1,2-Bis(imino)acenaphthene complexes of molybdenum and nickel[†]

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Molybdenum hexacarbonyl reacts with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (1, dpp-BIAN) and 1,2-bis[(trimethylsilyl)imino]acenaphthene (2, tms-BIAN) in toluene to produce (dpp-BIAN)Mo(CO)₄ (3) and (tms-BIAN)Mo(CO)₄ (4), respectively. The reaction of [CpNi(CO)]₂ with 1 yields (dpp-BIAN)NiCp (5). Metathesis between Li₂(tms-BIAN) and NiCl₂(dppe) affords the Ni(0) complex (tms-BIAN)Ni(dppe) (6). The diamagnetic compounds 3, 4 and 6 have been characterized by ¹H, ²⁹Si and ³¹P NMR spectroscopy, IR spectroscopy and elemental analysis. The ESR spectrum of the paramagnetic compound 5 indicates the presence of Ni(1) coordinated by Cp and a neutral dpp-BIAN ligand. The molecular structures of 3–6 have been determined by single-crystal X-ray analysis.

Introduction

 α -Diimine ligands proved to be useful tools for fine tuning the reactions of metal complexes. In this context, 1,2bis(imino)acenaphthenes (BIANs) have attracted increasing attention during the last years. Although BIAN's have been known since 1960,¹⁻³ they were not used as ligands in transition metal chemistry before 1990. The pioneers in this field have been the teams around Elsevier, Brookhart and Coates. They could demonstrate that transition metal complexes with neutral BIAN ligands catalyze reactions like alkyne hydrogenation,4 C-C bond formation,5 cycloisomerisation,⁶ and polymerisation of olefins⁷ and acrylic monomers.8 In 1995, Brookhart and co-workers reported9 on BIAN supported nickel(II) complexes, which are extremely active catalysts for the conversion of ethylene and α -olefins into high molecular syndiotactic polymers.9 Furthermore, BIAN coordinated η^3 -allyl dicarbonyl molybdenum(II) derivatives represent a new class of catalysts for the epoxidation of cycloalkenes.¹⁰

In 2003, we started our investigations of BIAN complexes of main group metals. In a series of papers we reported on group I,¹¹ II¹² and XIII¹³ metal complexes coordinated by 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN). Over the course of these studies it turned out that dpp-BIAN can act as an efficient "electron sponge" by accepting up to four electrons.¹¹ Furthermore, the unique stereoelectronic properties of dpp-BIAN's allowed the isolation of complexes with direct

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Zn–Zn¹⁴ and Ga–Ga¹⁵ bonds and of the germylenes (dpp-BIAN)Ge¹⁶ and (dpp-BIAN)GeCl.¹⁷ Very recently, the previous development in the field of the coordination chemistry of BIAN ligands with s- and p-block elements has been reviewed.¹⁸

To date, there are only two examples of transition metal complexes with anionic BIAN ligands, *e.g.* $(F-BIAN)_2Ni$ and $(F-BIAN)_3Co$ $(F-BIAN = 1,2-bis[{3,5-bis(trifluoromethyl)-phenyl}imino]acenaphthene).¹⁹ The Ni complex comprises the divalent metal ion with pairs of radical-anionic ligands, whereas the Co complex is best described as a Co(1) complex with two neutral and one radical-anionic F-BIAN ligands. In this study, we intended the preparation of d-metal complexes with anionic BIANs by the reactions of Mo and Ni carbonyl complexes with dpp-BIAN and tms-BIAN. Here, we report on the synthesis and characterisation of (dpp-BIAN)Mo(CO)₄ (3), (tms-BIAN)Mo(CO)₄ (4), (dpp-BIAN)NiCp (5) and (tms-BIAN)Ni(dppe) (6).$

Results and discussion

Synthesis and characterisation of compounds 3-6

 $Mo(CO)_6$ reacts with equimolar amounts of dpp-BIAN (1) and tms-BIAN (2) (Scheme 1) in boiling toluene within 12 h to give (dpp-BIAN)Mo(CO)₄ (3) and (tms-BIAN)Mo(CO)₄ (4), respectively, in yields up to 80%. In the course of the reactions, the colour of the solutions change from initially orange to bright green (3) or deep blue (4) colours, which also show the isolated crystalline compounds. The reaction of Mo(CO)₆ with dpp-BIAN runs much faster in THF and is completed after 6 h. Furthermore, this reaction can be carried out in air, since the reactants as well



Scheme 1 Syntheses of compounds 3 and 4.

