
C(42)	0.8381(2)	0.09152(13)	0.3684(2)	0.056(3)

Table 2 continued

Atom	*x*	*y*	*z*	U_{eq}
C(421)	0.8770(3)	0.1199(2)	0.3086(2)	0.085(4)
C(422)	0.8731(3)	0.0810(2)	0.2404(3)	0.122(7)
C(423)	0.9864(3)	0.1436(2)	0.3448(3)	0.123(7)
C(43)	0.8876(2)	0.0434(2)	0.4062(2)	0.067(4)
C(44)	0.8557(3)	0.01692(14)	0.4613(2)	0.069(4)
C(45)	0.7708(3)	0.03652(13)	0.4787(2)	0.065(4)
C(46)	0.7175(2)	0.08408(12)	0.4425(2)	0.050(3)
C(461)	0.6243(3)	0.10467(13)	0.4625(2)	0.062(3)
C(462)	0.5423(3)	0.0594(2)	0.4495(3)	0.098(5)
C(463)	0.6576(4)	0.1275(2)	0.5466(2)	0.110(6)
C(5)	0.4749(2)	0.18002(10)	0.1649(2)	0.042(2)
C(6)	0.4659(2)	0.14046(12)	0.1069(2)	0.050(3)
C(7)	0.5316(2)	0.09342(12)	0.1377(2)	0.053(3)
C(8)	0.5924(2)	0.10082(11)	0.2163(2)	0.046(2)

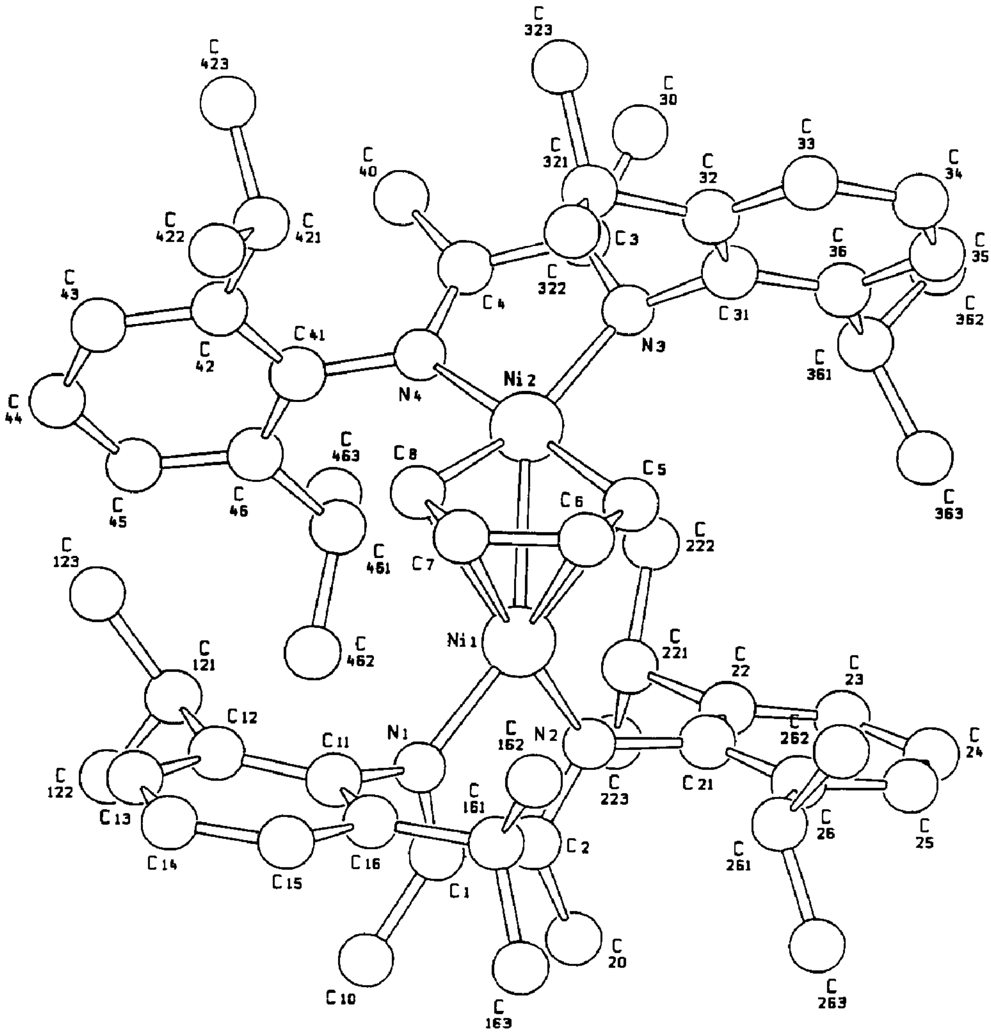

Fig. 1. SCHAKAL-plot of the molecular structure of 5 with the atomic numbering scheme

