Dinuclear 2,2'-biallyl nickel complexes containing square-planar nickel(I): crystal structure of $\mu(\eta^{3:3}$-$(CH_2)_2CC(CH_2)_2)$-*trans*-[Ni(dad)]$_2$ (dad = biacetylbis(2,6-dimethylphenylimine))

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Abstract

Diazadiene nickel butadiene complexes react with allene in a 1:1 ratio to give paramagnetic complexes **2**, of composition (dad)Ni(C_3H_4). A single-crystal structure determination in the case of **2a** has revealed the presence of a planar bridging tetramethyleneethane (2,2'-biallyl) ligand to which two (dad)Ni fragments are coordinated on opposite sides. The complex can be regarded as containing two independent nickel(I) centres, each having a square-planar coordination geometry.

Introduction

The behaviour of transition metal complexes towards organic substrates depends on the metal and also on the other ligands in the coordination sphere. In this respect the phosphine nickel(0) system [(P,P)Ni] [where (P,P) denotes two phosphine ligands)] differs significantly from the (diazadiene)nickel(0) system [(dad)Ni] (dad = RN=CR'CR'=NR). Thus [(P,P)Ni] coordinates with only one double bond to give the complexes [(Ph$_3$P)$_2$Ni(ethylene)] [1] or [(cyclohexyl$_3$P)$_2$Ni(η^2-isoprene)] [2], whereas with [(dad)Ni] two double bonds add, to give [(dad)Ni(ethylene)$_2$] [3] and [(dad)Ni(η^4-butadiene)] [4]. The complexes also show different behaviour in catalysis of coupling reactions of activated multiple bonds. Whereas [(P,P)Ni] is often rather unreactive in catalysis of reactions involving alkynes [5], [(dad)Ni(0)] species are excellent catalysts for the selective formation of tetrasubstituted cyclooctatetraenes from 1-alkynes [6], and intermediates in the coupling of two alkynes (including acetylene itself) to a C_4 fragment have been characterized by X-ray diffraction studies [4,7]. We thought it of interest to examine the behaviour of the very reactive double bond system of allene (1,2-propadiene) towards the (dad)nickel system, since its reaction with [(P,P)Ni] is known to give a 2,3-bis(methylene)nickelacyclopentadiene [8]. Bis(alkylidene)platinacyclopentadienes are also obtained from

corresponding [(P,P)Pt] and [(dad)Pt] precursors and allenes [9,10]. We report here on the different results observed with the diazadiene nickel system.

Results and discussion

When allene was bubbled in excess into a pentane solution of (dad)nickel(butadiene) **1** (i.e. either **1a** or **1b**), a white, gum-like polyallene was formed, together with an organonickel complex. However, when the pentane solution of **1** was exposed to an atmosphere of allene (an equimolar amount with respect to Ni) without stirring, a colour change from red-violet to brown was observed and large dark-coloured crystals of the product **2** separated after standing overnight. Product **2** has composition (dad)Ni(C_3H_4); it is moderately air sensitive, and its solutions turn red in contact with air, and polyallene formation is again observed. Complex **2** is paramagnetic, and no structural information could be obtained from its NMR spectra. The solid state ESR spectrum shows an intense signal at a central field of 3371.9 G, but no hyperfine splitting, indicating a Ni(I) species. In addition to bands from the coordinated dad, the IR spectrum shows new bands in the range 1500–1450 cm^{-1}, typical of η^3 coordinated allyl groups [11], while there are no absorptions in the range 1900–1700 cm^{-1} for a coordinated allene. We thus concluded that dimerization of the allene via the central carbon atom had taken place and that the complex must be dinuclear. Such dinuclear complexes with the C_6H_8-ligand in an $\eta^{3:3}$ coordination mode are well established for Mn[12], Fe [13], Ni [14] or Pd [14], but all such cases involved 18e$^-$ (or 16e$^-$ for d^8 metals) configurations. The paramagnetism of **2** was intriguing, and a single-crystal X-ray diffraction study was performed in the case of **2a**.
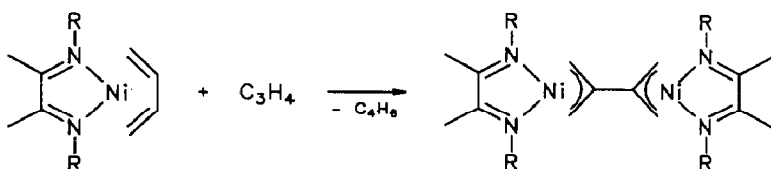
1a   R = 2,6-dimethylphenyl   2a, b
1b   R = 2,6-diisopropylphenyl

X-Ray structure determination of μ-($\eta^{3:3'}$-tetramethyleneethane)-trans-bis(diazadienenickel), 2a

A crystal of brown **2a**, mounted in a Lindemann capillary on a Syntex P2$_1$ diffractometer, was used. Details of the data collection and reduction are given in the experimental part. Figure 1 shows the molecular structure of **2a** with the atomic numbering scheme. The atomic positional parameters of the non-hydrogen atoms are listed in Table 1, and some important bond lengths and angles in Table 2.

