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Synthesis of 2-(*N*-arylimino-κ*N*-methyl)pyrrolide-κ*N* complexes of nickel

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ABSTRACT

2-(*N*-aryliminomethyl)pyrrole precursors (2,6-R_2-C_6H_3-N=CH-2-C_4H_3NH) (R = Me, **IH**; R = ^{i}Pr, **IIH**) were prepared and transformed into their corresponding sodium salts (**Na$^+$I$^-$** and **Na$^+$II$^-$**) by treatment with NaH. Both salts readily react with [$NiBr_2$(DME)] (DME = 1,2-dimethoxyethane) to give the respective bis{2-(*N*-arylimino-κ*N*-methyl)pyrrolide-κ*N*}nickel(II) complexes (**1**, **2**) in almost quantitative yields. The oxidative addition of **IH** to [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) results in the formation of **3**, which is a mono(iminomethylpyrrolide)-η^3-(cyclic-allyl)-type organonickel(II) complex. The crystal structure of compound **1** has been established by X-ray diffraction studies.

1. Introduction

The synthesis of new transition-metal complexes containing chelating imine ligands was stimulated by the reports of Brookhart [1], Gibson [2], Fujita [3] and Coates [4] regarding their usefulness in catalysis. Considerable effort has since been made to expand the number of both late and early transition-metal complexes with different chelating ligand frameworks [5]. For instance, asymmetrical *N*/*N* pyridylimine-type compounds have been synthesised and used in catalysis [6], organic synthesis [7], and biomedical studies [8], and we have recently also applied such metal complexes in dendrimer chemistry [9]. The number of closely related iminomethylpyrrolide metal complexes is, however, relatively scarce, despite the fact that these complexes contain an isosteric fragment of pyrromethenes and porphyrins. Significant results have been reported for bis(chelate) group 4 [10], or chromium [11], as well for mono(chelate) group 10 metal complexes and closely related species [12]. Herein we describe the straightforward synthesis and characterisation of bis{2-(*N*-arylimino-κ*N*-methyl)pyrrolide-κ*N*} complexes of nickel, as well as the identification of a mono-chelate derivative.

2. Results and discussion

2.1. Synthesis and characterisation

The 2-(*N*-aryliminomethyl)pyrrole precursors **IH** and **IIH** were synthesised according to previously described procedures [12] and deprotonated with NaH in THF (Scheme 1). After filtration and removal of the solvent in vacuum, **Na$^+$I$^-$** and **Na$^+$II$^-$** were isolated as white, solvent-free solids which can be stored indefinitely in a dry-box. However, they are moisture-sensitive in both the solid state and in solution, and hydrolyse back to the protonated precursors upon exposure to air.

The nickel complexes **1** and **2** were prepared by treatment of [$NiBr_2$(DME)] (DME = 1,2-dimethoxyethane) with the corresponding iminomethylpyrrolide ligand in a 1:2 molar ratio in acetonitrile (Scheme 1). These bis-chelate metal complexes were isolated in very high yields (>90%) as red, crystalline, air-stable solids which are soluble in chlorinated solvents and acetonitrile. The Holm and Barbier groups have described the synthesis of related *N*-aryl or *N*-alkyl bis(iminomethylpyrrolide)nickel(II) complexes by treatment of [NEt_4]$_2$[$NiBr_4$] with the appropriate Schiff base (deprotonated in situ with KO^{t}Bu) in dry THF [13]. However, the yields reported are below 30% and the workup procedure is more complicated. More recently, Gomes [12b], Dyer [12f] and Bochmann [12g] have also reported the incidental formation of bis(*N*-mesityliminopyrrolide)nickel(II) complexes. In fact, the latter author characterised compound **2** by ^{1}H NMR, which was isolated in much lower yield (15%) after the reaction of one equivalent of **Li$^+$II$^-$**