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms of **6** (esd's)

Atom	x	y	z	U_{eq}
Ni(1)	0.20172(4)	0.22830(3)	0.19661(3)	0.0345(5)
C(111)	0.0480(2)	0.3030(2)	0.2018(2)	0.033(2)
C(112)	0.0360(2)	0.17829(14)	0.2277(2)	0.034(2)
C(113)	0.0174(3)	0.2667(2)	0.1248(2)	0.039(2)
C(114)	0.0095(3)	0.1941(2)	0.1395(2)	0.039(2)
C(12)	0.3228(3)	0.2361(2)	0.2974(2)	0.041(2)
O(12)	0.4103(2)	0.2395(2)	0.3567(2)	0.054(2)
C(13)	0.2860(3)	0.2119(2)	0.1167(2)	0.050(3)
O(13)	0.3485(3)	0.2012(2)	0.0710(2)	0.075(3)
Ni(2)	0.07353(3)	0.25307(2)	0.30696(2)	0.0245(4)
C(3)	0.1188(2)	0.23867(12)	0.4844(2)	0.025(2)
C(30)	0.1399(3)	0.21015(13)	0.5745(2)	0.034(2)
C(4)	0.1248(2)	0.31153(12)	0.46931(14)	0.024(2)
C(40)	0.1496(2)	0.36125(13)	0.5435(2)	0.031(2)
N(3)	0.0875(2)	0.20290(10)	0.41216(120	0.0237(15)
C(31)	0.0577(2)	0.13142(12)	0.41370(14)	0.024(2)
C(32)	0.1553(2)	0.08179(13)	0.4272(2)	0.029(2)
C(321)	0.2985(2)	0.09980(13)	0.4528(2)	0.033(2)
C(322)	0.3635(3)	0.0764(2)	0.3826(2)	0.043(3)
C(323)	0.3689(3)	0.0679(2)	0.5413(2)	0.041(2)
C(33)	0.1175(3)	0.01390(13)	0.4146(2)	0.034(2)
C(34)	−0.0124(3)	−0.00497(14)	0.3902(2)	0.036(2)
C(35)	−0.1069(2)	0.04498(14)	0.3803(2)	0.034(2)
C(36)	−0.0750(2)	0.11324(13)	0.3927(2)	0.029(2)
C(361)	−0.1812(2)	0.16643(14)	0.3839(2)	0.032(2)
C(362)	−0.2584(3)	0.1532(2)	0.4509(3)	0.051(3)
C(363)	−0.2717(3)	0.1681(2)	0.2910(2)	0.048(3)
N(4)	0.0992(2)	0.32847(10)	0.38686(12)	0.0234(15)
C(41)	0.0816(2)	0.39946(12)	0.36355(14)	0.025(2)
C(42)	0.1844(2)	0.43667(14)	0.3473(2)	0.033(2)
C(421)	0.3174(3)	0.4053(2)	0.3596(3)	0.050(3)
C(422)	0.3679(3)	0.4127(2)	0.2790(3)	0.064(4)
C(423)	0.4126(3)	0.4395(3)	0.4387(3)	0.066(4)
C(43)	0.1637(3)	0.5048(2)	0.3229(2)	0.039(2)
C(44)	0.0425(3)	0.53500(14)	0.3125(2)	0.039(2)
C(45)	−0.0575(2)	0.49696(14)	0.3280(2)	0.035(2)
C(46)	−0.0405(2)	0.42930(13)	0.3548(2)	0.027(2)
C(461)	−0.1527(2)	0.38947(13)	0.3718(2)	0.032(2)
C(462)	−0.2242(3)	0.4303(2)	0.4264(3)	0.053(3)
C(463)	−0.2443(3)	0.3658(2)	0.2858(3)	0.050(3)