A centre of inversion connects the two halves of the molecule, which contains the bisallyl ligand in a bridging position and the two (dad)Ni moieties on opposite sides. The distances in the allyl part (C(31)–C(32), C(32)–C(33)) are equal, and comparable with those in a similar complex containing a cyclopentadienyl instead of dad ligand, [14]. The distance C(32)–C(32′) (1.51(1) Å) corresponds with a normal single
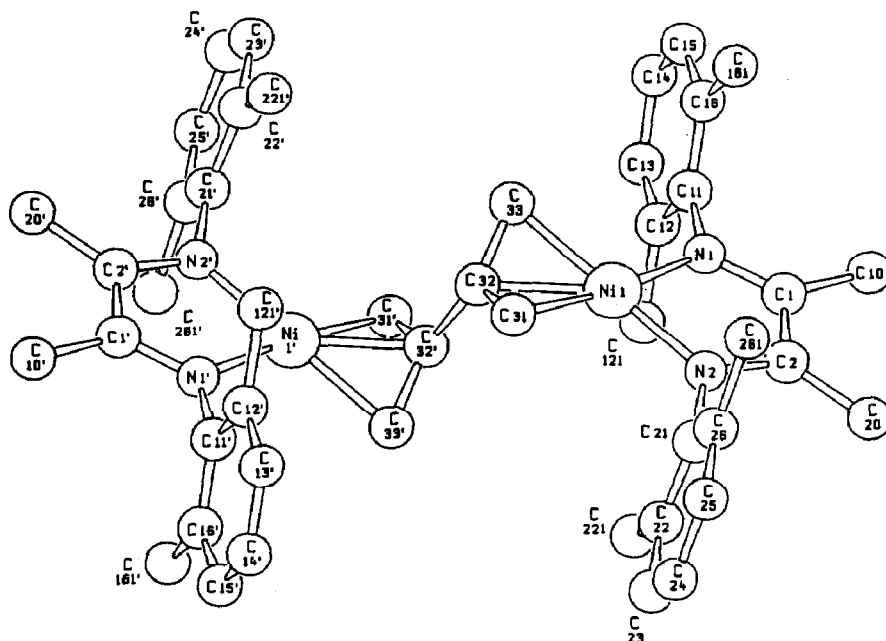
Fig. 1. Molecular structure of **2a** (SCHAKAL plot) with atomic numbering scheme.

Table 1

Atomic coordinates for **2a** (esd's in parentheses)

Atom	x	y	z	U_{eq}
Ni(1)	0.1072(1)	0.08630(3)	0.03480(8)	0.0543(3)
N(1)	0.1599(6)	0.1238(2)	0.1945(4)	0.048(1)
N(2)	0.0166(7)	0.1510(1)	−0.0261(4)	0.052(1)
C(1)	0.1210(8)	0.1737(2)	0.1878(6)	0.051(2)
C(2)	0.0369(8)	0.1900(3)	0.0636(6)	0.053(2)
C(10)	0.1585(9)	0.2120(3)	0.3025(6)	0.070(3)
C(11)	0.2273(7)	0.1007(2)	0.3180(5)	0.051(2)
C(12)	0.1196(8)	0.0806(3)	0.4017(6)	0.059(2)
C(13)	0.184(1)	0.0574(3)	0.5179(7)	0.081(3)
C(14)	0.348(1)	0.0532(3)	0.5537(7)	0.088(4)
C(15)	0.450(1)	0.0717(3)	0.4703(8)	0.083(3)
C(16)	0.3919(8)	0.0966(3)	0.3523(6)	0.063(3)
C(20)	−0.0235(9)	0.2451(3)	0.0334(7)	0.070(3)
C(21)	−0.0790(8)	0.1606(2)	−0.1515(6)	0.055(2)
C(22)	−0.2431(9)	0.1511(3)	−0.1668(7)	0.066(3)
C(23)	−0.334(1)	0.1607(3)	−0.2875(9)	0.090(4)
C(24)	−0.264(1)	0.1797(4)	−0.3920(8)	0.092(4)
C(25)	−0.101(1)	0.1879(3)	−0.3779(7)	0.085(3)
C(26)	−0.0040(9)	0.1784(3)	−0.2591(6)	0.064(3)
C(31)	0.079(1)	0.0430(3)	−0.1291(8)	0.073(4)
C(32)	0.0768(8)	0.0122(3)	−0.0178(6)	0.057(3)
C(33)	0.212(1)	0.0172(3)	0.0785(9)	0.073(3)
C(121)	−0.0597(8)	0.0850(3)	0.3601(7)	0.084(3)
C(161)	0.5050(9)	0.1172(4)	0.2619(8)	0.097(4)
C(221)	−0.3230(9)	0.1293(3)	−0.0533(8)	0.084(3)
C(261)	0.1759(9)	0.1854(3)	−0.2444(7)	0.087(3)

