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1-Azadienes as bridging ligands in nickel(0) complexes of the type [(1-aza-1.3-diene)Ni(L)]$_2$ (L = 1-aza-1.3-diene, alkyne, triphenylphosphine)

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Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday.

Abstract

Dinuclear nickel(0) complexes of the type [(R^1–CH=CH–CH=N–R^2)$_2$Ni]$_2$ have been prepared from 1-aza-1.3-dienes and (cod)$_2$Ni. Reactions of both [Ni(**A**)$_2$]$_2$ (**1**) and [Ni(**B**)$_2$]$_2$ (**2**) (**A**: 1-aza-1.3-diene with R^1 = 2-furyl, R^2 = phenyl; in **B**: R^1 = 2-furyl, R^2 = furfuryl) with Ph$_3$P result in the formation of the complexes [Ni(**A**)(PPh$_3$)]$_2$ (**3**) and [Ni(**B**)(PPh$_3$)]$_2$ (**4**). According to the X-ray analyses, **1**, **3** and **4** contain two 1-aza-1.3-dienes, which act as bridging ligands yielding a diaza-dinickela eight-membered ring in the boat conformation. A variety of alkynes react with bis(1-aza-1.3-diene)nickel(0) complexes to form complexes of the type [(R^1–CH=CH–CH=N–R^2)Ni(alkyne)]$_2$. The molecular structures of [(**B**)Ni(HOC(Me)$_2$–C≡C–C(Me)$_2$OH)]$_2$, [(**A**)Ni-(Ph–C≡C–C(Me)$_2$OH)]$_2$ and [(**B**)Ni(Ph–C≡C–C(Me)$_2$OH)]$_2$, determined by X-ray analyses, also show that in these complexes both 1-azadienes bridge the Ni(0) centres. The inner dimetalla ring exhibits a chair conformation and the alkynes are terminally coordinated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel(0); 1-Aza-1.3-dienes; Alkynes; X-ray structure

1. Introduction

1-Aza-1.3-dienes are very flexible ligands, which cannot only coordinate in a '1.3-diene-like' manner (e.g. as 2π or 4π electron donors or under formation of metal-lacyclopentene rings) but also via the free electron pair of the nitrogen atom [1–23].

An unexpected ligand behaviour toward Ni(0) was found for cinnemaldehyde-*N*-phenylimine (L), which forms a dimeric complex of the type [NiL$_2$]$_2$. In this compound two cinnemaldehyde-*N*-phenylimines bridge two metal centres, while two other 1-aza-1.3-dienes act as monodendate ligands. The inner part of the complex can be described as a substituted diaza-dinickela-cyclooctadiene ring [20] (Fig. 1, L = cinnemaldehyde-*N*-phenylimine). To our knowledge the formation of a dimetallic ring connected by two 1-aza-1.3-dienes is limited to nickel(0) [5,6,20].

The question then arises as to whether the formation of such an unusual ring system is a general stabilizing principle for nickel(0) centres in 1-aza-1.3-diene complexes.

In this article we report on the organometallic chemistry of some furane-substituted 1-aza-1.3 dienes, which bear additional olefinic groups as possible competitive ligands toward Ni(0) (Scheme 1).

Reactions in the presence of alkynes should open the way for the preparation of mixed complexes of the type [(alkyne)Ni(μ-1-aza-1.3-diene)$_2$Ni(alkyne)] in which the Ni(0) centre is stabilized by three different groups: one olefinic groups, one azomethine and one alkyne. Such arrangements around Ni(0) are hitherto unknown.

1.1. Dinuclear 1.3-azadiene–nickel(0) complexes of the type [(1-aza-1.3-diene)$_2$Ni]$_2$ and [(1-aza-1.3-diene)Ni-(PPh$_3$)]$_2$

Reactions of the 1-aza-1.3-dienes **A** with Ni(cod)$_2$ (in the molar ratio 2.5:1) in THF at ambient temperature

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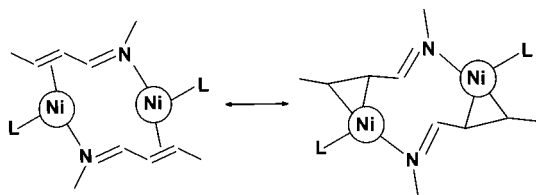* Corresponding author. Fax: + 49-36-4194-8102.

Fig. 1. The inner diaza-dinickela-cyclooctadiene ring in bis(bis(cinnemaldehyde-*N*-phenylimine)nickel(0) (L = cinnemaldehyde-*N*-phenylimine) and in related complexes.

resulted in the formation of a deep-blue, extremely air-sensitive solution from which the deep-blue micro-crystalline complex **1** of the composition [(1-aza-1.3-diene)$_2$Ni]$_2$ was isolated (Scheme 1). This complex is highly soluble in THF or diethyl ether, giving deep-blue or green solutions, and less soluble in hexane. The solutions are thermally unstable and tend to decompose under formation of traces of nickel.

NMR measurements show that there is only a slight difference in the ^{1}H and ^{13}C resonances of the coordinated 1-azadiene compared with those in the free ligand corresponding to the same observations in the structurally known complex bis[bis(cinnemaldehyde-*N*-phenylimine)]nickel(0) [20].

For example, in complex **1** the resonances for the CH=N groups ($\delta = 8.08$ and 8.46 ppm in DMF-d_7) lie in the same region as those of the bis[bis(cinnemaldehyde-*N*-phenylimine)]nickel(0) ($\delta = 7.9$ and 8.3 ppm).

The examination of the ^{13}C resonances of the ^{13}C-NMR spectra also reveals the coordination of ligand **A** to be very similar to that of bis[bis(cinnemaldehyde-*N*-

phenylimine)nickel(0)]. In comparison with the free ligand **A** in complex **1** the double signal set is observed, indicating two different types of 1-azadiene coordination. As expected, the signals of the ^{13}C atoms of the azomethine groups are found within the range of typical values for end-on-coordinated azomethines ($\delta = 161.1$ and 162.5 ppm) in agreement with the resonances in the compound bis[[bis(cinnemaldehyde-*N*-phenylimine)nickel(0)] [20]. The signals are almost unchanged when the NMR spectrum is monitored between -60 and $+60°C$, indicating that the structure is stable in a wide temperature range.