into the π^* levels of the diene must be stronger in **5** than in **6**. This is consistent with the bond distances within the metallacycles. Evidently, in **6** the two carbonyl ligands compete effectively in backbonding [10], and less electron density has to be distributed. If only σ-bonding were taken into account, one would expect longer bonds between the electron-rich Ni(1) and the ring carbon atoms in **5**. In contrast to **7**, the structure of which was reported by Diercks et al. [8], which has symmetrical flyover geometry, in which the two nickel atoms are only bonded to the two terminal carbon atoms of the C_4 fragment, in both **5** and **6** the distances between

Table 4

Selected bond lengths (Å) and angles (°) in **5** (esd's)

Bond lengths	
Ni(1)–Ni(2)	2.677(8)
Ni(1)–N(1)	1.912(2)
Ni(1)–N(2)	1.911(2)
Ni(1)–C(5)	2.087(3)
Ni(1)–C(6)	2.076(3)
Ni(1)–C(7)	2.046(3)
Ni(1)–C(8)	2.136(3)
Ni(2)–C(5)	1.891(3)
Ni(2)–C(8)	1.856(3)
Ni(2)–N(3)	1.897(2)
Ni(2)–N(4)	1.935(2)
N(1)–C(1)	1.333(4)
N(1)–C911)	1.438(3)
N(2)–C(2)	1.343(4)
N(2)–C(21)	1.443(3)
N(3)–C(3)	1.338(3)
N(3)–C(31)	1.443(3)
N(4)–C(4)	1.327(3)
N(4)–C(41)	1.436(3)
C(1)–C(2)	1.404(4)
C(1)–C(10)	1.505(4)
C(2)–C(20)	1.512(5)
C(3)–C(4)	1.423(4)
C(3)–C(30)	1.496(4)
C(4)–C(40)	1.507(4)
C(5)–C(6)	1.388(4)
C(6)–C(7)	1.433(4)
C(7)–C(8)	1.406(4)
Bond angles	
Ni(2)–Ni(1)–N(1)	145.15(7)
Ni(2)–Ni(1)–N(2)	112.76(6)
Ni(2)–Ni(1)–C(5)	44.67(7)
Ni(2)–Ni(1)–C(6)	70.66(8)
Ni(2)–Ni(1)–C(7)	70.39(8)
Ni(2)–Ni(1)–C(8)	43.58(7)
N(1)–Ni(1)–C(5)	160.63(10)
N(1)–Ni(1)–C(6)	121.88(10)
N(1)–Ni(1)–C(7)	97.89(10)
N(1)–Ni(1)–C(8)	107.04(10)
N(2)–Ni(1)–C(5)	108.69(10)
N(21)–Ni(1)–C(6)	132.69(10)
N(2)–Ni(1)–C(7)	172.30(10)
N(2)–Ni(1)–C(8)	147.57(10)
Ni(2)–C(5)–C(6)	115.90(20)
C(5)–C(6)–C(7)	110.50(20)
C(6)–C(7)–C(8)	112.60(20)
Ni(2)–C(8)–C(7)	115.60(20)

the Ni(1) atoms and the central carbon atoms are shorter than those to the terminal carbon atoms. In Fig. 3 the conformations of three complexes are compared. The dispositions of the two dad ligands are almost identical in **5** and **7**.

Table 5

Selected bond lengths (Å) and angles (°) in **6** (esd's)