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as product **3** are air-stable compounds. In contrast, tms-BIAN (**2**) is sensitive to moisture and therefore the synthesis of complex **4** has to be carried out under an inert atmosphere. Analytical grade samples and crystals suitable for single-crystal X-ray analysis of **3** and **4** have been obtained by crystallisation from hexane and toluene, respectively.

The IR spectra of **3** and **4** show the carbonyl stretching modes in the expected range (**3**: 2007, 1898 and 1859 cm⁻¹; **4**: 2008, 1873 and 1838 cm⁻¹). For comparison, in $[Mo(\eta^3 - C_3H_5)X(CO)_2(4-ClPh-BIAN)]^{10}$ (X = Cl, Br; 4-ClPh-BIAN = 1,2-bis[(4-chlorophenyl)imino]acenaphthene) these modes appear at 1928, 1869 (X = Cl) and 1946, 1869 cm⁻¹(X = Br). The ¹H NMR spectra of **3** and **4** show the expected signals for the protons of the BIAN ligands, even though they are somewhat shifted compared to the signals of free dpp-BIAN (**1**) and tms-BIAN (**2**). Thus, the signals of the methine protons of the isopropyl groups in **3** are centred at 3.50 ppm (*cf.* **1** 3.36 ppm²⁰) and the methyl protons of those groups give rise to two doublet signals at 1.50 and 0.80 ppm (*cf.* **1** 1.41 and 1.17 ppm²⁰).

The reaction of $[CpNi(CO)]_2$ with the twofold molar amount of dpp-BIAN (1) in boiling toluene is accompanied by a colour change of the solution from red-brown to green and is completed within 1 h. Work-up of the solution by evaporation of the solvent and recrystallisation of the remaining solid from hexane affords air stable, deep green crystals of (dpp-BIAN)NiCp (5) in almost quantitative yield (Scheme 2). The IR spectrum of 5 shows cyclopentadienyl ring absorptions at 1003 and 831 cm⁻¹ and the $v_{C=N}$ stretching mode of the dpp-BIAN ligand at 1650 cm⁻¹.



Scheme 2 Synthesis of compound 5.

Complex 5 is paramagnetic in the solid state as well as in solution. The anisotropic ESR signal of 5 in toluene (120 K) exhibits an orthorhombic symmetry of the *g*-tensor (Fig. 1).

The g_2 and g_3 tensor components reveal a hyperfine coupling to two equivalent ¹⁴N nuclei ($g_1 = 2.183$, $g_2 = 2.109$, $g_3 = 1.993$, $A_2 = 0.98$ mT, $A_3 = 1.30$ mT). These signal parameters are similar to those of (2,2'-bipy)NiCp.²¹ Thus, compound **5** represents a 19electron nickel(1) complex.

The addition of $(dppe)NiCl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) to the deep blue solution of Li₂(tms-BIAN), prepared *in situ* from **2** and excess lithium metal in toluene, causes a change in the colour of the reaction mixture to red brown. Appropriate work-up of this mixture allows the isolation of deep red crystals of (tms-BIAN)Ni(dppe) (**6**) in a yield of 58% (Scheme 3).

The 'N NMR spectrum of 6 in benzene-d₆ reveals nonequivalence of the two methylene groups of the dppe ligand.



Fig. 1 ESR signal of 5 (toluene, 120 K) (a) and its simulation (b).



Scheme 3 Synthesis of compound 6.

The methylene multiplets are broadened and appear at 1.90 and 1.63 ppm. Also the two phosphorus atoms of the dppe ligand are non-equivalent and give rise to two signals at 21.5 and 18.1 ppm in the ³¹P NMR spectrum. On the other hand, in the ¹H as well as in the ²⁹Si NMR spectrum of **6**, the trimethylsilyl groups of the tms-BIAN ligand give rise for a singlet signal at 0.39 ppm and -5.3 ppm, respectively (*cf.* **2**²² 0.51 ppm and -1.1 ppm), thus suggesting a mirror plane dividing the tms-BIAN ligand in **6** into two equal parts. The IR spectrum shows the $v_{C=N}$ stretching mode of the tms-BIAN ligand at 1646 cm⁻¹, thus indicating the neutral form of the tms-BIAN ligand in **6**.