In addition, complex **1** shows the expected characteristic IR features in Nujol ($\nu_{C=N} = 1627$, $\nu_{C-C} = 1585$ cm^{-1}).

The close similarity of the ^{1}H-, ^{13}C-NMR and IR data with those of the structurally elucidated complex bis[[bis(cinnemaldehyde-*N*-phenylimine)nickel(0) [20], suggests that complex **1** has an identical structure (Fig. 1; L = α-furylacrolein-*N*-phenylimine). The X-ray analysis of **1** (crystallized from THF–hexane) also confirms this structure in the solid state. Fig. 2 shows that a boat conformation is formed. Table 1 contains some relevant bond lengths and angles.

Complex **2** could be isolated as a deep-blue powder from a 1:2.5 mixture of Ni(cod)$_2$ and **B**. Its IR data (1620 ($\nu_{C=N}$), 1564 (ν_{C-C})) and the reactions towards phosphines and alkynes suggest that **2** should have the same structure as **1**.

Moreover, **1** as **2** react in diethyl ether or THF with Ph$_3$P at ambient temperature. The substitution of one 1-aza-1.3-diene proceeded very smoothly when 1:1 stoi-
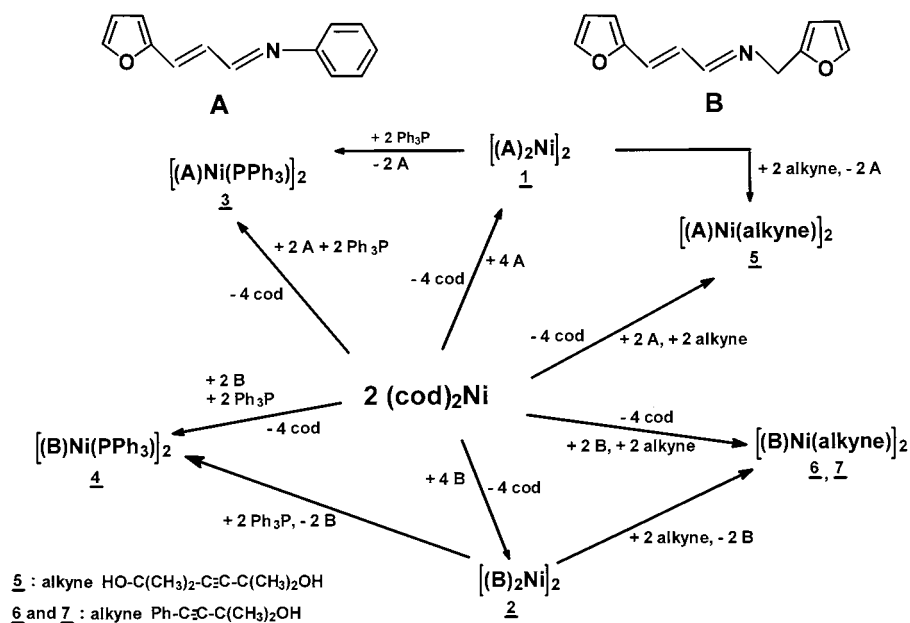
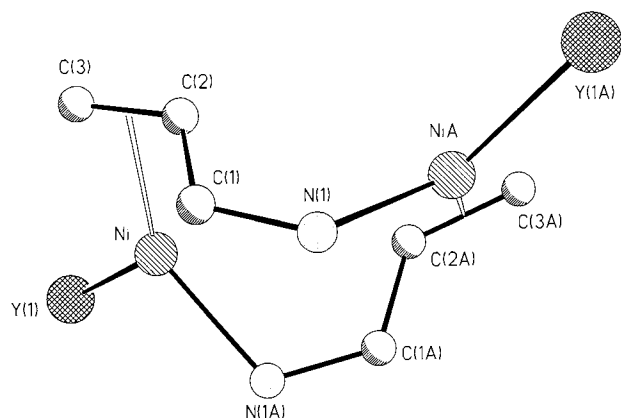Scheme 1. Formation reactions of 1-aza-1.3-diene complexes of Ni(0).

Fig. 2. The boat form of **1** (Y = N), **3** and **4** (Y = P).

Table 1
Selected bond distances (Å) and bond angles (°) for the boat form of **1**, **3** and **4** [a]

	1 Y = N	**3** Y = P	**4** Y = P
Bond lengths			
Ni–Y(1)	1.943(4)	2.151(1)	2.145(2)
Ni–N(1A)	1.993(4)	1.961(3)	1.961(6)
Ni–C(3)	1.982(5)	1.977(4)	1.990(8)
Ni–C(2)	2.000(5)	2.015(4)	2.017(7)
Ni–X(1)	1.858(4)	1.865(4)	1.865(7)
(centroid C(2)/C(3))			
C(2)–C(3)	1.430(7)	1.425(6)	1.439(11)
C(1)–C(2)	1.424(7)	1.395(6)	1.406(12)
C(1)–N(1)	1.334(7)	1.328(5)	1.316(10)
Bond angles			
Y(1)–Ni–N(1A)	101.9(2)	106.8(1)	110.5(2)
C(3)–Ni–C(2)	42.1(2)	41.8(2)	42.1(3)
X(1)–Ni–Y(1)	128.0(2)	123.7(1)	122.4(2)
X(1)–Ni–N(1A)	129.8(2)	129.5(2)	127.1(3)
C(1)–C(2)–C(3)	123.0(5)	125.6(4)	126.2(7)
C(2)–C(1)–N(1)	123.0(5)	121.2(4)	122.5(7)
C(1)–N(1)–NiA	118.4(4)	115.6(3)	118.6(5)

[a] Symmetry transformations used to generated equivalent atoms: $-x+1/2, y, -z+1$.
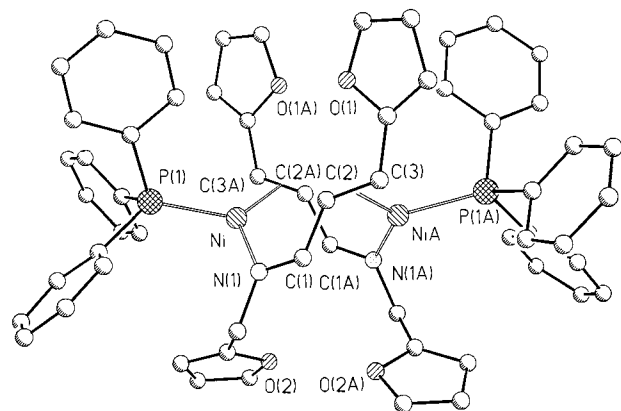

Fig. 3. Molecular structure of **4**.

chiometry (Ph_3P:Ni) was used, resulting in the formation of the deep-red complexes $[Ni(A)(PPh_3)]_2$ (**3**) and $[Ni(B)(PPh_3)]_2$ (**4**), which were isolated in good yields. The same complexes could be obtained by reacting a mixture of $(cod)_2Ni$ and the 1-aza-1.3-dienes **A** or **B** with triphenylphosphine (Scheme 1). Compounds **3** and **4** are much more thermally stable than the corresponding starting complexes **1** and **2**. They are sensitive towards air, but tolerate some moisture in the solvent. Both complexes are sparingly soluble in diethyl ether and THF.