Table 2

Important bond lengths and angles in **2a** (esd's in parentheses)

Bond lengths (Å)			
Ni(1)–N(1)	1.885(5)	Ni(1)–N(2)	1.877(5)
Ni(1)–C(31)	1.987(8)	Ni(1)–C(32)	1.961(8)
Ni(1)–C(33)	1.982(8)	N(1)–C(1)	1.306(7)
N(1)–C(11)	1.432(7)	N(2)–C(2)	1.341(8)
N(2)–C(21)	1.432(8)	C(1)–C(2)	1.423(9)
C(1)–C(10)	1.519(9)	C(2)–C(20)	1.50(1)
C(31)–C(32)	1.38(1)	C(32)–C(33)	1.40(1)
C(32)–C(32')	1.51(1)		

Bond angles (°)			
N(1)–Ni(1)–N(2)	83.1(2)	N(1)–Ni(1)–C(31)	172.9(4)
N(1)–Ni(1)–C(32)	136.5(2)	N(1)–Ni(1)–C(33)	102.0(3)
N(2)–Ni(1)–C(31)	102.1(3)	N(2)–Ni(1)–C(32)	135.7(2)
N(2)–Ni(1)–C(33)	173.2(3)	C(31)–Ni(1)–C(32)	40.9(3)
C(31)–Ni(1)–C(33)	72.4(4)	C(32)–Ni(1)–C(33)	41.5(3)
Ni(1)–N(1)–C(1)	114.6(4)	Ni(1)–N(1)–C(11)	124.8(4)
C(1)–N(1)–C(11)	120.5(5)	Ni(1)–N(2)–C(2)	114.3(4)
Ni(1)–N(2)–C(21)	126.4(4)	C(2)–N(2)–C(21)	119.1(5)
N(1)–C(1)–C(2)	114.6(5)	N(1)–C(1)–C(10)	123.7(5)
C(2)–C(1)–C(10)	121.6(5)	N(2)–C(2)–C(1)	113.2(6)
N(2)–C(2)–C(20)	122.5(6)	C(1)–C(2)–C(20)	124.3(6)
Ni(1)–C(31)–C(32)	68.5(4)	Ni(1)–C(32)–C(31)	70.6(5)
Ni(1)–C(32)–C(33)	70.1(4)	Ni(1)–C(32)–C(32A)	114.1(5)
C(31)–C(32)–C(33)	115.2(8)	C(31)–C(32)–C(32A)	122.4(7)
C(33)–C(32)–C(32')	120.0(6)	Ni(1)–C(33)–C(32)	68.4(5)

bond, as expected for the 2,2'-biallyl diradical (6 π electrons) and also for the dianion (8 π electrons) on the basis of MO considerations. The stereochemistry of the Ni atom is almost perfectly square planar, and seems to imply the oxidation state Ni(II). This would require an anionic dad ligand. The bond lengths within the nickel-diazadiene cycle, on the other hand, argue against such a description. The alternating short and long bonds in the NCCN part are more pronounced than in a Ni(dad)$_2$ complex containing a similar dad ligand [15], and resemble those in the recently described (dad)Ni complexes with acetylene dimers as ligands [4]. The rather short Ni–N distances (average 1.88 Å), compared with those in the above-mentioned (dad)Ni complexes, indicate that the unpaired electron might not occupy the σ^* orbital $d_{x^2-y^2}$ but instead a bonding combination of p_z(Ni) + π^*(dad), and thus give rise to some delocalization. Nevertheless it is surprising that the dimerization of allene does not depend on the concomitant formation of closed-shell organometallics, as was previously thought. Obviously this is related to the easy comproportionation of (dad)Ni(0) with (dad)Ni(II) to give dimeric Ni(I) [16]. The stereochemistry of Ni(I) in the complexes **2** resembles that of isoelectronic four-co-ordinate copper(II). So far no planar Ni(I) complex with N-donor ligands has been described.