Bond lengths	
Ni(1)–Ni(2)	2.561(2)
Ni(1)–C(12)	1.782(3)
Ni(1)–C(13)	1.783(3)
Ni(1)–C(111)	2.229(3)
Ni(1)–C(112)	2.208(3)
Ni(1)–C(113)	2.142(3)
Ni(1)–C(114)	2.132(3)
Ni(2)–C(111)	1.897(3)
Ni(2)–C(112)	1.907(3)
Ni(2)–N(3)	1.916(2)
Ni(2)–N(4)	1.923(2)
O(12)–C(12)	1.142(4)
O(13)–C(13)	1.138(5)
N(3)–C(13)	1.313(3)
N(3)–C(31)	1.440(3)
N(4)–C(4)	1.312(3)
N(4)–C(41)	1.440(3)
C(3)–C(4)	1.454(3)
C(3)–C(30)	1.502(3)
C(4)–C(40)	1.501(3)
C(111)–C(113)	1.380(4)
C(112)–C(114)	1.393(4)
C(113)–C(114)	1.451(5)
Bond angles	
C(12)–Ni(1)–C(13)	105.71(15)
C(12)–Ni(1)–C(111)	106.25(13)
C(12)–Ni(1)–C(112)	105.90(13)
C(12)–Ni(1)–C(113)	142.98(14)
C(12)–Ni(1)–C(114)	143.27(14)
C(13)–Ni(1)–C(111)	132.25(14)
C(13)–Ni(1)–C(112)	132.80(14)
C(13)–Ni(1)–C(113)	104.99(14)
C(13)–Ni(1)–C(114)	105.12(14)
C(11)–Ni(1)–C(112)	68.27(11)
C(111)–Ni(1)–C(113)	36.74(11)
C(111)–Ni(1)–C(114)	65.04(12)
C(112)–Ni(1)–C(113)	65.66(12)
C(112)–Ni(1)–C(114)	37.39(11)
C(113)–Ni(1)–C(114)	39.68(13)
Ni(1)–C(12)–O(12)	172.20(30)
Ni(1)–C(13)–O(13)	174.60(30)

The structures of **5** and **6** are consistent with the cyclotetramerization mechanism proposed by Wilke [11] in which bimetallic Ni complexes are involved. Compounds **5** and **6** can cyclotetramerize alkynes such as propargylic alcohols and ethers or propiolic esters, but so far have not been found to bring about tetramerization of acetylene itself. However, traces of cyclooctatetraene are detected, when these complexes are decomposed. Compounds **5** and **6** represent one extreme of possible conformations, with the flyover complex of Diercks et al. **7** [8], involving a