Single crystals of **3**, crystallizing with hexane and water, suitable for X-ray crystal structure analysis could be isolated from diethyl ether–hexane solutions containing a small amount water. Single crystals of **4** were obtained from THF.

Fig. 2 shows the principal structure motif found in both complexes; Fig. 3 displays the molecular structure of complex **4**, as an example, and Table 1 contains selected bond distances and angles for both complexes in comparison with those of complex **1**.

The most important information is that the inner part of the complexes also consists of the eight-membered ring, according to Fig. 1 (L = Ph_3P, see [6]). This ring shows a boat conformation, which was also found in complex **1**. Bond lengths and angles lie within the range of typical values and are very similar to those recently found for other 1-aza-1.3-diene complexes [5,6,20]. There is no M–M interaction between both metal centers.

1.2. Binuclear alkyne complexes with 1-aza-1.3-dienes as bridging ligands

Reactions of the complexes **1** and **2** with a variety of disubstituted alkynes result in the formation of intense green solutions from which dark green crystalline complexes of the composition [Ni(1-aza-1.3-diene)-(alkyne)]$_2$ were isolated in good yields. The same type of compounds can also be obtained by reacting bis(alkyne)Ni(0) complexes with alkynes or from mixtures of $(cod)_2Ni$, alkyne and 1-aza-1.3-diene (Scheme 1).

Table 2 lists some complexes and their selected spectroscopic data.

The ^{1}H-NMR spectra of **5**–**7** are similar to those of other complexes with bridging 1-aza-1.3-dienes. The typical resonance for a CH=N group of the investigated alkyne complexes was found between 8 and 8.4 ppm. In addition, one characteristic absorption for the ^{13}C atom of this group between $\delta = 161$ and 163.5 ppm was observed. Moreover, these signals, as with the other resonances of the 1-aza-1.3-diene ligand, show only small shifts compared with the free ligand — in agreement with the results for the above-mentioned complexes containing 1-aza-1.3-dienes as bridging ligands.

Table 2
Selected bond distances (Å) and bond angles (°) for the chair form of **5–7** [a]

	5	6	7
Ni–L(1) centroid alkyne	1.795(4)	1.797(3)	1.790(1)
Ni–C(3)	2.061(4)	2.025(2)	2.063(1)
Ni–C(4)	2.079(4)	2.034(2)	2.081(1)
Ni–X1 (centroid C(3)–C(4))	1.947(4)	1.905(2)	1.948(1)
C(3)–C(4)	1.404(5)	1.399(4)	1.409(2)
C(2)–C(3)	1.457(5)	1.445(3)	1.441(2)
N(1)–C(2)	1.299(5)	1.287(3)	1.307(2)
N(1)–C(1)	1.489(5)	1.485(3)	1.435(2)
L(1)–Ni–N(1A)	126.0(1)	118.4(1)	127.5(1)
L(1)–Ni–X(1)	131.7(1)	135.8(1)	131.1(1)
N(1A)–Ni–X(1)	102.3(1)	105.5(1)	101.3(1)
N(1A)–Ni–C(4)	114.4(1)	117.1(1)	110.98(5)
N(1A)–Ni–C(3)	89.2(1)	92.6(1)	90.42(5)
C(2)–C(3)–C(4)	117.8(4)	121.0(2)	121.3(1)
N(1)–C(2)–C(3)	124.7(3)	122.5(2)	121.9(1)
C(1)–N(1)–C(2)	114.5(3)	119.4(2)	118.6(1)
NiA–N(1)–C(2)	119.3(2)	125.8(2)	121.34(9)
Ni–C(13)	1.897(4)	1.908(3)	1.891(1)
Ni–C(14)	1.909(4)	1.905(3)	1.909(1)
C(13)–C(14)	1.267(5)	1.274(4)	1.276(2)
C(16)–C(13)–C(14)	143.6(3)	158.2(2)	146.8(1)
C(13)–C(14)–C(15)	142.6(3)	145.6(2)	150.1(1)

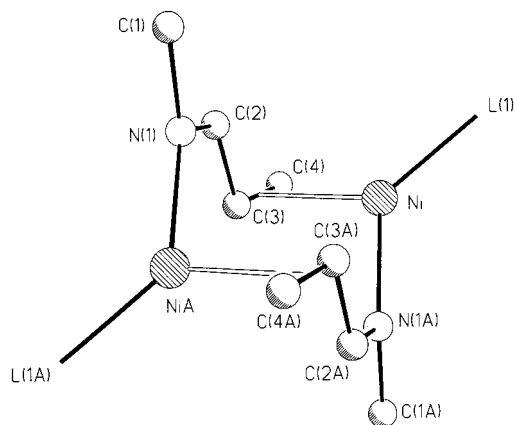[a] Symmetry transformations used to generated equivalent atoms: $-x+1$, $-y+1$, $-z$.

Fig. 4. The chair form of **5–7**.

For example, only one singlet for the CH$_3$ resonance at $\delta = 1.52$ ppm, one signal for the OH group ($\delta = 5.51$ ppm) and one doublet for the CH=N proton ($\delta = 8.03$ ppm) were observed in the DMF-d_7 solution of the complex [Ni(**A**)(Ph–C≡C–C(CH$_3$)$_2$OH)]$_2$ (**7**). The resonances for the protons of the phenyl group and of the furane ring were found between 6.9 and 7.9 ppm. Due to the simple pattern of the NMR spectra, a highly symmetrical structure is indicated.