Molecular structures of compounds 3-6

The molecular structures of compounds 3, 4, 5 and 6, determined by single-crystal X-ray diffraction, are depicted in Fig. 2, 3, 4, and 5, respectively. X-Ray quality crystals were obtained from hexane (3, 5, 6) and toluene (4). The crystal data are presented in Table 1, selected bond distances and bond angles are listed in Table 2.

Compounds **3** and **4** represent octahedral Mo(0) complexes. The CCDC search reveals three diazadiene-, ten bipyridyl- and two phenantrolinetetracarbonylmolybdenum analogues of complexes **3** and **4** (see ESI).† The unit cell of **3** consists of two crystallographically independent molecules those geometrical parameters are very similar. The deviation of the Mo atoms from the N(1)–C(1)–C(2)–N(2) plane in **3** and **4** are 0.383/0.026 and 0.772 Å, respectively. For comparison, in the complex (Me₂bipy)Mo(CO)₄ (Me₂bipy = 6,6'-dimethyl-2,2'-bipyridyl) this value is 0.477 Å.²³ In both **3** and **4** the sum of the angles formed by the bonds of the metal to its equatorial ligand atoms is very close to the ideal value of 360° (**3**, 359.9°; **4**, 359.7°). Due to the higher steric bulk of the two 2,6-*i*-Pr₂C₆H₃ substituents of the dpp-BIAN ligand in **3** compared to the two Me₃Si groups of the tms-BIAN ligand in **4**, the angle



Fig. 2 Molecular structure of complex **3**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability.



Fig. 3 Molecular structure of complex **4**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability.



Fig. 4 Molecular structure of complex **5**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% probability.



Fig. 5 Molecular structure of complex **6**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 40% probability.

between the axially positioned carbonyl groups is smaller in **3** (C(39)–Mo–C(40), 163.2°) than in **4** (C(19)–Mo–C(20), 172.1°). In **3** the phenyl ring planes are orthogonal to the diimine plane as it is the case in free dpp-BIAN and in all its metal complexes. The bonds C(1)–N(1), C(2)–N(2), and C(1)–C(2) of the diimine moiety in **3** and **4** correspond quite well with those of the free BIAN ligands **1** and **2**, *e.g.* **3**, C(1)–N(1) (1.293(4) Å), C(2)–N(2) (1.300(4) Å) and C(1)–C(2) (1.480(5) Å); **1** (C(1)–N(1) and C(2)–N(2) both 1.282(4) Å, C(1)–C(2) 1.534(6) Å)²⁰ as well as with the data obtained for the antimony complex (dpp-BIAN)SbCl₃ (N(1)–C(1) 1.288(2), N(2)–C(2) 1.277(3), C(1)–C(2) 1.524(3) Å),²⁴ which also contains the dpp-BIAN ligand in its neutral form.

The nickel atom in 5 is η^5 -coordinated by the Cp ring in a quite symmetric fashion since the Ni-C(Cp) distances lie in the narrow range of 2.160(1)–2.184(1) Å. Together with N(1)–C(1)–C(2)–N(2) the nickel atom forms an almost perfect plane, which is orthogonal to the plane of the Cp-ring. Compared to free dpp-BIAN (1), the C-N bond distances within the metallacycle are elongated while the C-C bond is shortened (5, (C(1)-N(1) 1.312(1), C(2)-N(2) 1.314(1) and C(1)–C(2) 1.4491(17) Å; 1 cf. above), a situation, which might be interpreted in the sense of a radical anionic nature of the dpp-BIAN ligand.¹⁸ In (dpp-BIAN)Zn-Zn(dpp-BIAN), which contains two dpp-BIAN radical-anions, the C(1)-N(1) and C(2)–N(2) distances are 1.324(1) and 1.336(1) Å).¹⁴ However, the ESR spectrum of 5 indicates the presence of Ni(I) and shows no signal attributable to an dpp-BIAN radical-anion. Therefore, the elongation of the C-N distances in 5 compared to those in free dpp-BIAN may be interpreted by a strong back donation from the electron-rich Ni(I) centre to the dpp-BIAN π orbitals.

The molecular structure of **5** can be compared with that of the related complex $(2,2'-bipy)NiCp.^{21}$ Whereas the lengths of the Ni–N bonds in **5** (1.951(1), 1.953(1) Å) and in (2,2'-bipy)NiCp (1.955(3), 1.958 (4) Å) are very similar, the Ni–C(Cp) distances are shorter in **5** (1.951(1)–1.953(1) Å) than in (2,2'-bipy)NiCp (2.17(4)–2.22(4) Å), thus indicating a stronger electron back donation of the metal to the dpp-BIAN ligand than to the 2,2'-bipy ligand.