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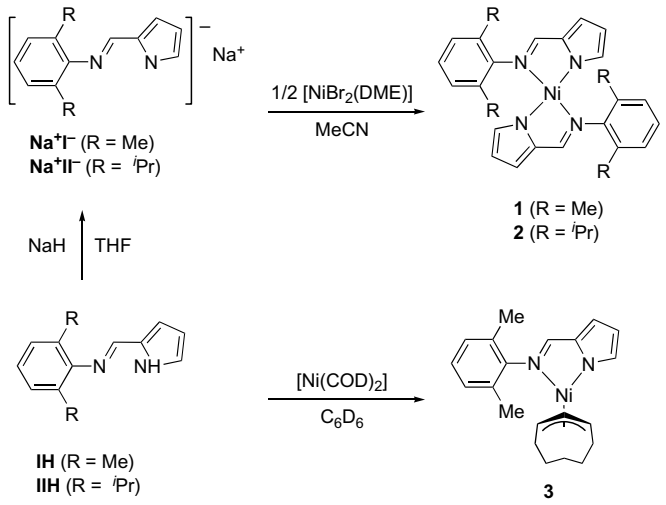


Scheme 1.

(generated *in situ* from **IIH** and Li^{n}Bu) and [$NiBr_2$(DME)] in diethyl ether at 0 °C.

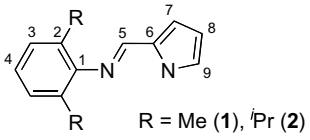
Complexes **1** and **2** were characterised by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses and mass spectrometry (see Section 4 for details). The crystal structure of **1** was determined by X-ray diffraction studies (see below). Both bidentate ligands are equivalent in the ^{1}H and ^{13}C NMR spectra, but the methyl groups of each isopropyl substituent in compound **2** are diastereotopic due to slow rotation around the *N*-aryl bond on the NMR time scale.

It has been documented that bis(iminomethylpyrrolide) nickel(II) complexes experiment planar ↔ tetrahedral endothermic equilibria, with topological populations intermediate or at either of the two extremes, depending on the steric properties of the N–R substituent [13]. The ^{1}H and ^{13}C chemical shifts observed for **1** and **2** are in the normal diamagnetic range, which is in agreement with a square-planar coordination for nickel in solution similar to that observed in the solid state for **1** (see below). On the other hand, important CIS effects (CIS = coordination-induced shift) are observed for the proton and carbon-13 resonances of the coordinated ligands when compared with their protonated precursors due to factors such as rehybridisation to accommodate the bite angle of the ligand, charge changes in the monoanionic pyrrolyl ring and in the coordinated imine group, or ring current and conjugation perturbations. The sign of the CIS effects is opposite for protons ($\Delta\delta < 0$) and carbon atoms ($\Delta\delta > 0$) and, as expected, the most affected shifts are those of the metallacycle and the proton in position 9 of the pyrrolide ring (Table 1).

Access to mono(iminomethylpyrrolide) nickel complexes is more difficult because the formation of bis(chelate) complexes seems to be favoured, which means that these latter compounds often appear as impurities or even as the only product during attempts to prepare mono(chelate) complexes [12b,c]. The only effective procedures reported to date are those by Gomes [12b] and Li [12c]. We attempted the reaction of equimolar amounts of **Na$^+$I$^-$** or **Na$^+$II$^-$** with [$NiBr_2$(DME)] in the presence of PPh_3 but only obtained mixtures of the corresponding bis-chelate **1** or **2** together with [$NiBr_2(PPh_3)_2$]. The reaction of pyrrole **IH** with [$Ni(COD)_2$] (COD = 1,5-cyclooctadiene) in an NMR tube proved more successful however. The spectra of an equimolar mixture in C_6D_6 showed no reaction at room temperature or at 60 °C, but complete transformation into a new compound, subsequently identified as complex **3**, and free COD was observed after heating at 120 °C for 30 min (Scheme 1). Compound **3** formally results from decoordination of a COD ligand in [$Ni(COD)_2$], oxidative addition of **IH** to the nickel centre, insertion of one double bond of the coordinated COD ligand into the Ni–H bond, and isomerisation of the resulting cyclooctenyl ligand to give an η^3-allyl-type organonickel complex. Similar species have been proposed as intermediates in catalytic reactions and have been identified by NMR spectroscopy from the in situ oxidative addition of phosphanylphenols (P, O ligand precursors) to [$Ni(COD)_2$] [14]. Unfortunately, the same reaction carried out on a larger scale at 120 °C in toluene led to the formation of a Ni(0) mirror and a solution containing a mixture of **3** (minor) and **IH** which could not be separated.