The alkyne complexes **5–7** also display the expected characteristic IR features. The bands assigned to the stretching vibrations of terminally coordinated C≡C bonds are found between 1815 and 1830 cm^{-1} (Table 2), indicating that the extent of π-back donation from Ni to the alkynes is greater than in the corresponding complexes of the type bis(alkyne)Ni(0), in which the stretching vibrations of the coordinated alkynes were found at 1880–1910 cm^{-1} [24–26]. The $\nu_{CH=N}$ bands appear between 1600 and 1630 cm^{-1}, depending on the nature of the alkyne and the 1-aza-1.3-diene.

The IR as well as the NMR data correspond well with a dimeric structure of the alkyne complexes containing both Schiff base ligands as bridges between the metal centres, while the alkynes are terminally coordinated.

X-ray diffraction studies of complexes **5–7** were carried out to establish the molecular structures. Green crystals suitable for structure determination were grown from mixtures of THF and diethyl ether. Under these conditions complex **5** crystallized with two equivalents of THF and complex **7** with two equivalents of diethyl ether, which do not coordinate to the metal centres. Fig. 4 displays the general structural principle, which indicates that in all three complexes dinuclear structures are also formed containing the 1-aza-1.3-dienes as bridging ligands. This confirms the high tendency to form such dimetallic ring systems.

Remarkably, the inner diaza-dinickela eight-membered ring in the three alkyne complexes exhibits a chair conformation — in contrast to the above-discussed complexes **1**, **3** and **4** containing the boat conformation. The stabilizing of different conformations by the different ligands cannot easily be explained; however a boat form of complexes **5–7**, containing bulky alkynes, would be unfavourable from steric reasons.

A drawing of the molecular structure of complex **5** is depicted in Fig. 5. Table 3 summarizes relevant bond distances and angles for complexes **5–7**, showing that the C=N, C=C– and the C≡C bond lengths are in the typical range of values for these bonds.
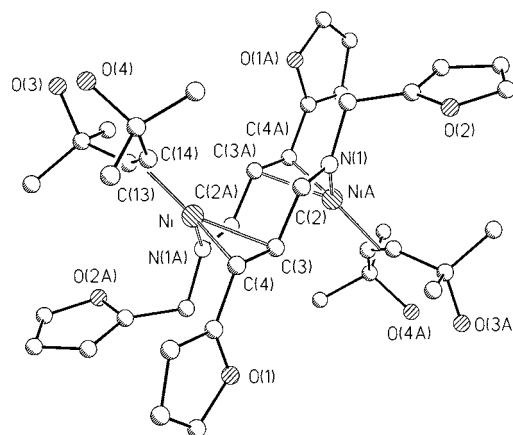

Fig. 5. Molecular structure of **5**.

Table 3
Some spectroscopic data of complexes of the type [(alkyne)Ni(μ-1-aza-1.3-diene)$_2$Ni(alkyne)] (complex **8** was only spectroscopically investigated)

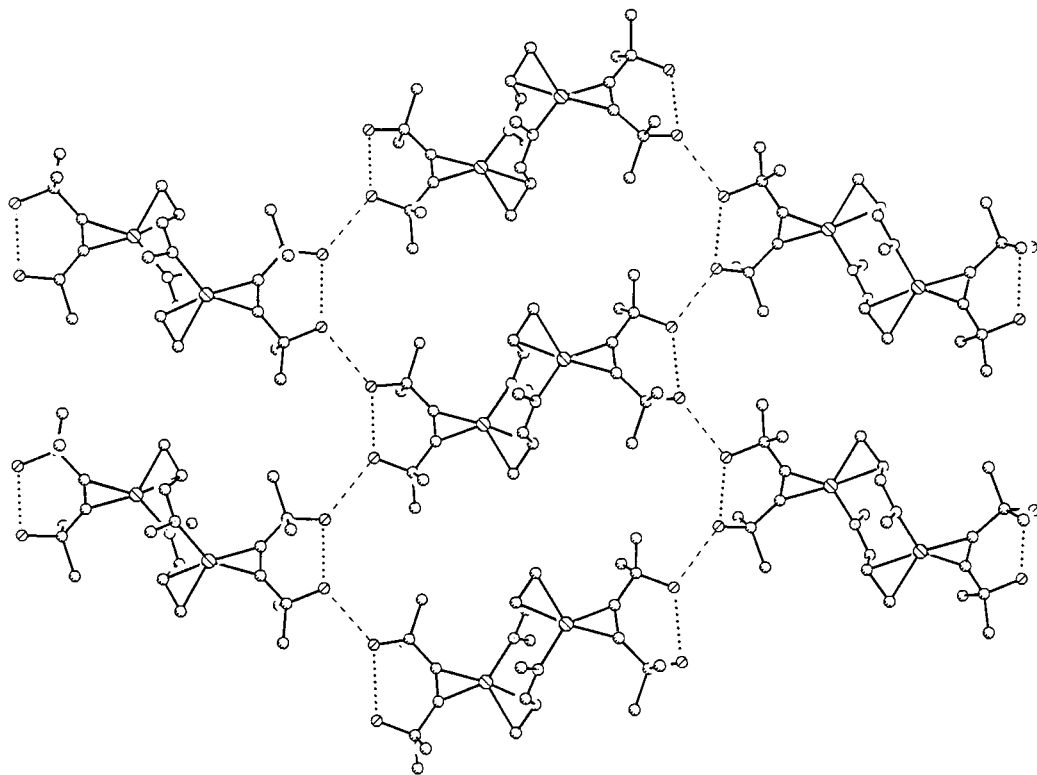| Complex	1-Aza-diene	Alkyne	$\delta_{CH=N}$	$v_{C\equiv C}$	$v_{C=N}$
5	**B**	HOC(Me)$_2$C≡C(Me)$_2$OH	162.3	1826	1628
6	**B**	Ph–C≡C(Me)$_2$OH	160	1819	1603
7	**A**	Ph–C≡C(Me)$_2$OH	162	1824	1593
8	**B**	HOC(Et)(Me)C≡C(Et)(Me)OH	163.8	1822	1629

Fig. 6. The layer arrangement of **5** in the packing (without the furfuryl groups for a better view).