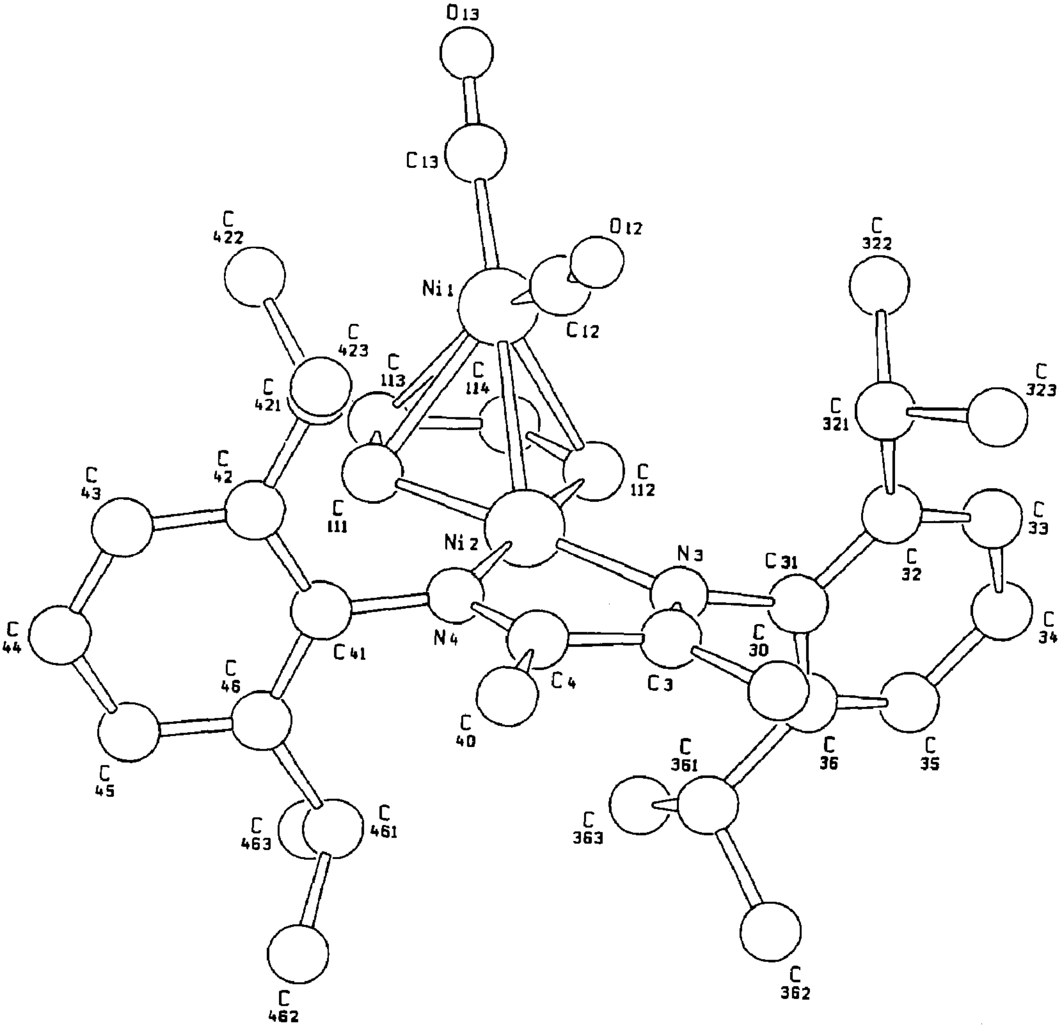

Fig. 2. SCHAKAL-plot of the molecular structure of **6** with the atomic numbering scheme

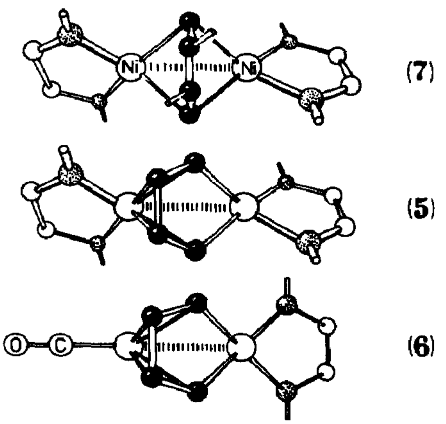

Fig. 3. Comparison of partial structures of complexes **5**, **6** and **7** with the same in-plane orientation of the Ni–Ni vectors

σ,σ-bridging alkyne dimer (butadienediyl) between two nickel(I) centres, representing the other limit. The influence of the other ligands on the nickel atoms is very important in respect of the types of intermediate which can be isolated in reactions with acetylene. Thus, Pörschke could isolate a nickelacyclopentadiene with a bridging acetylene [12], whereas Carpenter et al. [13] recently prepared bimetallic nickel complexes containing only σ bonds. This supports the conclusion of Reppe et al. many years ago that the outcome of the alkyne tetramerization strongly depends upon the nature of the ligands [14].

Experimental

All manipulations were carried out under purified nitrogen. Solvents (pentane, THF), including the NMR solvents, were distilled from Na/K alloy and saturated with nitrogen. NMR spectra were recorded on a Bruker WP-80 SYFT AM 100 or AM 360 spectrometer. Chemical shifts were determined relative to the solvent signal (benzene $\delta = 7.15$). IR spectra were recorded as Nujol mulls between KBr disks on Perkin Elmer spectrophotometer model 325. UV/VIS spectra were recorded on a Perkin Elmer spectrophotometer model 554. Elemental analyses were carried out by the Analytical Service Laboratory of our Institute. The syntheses of the dad ligands and the complexes (dad)NiX$_2$ were described earlier [9].

*Biacetylbis(2,6-diisopropylphenylimin)(1,3-butadiene)nickel (**4a**)*

To a suspension of 4.6 g (7.4 mmol) of **3a** in 100 ml of pentane were added 2.0 g (9.0 mmol) of $MgC_4H_6 \cdot 2THF$. The mixture was stirred overnight, during which the mixture changed from a yellow suspension to a red-violet solution. Filtration of the solution and subsequent evaporation of the pentane yielded 3.6 g (7.0 mmol, 96%) of **4a** as a reddish-violet microcrystalline solid. ^{1}H NMR (C_6D_6): δ 7.45–7.37 (m, 6H(Ph)); 5.17 (dd, 2H ^3J 7.8 and 11.4 Hz); 3.42 (m, 4H(iso), ^3J 6.6 Hz); 2.54 (d, 2H, ^3J 7.8 Hz); 1.49 (d, 6H, CH$_3$, ^3J 6.6 Hz); 1.24 (d, 6H, CH$_3$, ^3J 6.6 Hz); 1.11 (d, 2H, ^3J 11.4 Hz); 0.79 (s, 6H, CH$_3$(biacetyl)). ^{13}C NMR (C_6D_6): δ 139.10 (broad, N–C); 125.4 (broad, CPh); 123.48 (CPh); 90.17 (*C*H=CH$_2$); 49.10 (CH=*C*H$_2$); 27.80 (CH(isopropyl)); 26.26, 24.60 (CH$_3$). IR (cm^{-1}): 740 (s), 790 (s), 980 (m), 1260 (m), 1580 (m). UV/VIS (pentane), λ_{max}: 504 nm. Analysis. Found: C, 74.14; H, 8.91; N, 5.92. $C_{32}H_{46}N_2Ni$ (517.45) calcd.: C, 74.28; H, 8.96; N, 5.41%.