In contrast to complex 4, in which the molybdenum atom is coordinated by the two imino nitrogen atoms of the

Table 1Crystal structure data for 3, 4, 5 and 6

	3	4 ^{<i>a</i>}	5	6
Formula	$C_{40}H_{40}MoN_2O_4$	$C_{22}H_{24}MoN_2O_4Si_2$	$C_{41}H_{45}N_2Ni\cdot0.5C_6H_{14}$	$C_{44}H_{48}N_2NiP_2Si_2$
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	708.68	532.55	667.57	781.67
T/K	150(2)	150(2)	296(2)	100(2)
Crystal size/mm ³	$0.24 \times 0.21 \times 0.13$	$0.31 \times 0.07 \times 0.06$	$0.23 \times 0.18 \times 0.17$	$0.20 \times 0.05 \times 0.05$
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P\overline{1}$	$P2_1/c$
a/Å	21.1081(4)	6.8006(2)	12.3259(12)	17,7917(5)
h/Å	20.0378(3)	16 5995(3)	12,5980(13)	14 5028(4)
c/Å	18 0358(4)	20.8751(5)	13 4184(13)	17 5770(5)
$\alpha/^{\circ}$	90	20.8751(5)	69 714(4)	90
$\beta/^{\circ}$	106 820(2)	90	78 287(3)	118 579(1)
р/ у/°	90	90	79.081(4)	90
V/\dot{A}_{3}	7302 1(2)	2256 5(1)	1907 6(2)	2082 8(1)
7	/ 502.1(5) 8	2550.5(1)	1897.0(3)	3962.0(1)
$D / \alpha \text{ cm}^{-3}$	0	4	2 1 168	4
D_{calcd} / g CIII	0.71072	0.71072	1.100	1.304
$\mu(NOKG)/cm$	2044	1022	0.71073	1649
hkl range	2944 25 < h < 25	$\frac{1000}{8} - h - 8$	$\frac{16}{16} = h = 16$	1040 21 $- h - 21$
nki lange	$-23 \le h \le 23$	$-6 \le n \le 6$ $10 \le k \le 10$	$-10 \le h \le 10$ $17 \le h \le 17$	$-21 \le n \le 21$ $17 \le k \le 17$
	$-25 \le K \le 22$	$-19 \le k \le 19$	$-1 / \leq K \leq 1 /$ 18 < 1 < 18	$-1/ \le k \le 1/$ 20 < 1 < 20
0 Dan an fan data anllastian (°	$-10 \le l \le 21$	$-22 \le l \le 24$	$-10 \le l \le 10$	$-20 \le l \le 20$
θ Range for data collection/	2.80-23.00	3.14-23.00	1.04–29.00	2.01-23.00
Completeness to $\theta = 25.00$ (%)	99.8	99.7		99.0
Completeness to $\theta = 29.00$ (76)	-	-	99.1 0.012 and 0.885	— 0.0677 and 0.8701
Perfections measured	0.9498 and 0.9100	0.9398 and 0.8149	0.915 and 0.885	21 225
Reflections unique	12828	4140	20427	51 225 7005
Reflections unique	12 838	4140	0.022	/003
K _{int.}	0.092	0.0001	0.023	0.0055
$P(E)$ (, $P(E^2)$ [L = 2 – (1)]	003	200	433	400
$\frac{K(\Gamma)}{WK(\Gamma^{-})} [I > 2O(I)]$ $\frac{R(\Gamma)}{WK(\Gamma^{-})} [all data]$	0.0401/0.0/48	0.0303/0.0409	0.0330/0.0802	0.0430/0.0936
K(F) / WK(F) [all data]	0.099770.0804	0.0594/0.048/	0.0402/0.0901	0.0064/0.1051
$\operatorname{GOF}(F^{-})$	0.980	0.909	1.018	1.031
$\Delta \rho_{\rm fin} ({\rm max/min})/{\rm e}{\rm A}^{-3}$	0.3947-0.626	0.2557-0.244	0.512/-0.456	0.5/2/-0.293
^{<i>a</i>} Flack parameter 0.04(3).				