Characterisation of **3** in the C_6D_6 reaction solution was carried out by ^{1}H and {^{1}H,^{1}H} COSY NMR experiments. The ^{1}H NMR resonances assigned to the pyrrolide (δ 6.55, 5.98 and 5.05 for H^7, H^8 and H^9, respectively) and imine protons (δ 6.06) in **3** are shifted to high field upon coordination, in agreement with the CIS effects discussed above. The resonances at δ 5.09, 3.73 and 2.79, together with several multiplets observed in the aliphatic region, correspond to an allylic η^3-coordinated C_8H_{13} ring, as evidenced by selective ^{1}H,^{1}H decoupling and {^{1}H,^{1}H} COSY experiments. In addition to the corresponding cross-peaks between the pyrrolide protons, these experiments showed no coupling between the doublet of triplets at δ 2.79 and 3.73 (H$^{1'}$ and H$^{3'}$, Fig. 1). However, clear cross-peaks were observed between these resonances and the triplet at δ 5.09 (H$^{2'}$, J = 8.0 Hz), which appears partially overlapped by the H^9 pyrrolide proton. The chemical inequivalence of the allylic 1,3 protons means that the allyl ligand is not fluxional (rotation or π–σ–π conversion) at room temperature. Gomes has described the synthesis of two related [Ni(*N*-mesityliminomethylpyrrolide)(η^3-C_3H_5)] complexes by treatment of the sodium salt of the ligand and [Ni(η^3-C_3H_5)(μ-Br)]$_2$ [12b]. In agreement with this work, we tentatively assign the resonance

Table 1
Relevant CIS effects observed by NMR spectroscopy for compounds **1** and **2**.[a]



Complex	$\Delta\delta$[b]									
	H^5	H^7	H^8	H^9	C^5	C^6	C^7	C^8	C^9	C^1
1	−1.10	−0.02	−0.44	−1.74	+9.1	+10.5	+1.8	+2.5	+13.3	−3.4
2	−1.06	−0.05	−0.50	−1.83	+9.3	+9.8	+2.0	+2.3	+14.3	−3.6

[a] In $CDCl_3$ at 20 °C.
[b] $\Delta\delta$ in ppm with respect to the corresponding free ligands **IH** or **IIH**.

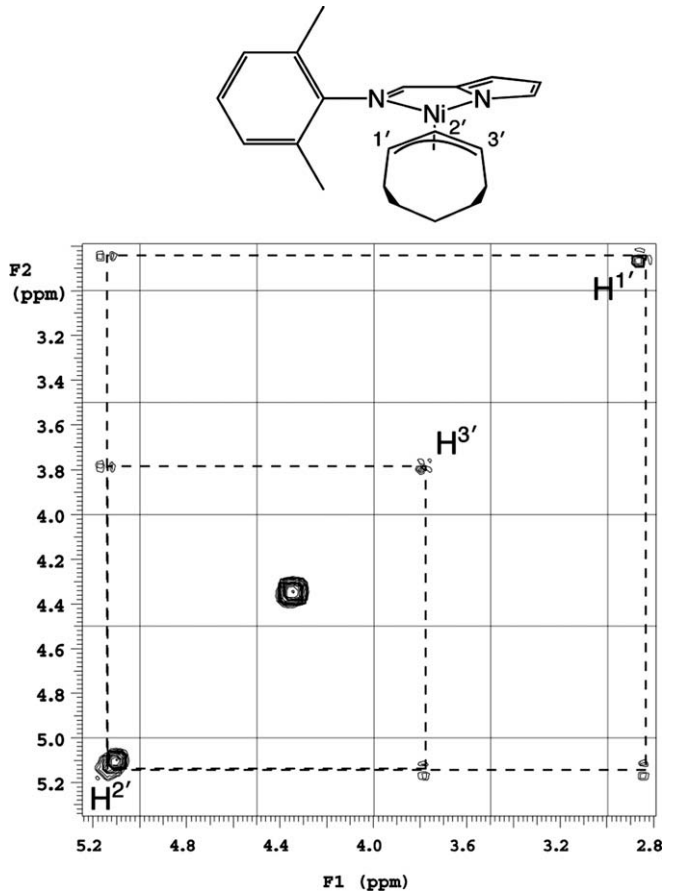


Fig. 1. {^{1}H,^{1}H} COSY spectrum of the η^3-allyl region for **3**.

found at δ 3.73 to the allylic *syn*-proton closest to the pyrrolide ring (H^3).