*Biacetylbis(2,6-dimethylphenylimin)(1,3-butadiene)nickel (**4b**)*

Starting from **3b**, the procedure used for **4a** was followed. Yield 78%. ^{1}H NMR (C_6D_6): δ 7.0–7.3 (m, 6H(Ph)); 4.87 (dd, 2H, ^3J 11.4 and 7.9 Hz); 2.31 (d, 2H, ^3J 7.9 Hz); 2.14 (s, 12H, CH$_3$); 0.84 (d, 2H, ^3J 11.4 Hz); 0.43 (s, 6H, CH$_3$(biacetyl)). ^{13}C NMR (C_6D_6): δ 90.00 (CH=*C*H$_2$); 45.51 (*C*H=CH$_2$). IR (cm^{-1}); 750 (s), 1230 (s), 1250 (s), 1570 (m). UV/VIS (pentane), λ_{max}: 494 nm. Analysis. Found: C, 69.13; H, 6.63; N, 6.56. $C_{24}H_{30}N_2Ni$ (405.23) calcd.: C, 71.14; H, 7.46; N, 6.91%.

*Biacetylbis(2,6-diisopropylphenylimin)(isoprene)nickel (**4c**)*

About 190 mg (0.36 mmol) of **4a** were stirred for 2 h with 0.5 ml of isoprene. The excess isoprene was then evaporated off and the remaining red powder recrystallised from 2 ml of pentane to yield 180 mg (0.3 mmol, 83%) of microcrystalline **4c**. ^{1}H NMR (C_6D_6): δ 7.61–7.42 (m, 6H(Ph)); 5.05 (m, 1H); 3.50 (sept, 2H(iso)); 3.11

(sept, 2H(iso)); 2.52 (d, 2H, H4(*syn*)); 2.50 (s, 1H, H1(*syn*); 1.91 (s, 3H, CH_3(isoprene)); 1.55 (d, 12H, CH_3, ^3J 7.7 Hz); 1.26 (broad, 12H, CH_3(isoprop)); 1.19 (s, 1H, H1(*anti*)); 1.10 (d, 1H, H4(*anti*), ^3J 12.03 Hz); 0.70 (s, 6H, CH_3(biacetyl)). ^{13}C NMR (C_6D_6): δ 152.20 (C=N); 139.70 (C–N); 126.00 (CPh); 124.16 (CPh); 105.50 (*C*=CCH_3); 90.35 (H_2C=CCH_3); 51.50 (CH_2=); 48.71 (CH_2=); 28.40 (CH(isopropyl)); 25.42, 24.89, 21.52, 20.86 (CH_3). IR (cm^{-1}): 750 (m), 795 (m), 990 (m), 1210 (w), 1290 (w) 1580 (m). UV/VIS (pentane), λ_{max}: 492 nm. Analysis. Found: C, 70.95; H, 9.15; N 4.89. $C_{33}H_{48}N_2Ni$ (531.47) calcd.: C, 74.58; H, 9.10; N, 5.27.