Experimental part

All manipulations were carried out under purified nitrogen. Solvents, including toluene-d_8 were distilled over Na/K alloy and saturated with N$_2$. IR spectra were

recorded with KBr or Nujol mulls between KBr disks on a Perkin-Elmer spectro-photometer model 325. Elemental analyses were carried out in the Analytical Service Laboratory of this department. The complexes (dad)Ni(C_4H_6) (**1**) were prepared as previously described [4].

μ-($\eta^{3;3'}$-2,2'-Biallyl)bis[biacetylbis(2,6-dimethylphenylimine)nickel] (2a)

A 100 ml Schlenk vessel containing a solution of 658.5 mg (1.63 mmol) of dadNi(butadiene) (**1a**) in 10 ml of pentane was cooled in liquid nitrogen and then evacuated. The solution was then allowed to warm up to room temperature and 45 ml ($\approx$ 2 mmol) of gaseous allene (Merck, used as supplied) were slowly introduced without stirring of the solution, and the rest of the space then filled with nitrogen. The colour of the mixture immediately changed from reddish-violet to brown. After ten minutes crystals began to separate from the solution, and after overnight standing the crystallisation was complete. The mother liquor was decanted, and the crystals were dried in vacuum to yield 500 mg (0.63 mmol, 78%) of **2a**. ^{1}H NMR (toluene-d_8, 360 MHz) at 296 K: δ 9.0–7.0 (br, $w_{1/2}$ = 470 Hz); 1.43 (br, $w_{1/2}$ = 36 hz); 0.89 (br, $w_{1/2}$ = 58 Hz). 190 K: 1.33 (24H, $w_{1/2}$ = 108 Hz); 0.89 (12H, $w_{1/2}$ = 72 Hz). IR (cm^{-1}): 760 (s), 890 (m), 1000 (w), 1090 (m), 1160 (w), 1210 (m), 1240 (s), 1260 (s), 1350–1480 br (s), 1590 (w), 1620 (w), 2900 br (m). Analysis: Found: C, 71.18; H, 7.35; N, 6.77%. $C_{46}H_{56}N_4Ni_2$ (782.40) calcd.: C, 72.41; H, 7.48; N, 6.50% ESR (solid, X-band, res. freq.: 9.449561 GHz); signal at central field 3371.90 G.

Table 3

Crystallographic data

Chemical formula of **2a**	$C_{46}H_{56}N_4Ni_2$
Crystal system	monoclinic
Space group no.	$P2_1/a$ (14 non-standard setting)
Z	2
a, Å	8.367(5)
b, Å	25.352(9)
c, Å	10.200(3)
β, °	97.98(4)
V, Å^3	2142(2)
d_{calc}, g/cm^3	1.212
λ(Mo-K_α), Å	0.71069
θ range, °	2.25–30
h range	$-10/9$
k range	0/33
l range	0/14
F(000), electrons	831.96
μ, cm^{-1}	8.61
Crystal dimensions (mm^3)	$0.1 \times 0.2 \times 0.05$
Temperature, K	298
No. of reflections	6707
Symm. independent refl.	4828
Significant refl.	2265
No. of refined parameters	256
Final R_f, $\Sigma(\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.0548
Final R_w, $[\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma\|wF_o^2\|]^{1/2}$	0.0570

μ-$(\eta^{3;3'}$-2,2'-Biallyl)bis[biacetylbis(2,6-diisopropylphenylimine)nickel] (**2b**)

The same procedure was used, but with **1b** instead of **1a**. Yield 79%. IR (cm^{-1}): 730 (s), 760 (w), 780 (s), 890 (s), 930 (w), 990 (w), 1050 (w), 1100 (w), 1220 (m), 1250 (s), 1320 (s), 1325 (s), 1375 (s), 1400 (s), 1580 (w). Analysis. Found: C, 73.88; H, 8.83; N, 5.20%. $C_{62}H_{88}N_4Ni_2$ (1006.84). Calcd.: C, 73.96; H, 8.81; N, 5.56%.

Crystallographic data for **2a** were collected on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator, and details are given in Table 3. The space group was shown to be $P2_1/a$ from the systematically absent reflections. The positions of the nickel atom were determined by a Patterson synthesis using SHELXS 86 [17]. Difference Fourier maps showed the nitrogen and carbon atoms. Hydrogen atoms were calculated in ideal positions. For the structure refinement the program SHELX 76 [18] was used. Refinement of the non-hydrogen atoms with anisotropic temperature factors, and of the hydrogen atoms with isotropic thermal parameters, lead to final R and R_w values given in Table 3. The graphic representation of the molecular structure was produced with the program SCHAKAL [19].

Further details of the crystal structure investigation are available on request from the FIZ Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54800, the names of the authors, and the journal citation.

Acknowledgements

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