Complexes **1** and **2**, activated by IPMAO, and **3** were evaluated as ethylene polymerisation catalysts (room temp., 2 bar, toluene, 24 h, Al/Ni = 1000). Only traces of sticky polymer were observed in the case of the bis(chelate) compounds.

2.2. Crystal structure of complex *1*

The molecular structure of complex **1** in the solid state, as determined by single-crystal X-ray diffraction studies, is shown in Fig. 2; selected bond lengths and angles are listed in Table 2. The molecule is monomeric, has non-crystallographic C_2 symmetry, and resembles that found for similar Cr(II) [11], Pd(II) [12a] or Ni(II) [12f] bis-chelate complexes. The geometry at the Ni atom is approximately square-planar, with *cis* angles in the range 83.48(11)–97.34(10)°. The four nitrogen atoms deviate slightly from the mean plane [N(1) and N(3) 0.11, N(2) −0.10, and N(4) −0.12 Å] with Ni(1) lying in the plane. The complex adopts a *trans* configuration, probably due to steric constraints, with N(1)–Ni(1)–N(3) and N(2)–Ni(1)–N(4) angles of 173.11(11)° and 173.28(11)°, respectively. The pyrrolide ring and the metallacycle of each ligand are co-planar to within 0.07 and 0.027 Å but have a dihedral angle of 13.13° between them. The 2,6-dimethylphenyl rings tend to lie orthogonal (76.05° and 73.60°) to the molecular plane, with Ni(1)–N(4)–C(21)–C(22) and Ni(1)–N(2)–C(11)–C(12) torsion angles of −66.2° and −71.3°, respectively. The Ni–N distances in complex **1** are slightly shorter than those of related mono-chelate complexes [12b,c], whereas the imine double bond is slightly longer,

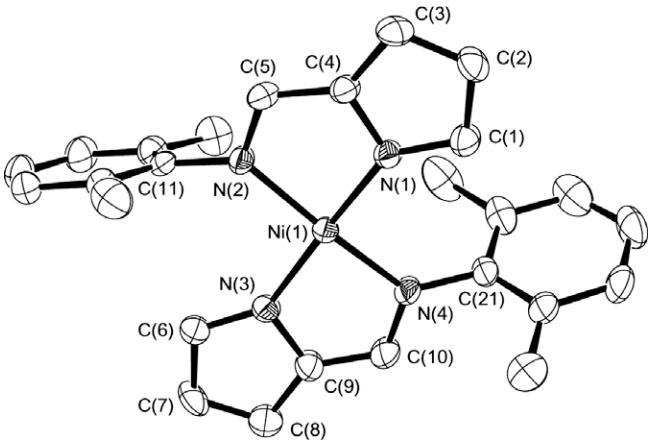


Fig. 2. Molecular structure of complex **1**.

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**.

Ni(1)–N(1)	1.914(2)	N(1)–Ni(1)–N(3)	173.11(11)
Ni(1)–N(3)	1.916(2)	N(2)–Ni(1)–N(4)	173.28(11)
Ni(1)–N(2)	1.929(2)	N(1)–Ni(1)–N(2)	83.53(10)
Ni(1)–N(4)	1.932(3)	N(3)–Ni(1)–N(4)	83.48(11)
N(1)–C(1)	1.365(4)	N(2)–Ni(1)–N(3)	97.34(10)
N(1)–C(4)	1.379(4)	N(1)–Ni(1)–N(4)	96.47(11)
N(2)–C(5)	1.313(4)	Ni(1)–N(1)–C(4)	113.00(19)
N(2)–C(11)	1.454(4)	Ni(1)–N(2)–C(5)	112.8(2)
C(4)–C(5)	1.411(4)	N(1)–C(4)–C(5)	113.3(3)
N(3)–C(6)	1.367(4)	C(4)–C(5)–N(2)	117.3(3)
N(3)–C(9)	1.385(4)	C(5)–N(2)–C(11)	116.7(3)
N(4)–C(10)	1.316(4)	C(9)–N(3)–Ni(1)	112.27(19)
N(4)–C(21)	1.439(4)	C(10)–N(4)–C(21)	118.5(3)
C(9)–C(10)	1.402(4)	C(10)–N(4)–Ni(1)	113.0(2)
		C(21)–N(4)–Ni(1)	128.2(2)
		N(3)–C(9)–C(8)	110.5(3)
		N(3)–C(9)–C(10)	113.8(3)
		N(4)–C(10)–C(9)	116.9(3)