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Table 2 Selected bond lengths (Å) and angles (°) for 3, 4, 5 and 6 with estimated standard deviations in parentheses

Complex	3	4	5	6
Distances/Å	M = Mo	M = Mo	M = Ni	M = Ni
M-N(1)	2.242(3)	2.283(2)	1.9528(10)	1.8976(17)
M-N(2)	2.246(3)	2.277(3)	1.9506(10)	_ ``
M-C(1)	_ ``	_ ``	_ ``	1.9856(19)
M-P(1)				2.1708(6)
M-P(2)				2.1865(5)
M-C(37)	1.963(4)		2.1675(14)	_ ``
M-C(38)	1.971(4)		2.1757(14)	
M-C(39)	2.051(4)		2.1847(13)	
M - C(40)	2.023(4)		2.1609(14)	
M - C(41)	_ ``		2.1688(14)	
M-C(19)		2.014(4)	_ ``	
M - C(20)		2.064(4)		
M - C(21)		1.953(4)		
M - C(22)		1.953(4)		
C(1) - N(1)	1.293(4)	1.294(4)	1.3125(16)	1.363(2)
C(2) - N(2)	1.300(4)	1.299(4)	1.3141(15)	1.279(2)
C(1)–C(2)	1.480(5)	1.514(4)	1.4491(16)	1.510(2)
Angles/°				
N(1)–M–N(2)	72.70(10)	74.25(8)	83.13(4)	
N(1)-M-C(1)				41.03(7)

tms-BIAN ligand, in complex 6 the nickel atom is coordinated to the C=N double bond of only one of the two imino functions of the ligand. According to the dihedral angles C(5)-C(1)-N(1)-Ni(99.9°) and C(2)-C(1)-N(1)-Ni (97.5°), the plane C(1)-Ni-N(1) is orthogonal to the plane C(2)-C(1)-C(5). Besides the coordination by the tms-BIAN ligand in this uncommon fashion, the nickel atom is coordinated by the two phosphorous atoms of the dppe ligand. The Ni-P bonds are of almost equal length (Ni(1)-P(1) 2.1710(6) and Ni(1)-P(2) 2.1867(6) Å). Whereas P(1) lies nearly perfect in the N(1)–C(1)–Ni plane (dihedral angle P(1)–C(1)– N(1)-Ni: 3.3°), P(2) deviates noticeably from this plane (P(2)- $C(1)-N(1)-Ni: 10.0^{\circ}$). The sum of the bond angles at the Ni atom is 360.2° . Complex 6 can be considered either as a Ni(II) containing metallocycloazapropane or as a Ni(0) complex π coordinated by the C=N double bond of the ligand. The latter model seems to be more plausible, since the Ni-P distances in 6 are larger than in the Ni(II) complex (dppe)NiCl₂²⁵ (Ni-P 2.154(4) and 2.153(4) Å). The Ni-P distances in 6 can be further compared with those in (dppe)₂Ni²⁶ (Ni-P 2.152(3)-2.177(3) Å) and in the monoazadiene complex (MAD)Ni(PPh₃) $_{2}^{27}$ $(MAD = PhCH = CHCH = NPr^{i})$ (Ni-P 2.195(1) and 2.192(5) Å). Concerning the last mentioned compound it has to be noted, that the nickel atom is not coordinated to the C=N, but to the C=C double bond of the MAD ligand. A comparison of the distances of the nickel atoms to the carbon atoms of the respective coordinating C=N and C=C double bond reveals, that the distance Ni–C(1) (1.985(2) Å) in **6** is close to the Ni–C bond lengths in (MAD)Ni(PPh₃)₂²⁷ (2.013(4) and 2.005(4) Å). In **6** the Ni–C(1) bond (1.985(2) Å) is larger than the Ni–N(1) distance (1.898(1) Å). Also the bonds N(1)–C(1) (1.361(3) Å) and N(2)– C(2) (1.279(2) Å) differ significantly between each other, with the latter value being in the range of the C=N bond distances in free tms-BIAN.²²