Fig. 6 shows the hydrogen-bonded network in **5** consisting of a sequence of inter- and intramolecular hydrogen bonds, which link the diol groups of the alkyne substituents to form layers. The intramolecular O···O distances in **5** are 2.763(2) Å, while the intermolecular separations are slightly longer (2.791(2) Å). A similar hydrogen-bonded network was found in the complex (cod)Ni(alkynediol), which we recently reported [24]. This is different from the packing motifs observed in complexes of the type bis(alkynediol)Ni(0), which exclusively form intermolecular hydrogen bonds [24,25]. This difference may be explained by the influence of the nitrogen ligand in the 1.3-azadiene complex **5**, which is a better donor ligand than the alkynediol in the corresponding bis(alkynediol) complex.

It is noteworthy that the oxygen atoms of the furane rings do not act as hydrogen acceptors in this compound; only the OH groups of the coordinated alkynediol form the hydrogen bonds. The formation of polymeric units in **5** via O–H···O bonds of the OH groups does not only maximize the O···O approach, but also generates a protected system where the hydroxyl groups are encapsulated within a sheath of carbon atoms. This might explain why the OH groups do not react with Ni(0) under oxidation of the metal centre. For this reason the Ni(0) complexes are stable in the solid-state even for a long time.

The larger charge transfer from Ni(0) into the π*-orbital of the alkyne in **5** leads to smaller C–C≡C bond angles compared with those in the bis(alkyne)Ni(0) complexes [26]; consequently the formation of intramolecular hydrogen bonds becomes more favourable in **5**.

Complexes **6** and **7** containing a substituted alkynol instead of an alkynediol have very similar molecular structures. However, the nature of the hydrogen bond is quite different. In case of the crystalline complex **6**, the oxygen groups of the furane ring in the 1-aza-1.3-diene act as hydrogen acceptors for the OH groups of the alkynol to form chains in which the O···O separa-

tion is 3.106(3) Å (Fig. 7), while in complex **7**, crystallizing with one molecule of diethyl ether per Nickel, hydrogen bonds between the OH groups of the alkynol and diethyl ether are solely formed.

2. Conclusions

In summary, we have synthesized a new series of dinuclear (1-aza-1.3-diene)nickel(0) complexes in which two 1-azadienes act as bridging ligands connecting two Ni(0) centres.

Six X-ray structural analyses (for **1**, **3**, **4**, **5**, **6**, **7**) demonstrate the outstanding stability of the inner part of the complexes, which can be described as substituted dinickela-diazaoctadiene ring existing in two conformations. Additional ligands at the Ni(0) centre can be either 1-aza-1.3-dienes or triphenylphosphine (stabilizing the chair conformation) or a variety of substituted alkynes, which stabilize the boat conformation. For the first time we were able to prepare nickel(0) complexes, where an olefinic ligand, an alkyne and an azomethine ligand surrounded the metal center all together.

3. Experimental

All operations were carried out in an inert atmosphere of argon using Schlenk techniques. Solvents were dried by usual methods and distilled under argon prior to use. For analytical characterizations we used a 200 MHz Bruker AC 200 F spectrometer for NMR (200 MHz and 50.3 MHz for ^{1}H and ^{13}C, respectively), a Perkin–Elmer spectrometer system 2000 FT for IR (spectra measured as Nujol mulls), a Chrompack CP 9000 (with methylsilicone CP-SIL-5CB) for GC, a Finnigan MAT SSQ 710 for GC–MS, a Perkin–Elmer AutoSystem XL for GC–IR measurements and for X-ray determination an Enraf–Nonius diffractometer.

Elemental analyses (C, H, N, Cl) were carried out in the Institut für Organische Chemie und Makromolekulare Chemie (Friedrich-Schiller-Universität Jena).

Primary amines and aldehydes used for the preparation of the 1-azadienes were purchased (Aldrich) and destillated. Complexes of the type [(alkyne)$_2$Ni] were prepared as described [24–26].

3.1. Bis[bis(α-furylacrolein-N-phenylimine)di-nickel(0)] (1)

α-Furylacrolein-*N*-phenylimin (**A**) was prepared from α-furylacrolein and aniline, according to described methods [20,27], as a white microcrystalline solid, yield 70%. ^{1}H-NMR (200 MHz, CDCl$_3$, 298 K): $\delta = 6.27$–7.45 (m, 10H, furyl, ph), 8.14 (d, 1H, CH=N); ^{13}C-NMR (50.3 MHz, CDCl$_3$, 298 K): $\delta = 112.2$, 112.6, 120.8, 126.0, 126.6, 129.1, 130.2, 144.2, 151.8, 151.9, (furyl, ph, CH=), 160.9 (CH=N). IR (Nujol, cm^{-1}): 1626 ($\nu_{C=N}$), 1583 ($\nu_{C=C}$).

The reaction of (cod)$_2$Ni (0.8 mmol, 220 mg) with 2.4 mmol (474 mg) of the ligand **A** in THF (30 ml) results in a deep-blue solution, which was stirred over a period of 4 h at ambient temperature. Upon distillation of the solvent, followed by removal of cod i.v. at 20°C, hexane was added. The precipitate was filtered off and washed three times with hexane to remove free ligand. Black, extremely air-sensitive microcrystalline solid of the composition [Ni(**A**)$_2$]$_2$, Yield 44.6%. ^{1}H-NMR (200 MHz, THF-d_8, 298 K, in situ): $\delta = 6.41$–7.84 (m, furyl, ph), 8.08, 8.46, (d, 1H, CH=N); ^{13}C-NMR (50.3 MHz, 298 K): $\delta = 112.3$,; 112.9, 113.1, 121.5, 122.4, 122.7, 126.3, 127.8, 128.7, 128.9, 129.5, 130.4, 139.1, 144.7, 145.1, 153.1, 153.3, 156.9 (furyl, ph, CH=), 161.1, 162.5 (CH=N). IR (Nujol, cm^{-1}): 1617 ($\nu_{C=N}$), 1591, 1567 ($\nu_{C=C}$). [Ni(**A**)$_2$]$_2$, C$_{52}$H$_{44}$N$_4$Ni$_2$O$_4$, $M = 906.3$ g mol^{-1}. Elemental analyses: Calc.: C, 68.9; H, 4.9; N, 6.2. Found: C, 69.0; H, 5.0; N, 5.9%.