which is consistent with a somewhat greater nickel-to-ligand π-back-donation in the bis-chelate compound. Gomes has analysed the structural differences between free and coordinated ligands and has found that coordination results in an acute N–Ni–N angle (*ca.* 83°) at the expense of different angle accommodations observed for the imine-pyrrolide moiety [12b]. Since the ligand bite angle in **1** [N(1)–Ni(1)–N(2) 83.52(10)° and N(3)–Ni(1)–N(4) 83.48(11)°] and the other angles in the -N=CH-C_4H_3N- moiety are fairly similar [*e.g.*, C(1)–N(1)–C(4) 105.7(3)°], we conclude that ligand distortion upon coordination also occurs in the bis(chelate)nickel(II) complexes described here.

3. Conclusions

An efficient and simple procedure for the synthesis of bis(iminopyrrolide)nickel(II) complexes, which involves treatment of the sodium salt of the N,N′-ligand with [$NiBr_2$(DME)], is reported in this work. The *N*-aryl-iminopyrrolide compounds **1** and **2** are found to be in a square-planar geometry both in the solid state and in solution. The mono(iminopyrrolide) complex **3** has been identified from the reaction of [Ni(COD)$_2$] and *N*-(2,6-dimethylphenyl)iminopyrrole, and its characterisation indicates the formal oxidative addition of the pyrrole to [Ni(COD)$_2$] to give an η^3-(cyclic allyl)-type organonickel(II) complex. This compound also displays a pseudo-planar symmetry with some rigidity of the coordinated cyclic allyl ligand.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under argon using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Compounds **IH** and **IIH** and their sodium salts (**Na$^+$I$^-$** and **Na$^+$II$^-$**) were synthesised by adapting reported procedures [12], and [$NiBr_2$(DME)] (DME = 1,2-dimethoxyethane) [15] was prepared as described in the literature. Solvents were dried prior to use and distilled under argon as described elsewhere [16]. NMR spectra were recorded with Varian Unity VR-300 or Varian Unity 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$, and were measured relative to the ^{13}C and residual ^1H resonances of the deuterated solvents. Assignments for the aryl-iminopyrrolide fragments are given according to the numbering depicted in Table 1. Elemental analyses and APCI mass spectra were performed by the Microanalytical Laboratories of the University of Alcalá with a Heraeus CHN-O-Rapid microanalyzer and a Thermo Quest Finningan Automass Multi mass spectrometer, respectively.