Two further features of complex 6 are remarkable. The unit cell of 6 contains two mirror isomers: in one the Ni atom is positioned left from the plane running the middle of the C(1)–C(2) bond and atom C(4) whereas in the other one the Ni atom is positioned on the opposite side of this plane. However, the NMR spectroscopic data of 6 suggest the presence of the symmetric molecule with two equivalent imino functions in solution. We suppose that in solution the fragment Ni(dppe) migrates fast (on the NMR time scale) between two C=N bonds. Furthermore, the molecules of complex 6 show π -stacking between the phenyl ring [C(19)–C(24)] of the dppe ligand and the co-planar naphthalene part of the tms-BIAN ligand. The atoms C(19), C(21) and C(23) are located exactly above the atoms C(4), C(8) and C(10), respectively, and the distances $C(4) \cdots C(19)$ (3.422 Å), $C(8) \cdots C(21)$ (3.380 Å), and $C(10) \cdots C(23)$ (3.436 Å) are comparable with the interlayer distance in graphite (3.35 Å).²⁸

Conclusions

The mononuclear molybdenum and nickel complexes **3–6** with two different acenaphthene-1,2-diimine ligands have been synthesised either by ligand substitution reactions using appropriate metal carbonyl complexes and free BIAN ligands (**3–5**), or by metathesis between NiCl₂(dppe) and Li₂(tms-BIAN) (**6**). In all four complexes the respective BIAN ligand acts as a neutral N- (**3–5**) or π donor (**6**). The NMR data of **6** suggest a fast migration of the Ni(dppe) fragment between the two C=N double bonds of the tms-BIAN ligand.

Experimental

General procedures

All manipulations were carried out using Schlenk techniques. tms-BIAN²¹ and dpp-BIAN²⁹ have been prepared according to literature procedures. Melting points were measured in sealed capillaries and are uncorrected. The solvents were distilled from sodium-benzophenone prior to use. The ¹H, ²⁹Si and ³¹P NMR spectra were recorded on Bruker DPX-200 NMR and Bruker Advance III 400 spectrometers; IR spectra on a FSM-1201 spectrometer; ESR spectra on a Bruker EMX instrument.

1,2-Bis [(2,6-diisopropylphenyl) imino]acenaphthene - molybdenumtetracarbonyl (dpp-BIAN)Mo(CO)₄ **(3).** To a solution of dpp-BIAN (0.50 g, 1.0 mmol) in toluene (50 mL) Mo(CO)₆ (0.26 g, 1.0 mmol) was added. Within 12 h of reflux, the mixture changed colour from orange to bright green. The solvent was then evaporated under vacuum. Crystallization of the residual solid from hexane gave 0.55 g (78%) of complex **3** as deep green crystals. M.p. 275–280 °C (decomposition). Anal. calcd for $C_{40}H_{40}MoN_2O_4$: C 67.79, H 5.69; found: C 68.47, H 5.72. ¹H NMR (200 MHz, C_6D_6) δ /ppm: 7.28–7.11 (m, 6 H_{arom.}), 7.07 (d, 2 H_{arom.}, 8.3 Hz), 6.61 (dd, 2 H_{arom.}, 7.3 and 8.3 Hz), 6.35 (d, 2 H_{arom.}, 7.3 Hz), 3.50 (sept, 4 H, CHMe₂, 6.8 Hz), 1.50 (d, 12 H, CH(CH₃)₂, 6.8 Hz), 0.8 (d, 12 H, CH(CH₃)₂, 6.8 Hz). IR (Nujol, cm⁻¹): v = 2007 vs, 1898 vs, 1859 s, 1602 w, 1535 w, 1294 m, 844 w, 831 w, 804 w, 777 m, 762 m, 641 s, 572 m, 532 m, 505 m.