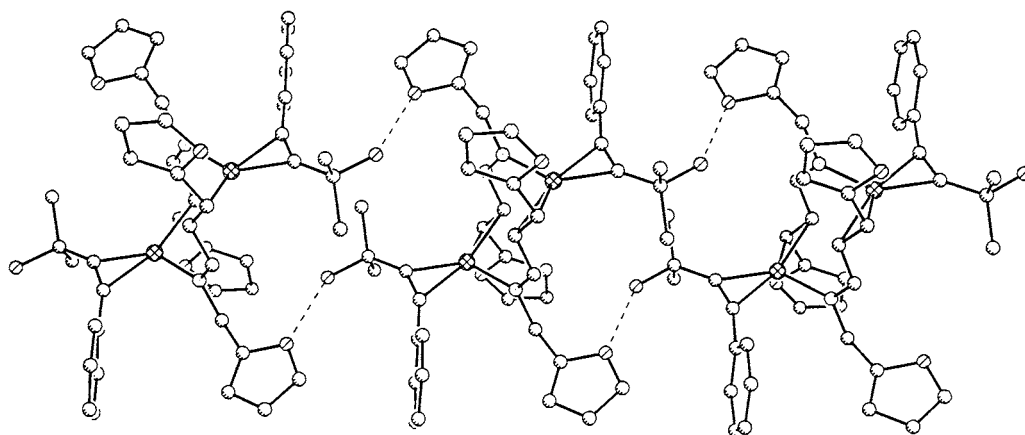Fig. 7. The chain arrangement of **6** in the packing.

3.2. Bis[bis(α-furylacrolein-N-furfurylimine)-di-nickel(0)](diethyl ether) (2)

α-Furylacrolein-*N*-furfurylimine (**B**) was prepared from α-furylacrolein and furfurylamine, according to described methods [20,27], as a white microcrystalline solid, yield 75%. ^{1}H-NMR (200 MHz, CDCl$_3$, 298 K): $\delta = 4.64$ (s, 2H, CH$_2$), 6.20–6.87 (m, 6H), 7.35 (2H; d(d)), furyl, ph); 8.14 (d(d), 1H, CH=N); ^{13}C-NMR (50.3 MHz, CDCl$_3$, 298 K): $\delta = 57.1$ (–CH$_2$), 107.2, 110.3, 111.7, 111.9, 126.1, 128.9, 142.1, 143.8 (furyl, ph, CH=), 151.8, 152.4 (C=), 163.8 (CH=N). IR (Nujol, cm^{-1}): 1635, 1623, 1553, 1505 ($v_{C=N}$, $v_{C=C}$).

The deep-blue nickel(0) complex **2** was prepared analogously to complex **1**. It tends to precipitate as a dark blue oily product containing different amounts of solvent. Dissolution in ether and treatment with an excess of hexane gives a microcrystalline powder of the composition [Ni(**B**)$_2$]$_2$(diethyl ether), C$_{52}$H$_{54}$N$_4$Ni$_2$O$_9$, $M = 996.3$ g mol^{-1}. Elemental analyses: Calc.: N, 5.6; Ni, 11.8. Found: N, 5.4; Ni, 12.0%. IR (Nujol, cm^{-1}): 1620 ($v_{C=N}$), 1564 ($v_{C=C}$).

3.3. Bis[(α-furylacrolein-N-phenylimine)-(triphenylphosphin)nickel(0)], [Ni(A)(PPh$_3$)]$_2$ (3)

(cod)$_2$Ni (0.8 mmol, 220 mg) was dissolved in THF (35 ml). At ambient temperature 0.8 mmol (158 mg) of ligand **A** was added, followed by addition of Ph$_3$P (210 mg) dissolved in THF (20 ml). Upon stirring of the reaction mixture (4 h) the volume of the dark red solution was reduced to 2–3 ml and 10 ml diethyl ether were added, followed by addition of 10 ml hexane. The product was isolated as deep-red crystals. Yield 299 mg (72.1%). ^{1}H-NMR (200 MHz, THF-d_8, 298 K): $\delta = 3.00$ (d,d), (CH=), 5.27 (d), 5.86 (s), 6.28–6.64 (furyl, CH=), 7.14–7.38 (ph, CH=N); ^{13}C-NMR (50.3 MHz, THF-d_8, 298 K): $\delta = 101.9$, 112.0, 120.8, 121.5, 128.1, 128.3, 128.4, 129.3, 134.2, 134.5, 134.9, 135.6, 138.7, 147.6, 154.8 (furyl, ph, CH=), 160.9 (CH=N). IR (Nujol, cm^{-1}): 1615 ($v_{C=N}$), 1583, 1547 ($v_{C=C}$). C$_{62}$H$_{52}$N$_2$Ni$_2$O$_2$P$_2$, $M = 1036.4$ g mol^{-1} Elemental analyses: Calc.: N, 2.7; Ni, 11.3. Found: N, 2.5; Ni, 11.1%.

Single crystals of the composition [Ni(A)-(PPh$_3$)]$_2$(hexane)$_{0.5}$(water)$_{1.5}$, suited for X-ray analysis, were obtained from diethyl ether–hexane solutions, which also contained a small amount water (from moisture in diethyl ether). The mother liquor was decanted off and the dark red single crystals were used for the X-ray analysis without removal of the solvents.

3.4. Bis[(α-furylacrolein-N-furfurylimine)-(triphenylphosphin)nickel(0)], [Ni(B)(PPh$_3$)]$_2$ (4)

Complex **4** was prepared from (cod)$_2$Ni, ligand **B** and Ph$_3$P, analogously to the procedure described for **3**.

Sparingly soluble dark red single crystals of the composition [Ni(B)(PPh$_3$)]$_2$, suited for the X-ray analysis, were obtained from the dark red solution. IR (Nujol, cm^{-1}): 1628 ($v_{C=N}$), 1566 ($v_{C=C}$). C$_{60}$H$_{52}$N$_2$Ni$_2$O$_4$P$_2$, $M = 1044.40$ g mol^{-1}, Elemental analyses: Calc.: C, 68.9; H, 5.1; N, 2.8. Found: C, 68.1; H, 5.8; N, 2.5%.

3.5. Preparation of the alkyne complexes 5–7

To the blue solution of 0.9 mmol (cod)$_2$Ni and 0.9 mmol of the corresponding 1-aza-1.3-diene in THF (35 ml) at ambient temperature 0.9 mmol of the alkyne were added. The colour of the reaction mixture changed after 5–10 min to deep green. The solution was stirred for 6–8 h. After this time the solution was concentrated to ca. 2–3 ml. Standing overnight resulted in the precipitation of green needles. Upon filtration the products were washed with diethyl ether and dried in high vacuum. Yield was ca. 70%.