η^{2-5}-(Biacetylbis(2,6-diisopropylphenylimin)nickela-(2,4-cyclopentadiene)-biacetylbis(2,6-diisopropylphenylimin)nickel(0) (5)

A 100 ml Schlenk vessel containing a solution of 620 mg (1.12 mmol) of **4a** in 20 ml of pentane was cooled in liquid nitrogen and then evacuated. The solution was then allowed to warm up to room temperature and acetylene (purified over molecular sieve 4 Å) was slowly introduced without stirring of the solution. The colour of the mixture immediately changed from reddish-violet to deep blue. After 10 min crystals began to separate from the solution, and after overnight standing the crystallisation was complete and the mother liquid was decanted. The crystals were dried in vacuo to yield 290 mg (0.29 mmol, 49%) of complex **5**. When THF was used as solvent only polyacetylene was isolated, and so the solution must not be stirred, because too high a concentration of acetylene leads to polyacetylene. Even in the pentane procedure it was not possible to recover another crop of crystals from the mother liquid because of contamination with polyacetylene. IR (cm^{-1}): 740 (m), 780 (m), 970 (m), 1260 (m), 1380 (s), 1580 (m), 1640 (m), 2980 (s). UV/VIS (pentane), λ_{max}: 645 nm. Analysis. Found: C, 73.28; H, 8.80; N, 5.54. $C_{60}H_{84}N_4Ni_2$ (978.79) calcd.: C, 73.63; H, 8.65; N, 5.72%. The very poor solubility of the complex in common solvents prevented the recording of NMR-spectra.

η^{2-5}-(Biacetyl-bis(2,6-diisopropylphenylimin)nickela-2,4-cyclopentadiene)dicarbonylnickel (6)

A suspension of 204.2 mg (0.21 mmol) of **5** in 25 ml of pentane was stirred under an atmosphere of CO for 8 h, after which the colour had changed from blue to green. The solution was then filtered and concentrated to 5 ml and kept overnight to give 80 mg (0.13 mmol, 60%) of dark green crystals of **6**. ^1H NMR (C_6D_6): δ 7.21–7.14 (6H(Ph)); 4.75 (pseudo-t, 2H, ^3J 4.7 Hz); 4.21 (pseudo-t, 2H, ^3J 4.7 Hz); 3.31 (sept, 2H, ^3J 7.7 Hz); 3.01 (sept, 2H, ^3J 7.7 Hz); 1.53 (d, 6H); 1.39 (d, 6H); 1.14 (d, 6H); 0.99 (d, 6H); 0.86 (s, 6H, CH_3(biacetyl)). ^{13}C NMR (C_6D_6): δ 216.17 (CO); 200.10 (CO); δ 162.40 (N=C); δ 147.18 (N–C); 141.18 (C(*ortho*)); 140.20 (C(*ortho*)); 128.42 (C(*para*)); 127.60, 124.4 (C(*meta*)); 120.54 (Ni–C=*C*–); 114.65 (Ni–*C*=C–); 29.11, 28.82 (CH(iso)); 26.52, 25.04, 24.90, 24.76 (CH_3(iso)); 20.36 (CH_3(biacetyl)). IR (cm^{-1}): 1950 (s), 2000 (s), 1680 (m). UV/VIS (pentane), λ_{max}: 652 nm. Analysis. Found: C, 65.20; H, 7.37; N, 4.72. $C_{34}H_{44}N_2Ni_2O_2$ (630.16) calcd.: C, 64.81; H, 7.04; N, 4.45%.

X-ray data collection, structure determination, and refinement for 5 and 6

A blue crystal of **5**, isolated from the reaction mixture, was mounted in a Lindemann glass capillary under nitrogen. The space group was shown to be $P2_1/n$ from the systematically absent reflections. The positions of the nickel atom were determined by a Patterson synthesis using SHELXS 86 [15]. Difference Fourier maps showed the nitrogen and carbon atoms. For structure refinement the program SHELX 76 [16] was used. Refinement of the non-hydrogen atoms with anisotropic temperature factors and of the hydrogen atoms with isotropic thermal parameters led to final values of $R = 0.047$ and $R_w = 0.047$. The final positional parameters for **5** are given in Table 2.

A green crystal of **6**, obtained by cooling of a saturated pentane solution to −25 ° C, was immersed in silicone oil and then, at a temperature of 220 K, mounted on a glass fibre. From the systematic absences the space group was shown to be $P2_1/n$. The procedure for solving and refinement of the structure was the same as that used for **5**. However, the crystals of **6** showed to be rather unstable, when exposed to X-rays and three crystals had to be used to give sufficient data. For the refinement of the structure it was necessary to incorporate the three separate sets of collected data into one set, leading to a final $R = 0.063$ and $R_w = 0.079$. The final positional parameters of **6** are given in Table 3.

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