1,2-Bis[(trimethylsily]) imono] acenaphthene-molybdenumtetracarbonyl (tms-BIAN)Mo(CO)₄ (4). To a solution of tms-BIAN (0.30 g, 0.9 mmol) in toluene (20 mL) Mo(CO)₆ 0.24 g (0.91 mmol) was added. Within 10 h of reflux, the reaction mixture changed colour from orange to deep blue. Slow cooling of the reaction mixture to ambient temperature causes precipitation of **4** as deep blue crystals. Yield 0.33 g (68%). M.p. 210 °C. Anal. calcd for $C_{22}H_{24}MoN_2O_4Si_2$: C 49.62, H 4.54; found: C 50.43, H 5.12. ¹H NMR (200 MHz, C_6D_6) δ /ppm: 7.61 (d, 2 H_{arom.}, 7.3 Hz), 7.35 (d, 2 H_{arom.}, 8.3 MHz), 7.01 (dd, 2 H_{arom.}, 7.3 and 8.3 Hz), 0.61 (s, 18 H, Si(CH₃)₃). IR (Nujol, cm⁻¹): v = 2008 s, 1873 s, 1838 s, 1584 m, 1522 w, 1419 w, 1377 m, 1272 w, 1253 m, 1180 w, 1095 m, 1042 m, 930 m, 838 s, 826 s, 780 m, 676 w, 630 w, 599 w, 580 w, 549 w, 526 w.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene-nickelcyclopentadienyl (dpp-BIAN)NiCp-0.5 C₆H₁₄ (5). To a solution of dpp-BIAN (0.50 g, 1.0 mmol) in toluene (50 mL) [CpNi(CO)]₂ (0.15 g, 0.5 mmol) was added. The reaction mixture was refluxed until its colour turned bright green (*ca.* 1 h). Evaporation of the solvent and crystallization of the crude product from hexane gave **5** as deep green crystals. Yield 0.59 g (89%). M.p. 240–245 °C. Anal. calcd for C₄₄H₅₂N₂Ni: C 79.17, H 7.85; found: C 78.87, H 7.63. IR (Nujol, cm⁻¹): v = 1650 w, 1529 s, 1511 m, 1418 m, 1363 w, 1330 m, 1309 m, 1257 m, 1191 w, 1112 w, 1003 w, 831 m, 783 s, 760 m, 550 w. ESR (toluene, 120 K): $g_1 = 2.183$, $g_2 = 2.109$, $g_3 = 1.993$, $A_2 = 0.98$ mT, $A_3 = 1.30$ mT.

1,2-Bis[(trimethylsilyl)imino]acenaphthenenickel[1,2-bis(diphenylphosphino)ethane (tms-BIAN)Ni(Ph₂PCH₂)₂ (6). A mixture of lithium (0.30 g, 43.2 mmol) and tms-BIAN (0.32 g, 1.0 mmol) in toluene (50 mL) was vigorously stirred at room temperature for 4 h. The deep blue solution of [(tms-Bian)Li₂]₂ was then decanted from excess lithium. NiCl₂(dppe) (0.53 g, 1.0 mmol) was added to this solution. The reaction mixture turned red brown within 4 h stirring. After evaporation of the solvent, the residue was dissolved in hexane and filtered off from lithium chloride. Complex 6 was separated from the concentrated hexane solution as deep red crystals. Yield 0.45 g (58%). M.p. >240 °C (decomposition). ¹H NMR (400 MHz, C_6D_6) δ /ppm: 7.94–7.89 (m, 4 H, C_6H_5 -P), 7.53 (d, 2 $H_{arom.}$, 7.0 Hz), 7.35 (d, 2 $H_{arom.}$, 8.0 Hz), 7.24–7.19 (m, 6 H, C₆H₅-P), 7.13–7.10 (m, 2 H_{arom}), 6.92–6.85 (m, 4 H, C₆H₅-P), 6.83 $(d, 2H, C_6H_5-P, 7.0Hz), 6.78-6.75 (m, 4H, C_6H_5-P), 1.92-1.88 (m, 4H, C_6H_5-P)$ 2 H, CH₂-P), 1.65–1.61 (m, 2 H, CH₂-P), 0.39 (s, 18 H, Si(CH₃)₃). ²⁹Si NMR (400 MHz, C₆D₆) δ/ppm: 5.33 (s, 2 Si, Si(CH₃)₃). ³¹P NMR (400 MHz, C_6D_6) δ /ppm: 21.5 (d, 1 P, C_6H_5 -P, 14.7 Hz), 18.1 (d, 1 P, C₆H₅-P, 14.7 Hz). IR (Nujol, cm⁻¹): v = 3046 w, 1646 s, 1619 m, 1603 w, 1484 w, 1434 s, 1407 s, 1360 m, 1303 w, 1261 m, 1242 s, 1203 w, 1095 s, 1049 m, 1026 m, 1007 w, 972 m, 903 m, 846 s, 826 s, 776 m, 749 m, 699 s, 684 s, 676 m, 618 w, 526 s, 480 m.

X-Ray structure determination

The intensity data for **3** and **4** were collected at 150 K on an Oxford Diffraction Xcalibur S Sapphire diffractometer, for **5** and **6** at 296 and 100 K, respectively, on a Bruker APEX I CCD diffractometer using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. SADABS³⁰ was used to perform areadetector scaling and absorption corrections. The structures were solved by direct methods using SHELXS-97³¹ and by full-matrix least squares techniques against F_o^2 using SHELXL-97.³² All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². Experimental details are given in Table 1.

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