The same products could be isolated from the reaction between the bis(alkyne)Ni(0) complexes and the corresponding 1-aza-1.3-dienes in THF or by reacting the bis[bis(1.3-azadiene)Ni(0)] complexes with the corresponding alkynes.

3.6. Bis[(α-furylacroleine-N-furfurylimine)-(tetramethylbutindiol)nickel(0)] (5)

^{1}H-NMR (200 MHz, DMF-d_7, 298 K): $\delta = 1.39$ (s, CH$_3$), 3.40 (OH), 4.30 (s, CH$_2$), 4.5–5.3, 5.7–6.5, 7.6–7.8 (m, furyl, CH=), 8.0 (CH=N); ^{13}C-NMR (50.3 MHz, DMF-d_7, 298 K): $\delta = 32.1$ (CH$_3$), 56.7 (CH$_2$), 65.9 (*C*(CH$_3$)$_2$OH), 58.8, 67.9, 71.0, 76.2, 107.0, 110.4, 111.2, 113.5, 142.2, 143.7 (furyl, CH=, C≡), 162.3 (CH=N); ^{15}N-NMR: $\delta = 102.8$. IR (Nujol, cm^{-1}): 1628 ($v_{C=N}$), 1826, ($v_{C≡C}$), 3313 (v_{OH}). C$_{40}$H$_{50}$N$_2$O$_8$Ni$_2$, $M = 948.45$ g mol^{-1}. Elemental analyses: Calc.: C, 59.7; H, 6.3; N, 3.5; Ni, 14.6. Found: C, 57.3; H, 6.4; N, 3.4; Ni, 14.6%.

Crystals of the composition [(A)Ni(tetramethyl-butindiol)]$_2$·2THF, suitable for the X-ray analysis, were obtained from dilute THF solutions at $-20°C$. They were used without evaporation of the solvent in vacuo.

3.7. Bis[(α-furylacroleine-N-furfurylimine)-(4-phenyl-2-methyl-but-3-yne-2-ol)nickel(0)] (6)

IR (Nujol, cm^{-1}): 1559, 1577, ($v_{C=C}$), 1603 ($v_{C=N}$), 1819, ($v_{C≡C}$), 3146 (v_{OH}).

Single crystals of **6** were isolated from dilute THF solutions at $-20°C$.

3.8. Bis[(α-furylacroleine-N-phenylimine)(4-phenyl-2-methyl-buty-3-yne-2-ol)nickel(0)](diethyl ether)$_2$ (7)

The compound crystallizes from a mixture of THF–diethyl ether at $-20°C$, depending on the conditions

for crystallization and drying with one to two equivalents diethyl ether per dimeric unit.

Single crystals containing two equivalents of diethyl ether were obtained from dilute solutions (1:5 THF–diethyl ether) at $-25°C$. ^1H-NMR (200 MHz, DMF-d_7, 298 K): $\delta = 1.11$ (t, CH_3, from diethyl ether); 1.52 (s, CH_3 from the alkyne), 1.40 (q, CH_2 from diethyl ether), 5.51 (s, OH), 6.90–7.40 (m, ph, furyl, CH=), 8.39 (d, CH=N); ^{13}C-NMR (50.3 MHz, DMF-d_7, 298 K, only resonances which do not overlap with the signals of the solvent could be assigned): 15.5 (CH_3), 65.6 ($C(CH_3)_2OH$), 113.2, 113.9, 121.9, 126.5, 127.0, 128.8, 129.2, 129.8 (CH=, phenyl), 131.2, 131.9, (C≡) 145.7, 152.7, (C) 161.9 (CH=N). IR (Nujol, cm^{-1}): 1559, 1587 ($v_{C=C}$), 1593 ($v_{C=N}$), 1824, ($v_{C≡C}$), 3457 (v_{OH}). $C_{52}H_{56}N_2Ni_2O_5$ (with one equivalent diethyl ether) $M = 906.4$ g mol^{-1}, Elemental analyses: Calc.: C, 68.9; H, 6.2; N, 3.1; Ni, 12.9. Found: C, 68.0; H, 5.6; N, 3.2; Ni, 12.7%.

3.9. Crystal structure determination

The intensity data for compounds **3** and **4** were collected on a Nonius CAD4 diffractometer and for the other compounds on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [28,29].

The structures were solved by direct methods (SHELXS [30]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [31]). For compounds **5** and **6**, and for the hydroxy group of **7**, the hydrogen atoms were located by difference Fourier synthesis and refined isotropically, the hydrogen atoms of the other structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [31]. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

3.9.1. Crystal data for **1**

$C_{52}H_{44}N_4Ni_2O_4$, $M_r = 906.3$ g mol^{-1}, black prism, size $0.20 \times 0.10 \times 0.08$ mm^3, orthorhombic, space group $Pbcn$, $a = 19.9488(6)$, $b = 13.0224(6)$, $c = 17.0322(8)$ Å, $V = 4424.6(3)$ Å^3, $T = -90°C$, $Z = 8$, $\rho_{calc.} = 1.361$ g cm^{-3}, μ(Mo–K$_\alpha$) = 9.02 cm^{-1}, $F(000) = 1888$, 9598 reflections in h ($-25/25$), k ($-16/16$), l ($-22/22$), measured in the range $3.35° \leq \Theta \leq 27.52°$, completeness $\Theta_{max} = 99.6\%$, 5069 independent reflections, $R_{int} = 0.125$, 2886 reflections with $F_o > 4\sigma(F_o)$, 277 parameters, nine restraints, $R^1_{obs} = 0.0964$, $wR^2_{obs} = 0.1729$, $R^1_{all} = 0.1848$, $wR^2_{all} = 0.2021$, GOF = 1.072, largest difference peak and hole: $0.787/-0.580$ e Å^{-3}.

3.9.2. Crystal data for **3**

$C_{62}H_{52}N_2Ni_2O_2P_2 \cdot 0.5C_6H_{12} \cdot 1.5H_2O$, $M_r = 1102.49$ g mol^{-1}, dark-red prism, size $0.40 \times 0.38 \times 0.38$ mm^3,

monoclinic, space group $I2/a$, $a = 18.366(4)$, $b = 16.601(3)$, $c = 21.344(4)$ Å, $\beta = 110.13(3)°$, $V = 6110(2)$ Å^3, $T = -90°C$, $Z = 4$, $\rho_{calc.} = 1.198$ g cm^{-3}, μ(Mo–K$_\alpha$) = 7.13 cm^{-1}, $F(000) = 2304$, 7168 reflections in h ($-23/21$), k ($-21/0$), l (0/27), measured in the range $2.36° \leq \Theta \leq 27.54°$, 6987 independent reflections, $R_{int} = 0.104$, 3724 reflections with $F_o > 4\sigma(F_o)$, 352 parameters, 0 restraints, $R^1_{obs} = 0.057$, $wR^2_{obs} = 0.147$, $R^1_{all} = 0.117$, $wR^2_{all} = 0.250$, GOF = 1.023, largest difference peak and hole: $0.921/-0.781$ e Å^{-3}.

3.9.3. Crystal data for **4**

$C_{60}H_{52}N_2Ni_2O_4P_2$, $M_r = 1044.40$ g mol^{-1}, dark-red prism, size $0.40 \times 0.38 \times 0.36$ mm^3, monoclinic, space group $I2/a$, $a = 18.585(4)$, $b = 14.998(3)$, $c = 22.648(5)$ Å, $\beta = 105.45(3)°$, $V = 6084(2)$ Å^3, $T = -90°C$, $Z = 4$, $\rho_{calc.} = 1.140$ g cm^{-3}, μ(Mo–K$_\alpha$) = 7.13 cm^{-1}, $F(000) = 2176$, 7063 reflections in h ($-24/20$), k ($-19/0$), l ($-29/20$), measured in the range $2.34° \leq \Theta \leq 27.41°$, 6910 independent reflections, $R_{int} = 0.036$, 2263 reflections with $F_o > 4\sigma(F_o)$, 316 parameters, 0 restraints, $R^1_{obs} = 0.067$, $wR^2_{obs} = 0.177$, $R^1_{all} = 0.185$, $wR^2_{all} = 0.330$, GOF = 1.153, largest difference peak and hole: $1.051/-0.477$ e Å^{-3}.

3.9.4. Crystal data for **5**

$C_{40}H_{50}N_2O_8Ni_2 \cdot 2C_4H_8O$; $M_r = 948.45$ g mol^{-1}, red–brown prism, size $0.38 \times 0.36 \times 0.32$ mm^3, monoclinic, space group $P2_1/n$, $a = 12.4654(3)$, $b = 9.2149(3)$, $c = 21.1194(8)$ Å, $\beta = 92.799(2)°$, $V = 2423.0(1)$ Å^3, $T = -90°C$, $Z = 2$, $\rho_{calc.} = 1.297$ g cm^{-3}, μ(Mo–K$_\alpha$) = 8.33 cm^{-1}, $F(000) = 1008$, 6321 reflections in h ($-13/13$), k ($-10/0$), l ($-23/23$), measured in the range $2.94° \leq \Theta \leq 23.27°$, completeness $\Theta_{max} = 99.3\%$, 3474 independent reflections, $R_{int} = 0.039$, 2924 reflections with $F_o > 4\sigma(F_o)$, 272 parameters, nine restraints, $R_{obs} = 0.050$, $wR^2_{obs} = 0.147$, $R^1_{all} = 0.060$, $wR^2_{all} = 0.156$, GOF = 0.942, largest difference peak and hole: $0.743/-0.646$ e Å^{-3}.

3.9.5. Crystal data for **6**

$C_{46}H_{46}N_2Ni_2O_6$, $M_r = 840.25$ g mol^{-1}, dark-green prism, size $0.35 \times 0.35 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $a = 9.4118(8)$, $b = 9.436(1)$, $c = 11.384(1)$ Å, $\alpha = 96.225(5)$, $\beta = 95.718(7)$, $\gamma = 94.312(7)°$, $V = 996.3(2)$ Å^3, $T = -90°C$, $Z = 1$, $\rho_{calc.} = 1.397$ g cm^{-3}, μ(Mo–K$_\alpha$) = 9.97 cm^{-1}, $F(000) = 438$, 5413 reflections in h ($-10/10$), k ($-10/0$), l ($-12/12$), measured in the range $3.44° \leq \Theta \leq 23.30°$, completeness $\Theta_{max} = 98.3\%$, 2713 independent reflections, $R_{int} = 0.054$, 2503 reflections with $F_o > 4\sigma(F_o)$, 341 parameters, 0 restraints, $R^1_{obs} = 0.034$, $wR^2_{obs} = 0.092$, $R^1_{all} = 0.038$, $wR^2_{all} = 0.097$, GOF = 1.024, largest difference peak and hole: $0.368/-0.532$ e Å^{-3}.

3.9.6. Crystal data for **7**

$C_{48}H_{46}N_2Ni_2O_4 \cdot 2C_4H_{10}O$, $M_r = 980.53$ g mol^{-1}, black prism, size $0.34 \times 0.32 \times 0.30$ mm^3, monoclinic, space group $P2_1/c$, $a = 12.1019(2)$, $b = 18.9249(3)$, $c = 12.9029(2)$ Å, $\beta = 117.228(1)°$, $V = 2627.67(7)$ Å^3, $T = -90°C$, $Z = 2$, $\rho_{calc.} = 1.239$ g cm^{-3}, $\mu(Mo-K_\alpha) = 7.66$ cm^{-1}, $F(000) = 1040$, 10103 reflections in h (0/15), k (0/23), l (−16/14), measured in the range $3.55° \leq \Theta \leq 26.33°$, completeness $\Theta_{max} = 99.3\%$, 5310 independent reflections, $R_{int} = 0.030$, 4895 reflections with $F_o > 4\sigma(F_o)$, 430 parameters, 0 restraints, $R_{obs}^1 = 0.0275$, $wR_{obs}^2 = 0.0742$, $R_{all}^1 = 0.031$, $wR_{all}^2 = 0.077$, GOF = 0.980, largest difference peak and hole: $0.238/-0.357$ e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134627 (for compound **1**), CCSD 134622 (for compound **3**), CCSD 134623 (for compound **4**), CCSD 134624 (for compound **5**), CCSD 134625 (for compound **6**), and CCSD 134626 (for compound **7**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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