4.2. Preparation of bis{2-[N-(2,6-dimethylphenyl)imino-κN-methyl]pyrrolide-κN}nickel (*1*)

NaH (60% in mineral oil; 202 mg, 5.05 mmol) was washed with pentane (2 × 10 mL) in a Schlenk tube and then treated with a THF solution (20 mL) of ligand **IH** (1000 mg, 5.04 mmol) at room temperature. A bubbler was fitted to the tube and, after gas evolution had ceased, the mixture was stirred for an additional 5 h. The resulting colourless solution was filtered, pumped to dryness under vacuum, and the crude residue washed with pentane (2 × 15 mL) to afford **Na$^+$I$^-$** as a white solid, which was stored in a dry-box. [$NiBr_2$(DME)] (375 mg, 1.22 mmol) was added to an orange solution of **Na$^+$I$^-$** (537 mg, 2.44 mmol) in MeCN (50 mL) at room temperature. The mixture changed instantaneously to a brownish colour and was stirred for 24 h. After filtration of the NaCl by-product, the red solution was concentrated to half of its initial volume and cooled to −20 °C overnight to afford complex **1** as a red-brown crystalline solid. Concentration and cooling of the mother liquor gave a second crop of crystals. Yield: 517 mg (94%, relative to Ni). Anal. Calc. for $C_{26}H_{26}N_4Ni$ (453.21): C, 68.90; H, 5.78; N, 12.36. Found: C, 68.97; H, 5.78; N, 12.31%. ^1H NMR ($CDCl_3$): δ 2.63 (s, 6H, Me), 4.65 (broad s, 1H, H^9), 5.74 (dd, $J_{8,7}$ = 3.7, $J_{8,9}$ = 1.6 Hz, 1H, H^8), 6.57 (dd, $J_{7,8}$ = 3.7, $J_{7,9}$ = 1.0 Hz, 1H, H^7), 6.87 (s, 1H, H^5), 7.0–7.2 (overlapped m, 3H, $H^{3,4}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2 (Me), 112.5 (C^8), 118.2 (C^7), 126.5 (C^4), 128.4 (C^3), 133.4 (C^2), 136.9 (C^9), 140.6 (C^6), 147.3 (C^1), 162.0 ppm (C^5). MS (APCI in CH_3CN): *m*/*z* 454 $[M+H]^+$, 338 $[M-\mathbf{I}+2MeCN]^+$, 297 $[M-\mathbf{I}+MeCN+H]^+$, 255 $[M-\mathbf{I}]^+$, 240 [**IH**+MeCN+H]$^+$, 199 [**IH**+H]$^+$.

Spectroscopic data for **Na$^+$I$^-$**: ^1H NMR ($CDCl_3$): δ 2.04 (s, 6H, Me), 6.28 (t, $J_{8,7} \approx J_{8,9} \approx 3.0$ Hz, 1H, H^8), 6.60 (d, $J_{7,8}$ = 3.0 Hz, 1H, H^7), 6.91 (m, 1H, H^4), 6.95 (broad s, 1H, H^9), 7.03 (overlapped m, 2H, H^3), 7.94 (s, 1H, H^5).

4.3. Preparation of bis{2-[N-(2,6-diisopropylphenyl)imino-κN-methyl]pyrrolide-κN}nickel (*2*)

The sodium salt **Na$^+$II$^-$** was prepared as described above for **Na$^+$I$^-$**, starting from NaH (60% in mineral oil; 157 mg, 3.93 mmol) and ligand **IIH** (1000 mg, 3.39 mmol), and isolated as a white solid, which was stored in a dry-box. Compound **2** was isolated as a red microcrystalline solid following a similar procedure to that described for **1**, starting from **Na$^+$II$^-$** (361 mg, 1.31 mmol) and [$NiBr_2$(DME)] (202 mg, 0.65 mmol) in MeCN (30 mL). Yield: 338 mg (92%). Anal. Calc. for $C_{34}H_{42}N_4Ni$ (565.43): C, 72.22; H, 7.49; N, 9.91. Found: C, 72.28; H, 7.40; N, 9.85%. ^1H NMR ($CDCl_3$): δ 1.19 (d, $J_{H,H}$ = 6.9 Hz, 6H, ^{i}Pr), 1.23 (d, $J_{H,H}$ = 6.9 Hz, 6H, ^{i}Pr), 4.41 (sept, $J_{H,H}$ = 6.9 Hz, 2H, ^{i}Pr), 4.68 (broad s, 1H, H^9), 5.71 (dd, $J_{8,7}$ = 3.7, $J_{8,9}$ = 1.8 Hz, 1H, H^8), 6.54 (dd, $J_{7,8}$ = 3.7, $J_{7,9}$ = 0.9 Hz, 1H, H^7), 6.87 (s, 2H, H^5), 7.13 (m, 1H, H^4), 7.28 (m, 4H, H^3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.7 and 24.7 ($CHMe_2$), 28.8 ($CHMe_2$), 112.3 (C^8), 118.0 (C^7), 123.8 (C^3), 127.2 (C^4), 137.6 (C^9), 140.0 (C^6), 143.5 (C^2), 145.0 (C^1), 161.5 ppm (C^5). MS (APCI in CH_3CN): *m*/*z* 566 $[M+H]^+$, 394 $[M-\mathbf{II}+2MeCN]^+$, 354 $[M-\mathbf{II}+MeCN+H]^+$, 296 [**IIH**+MeCN+H]$^+$, 255 [**IIH**+H]$^+$.

Spectroscopic data for **Na$^+$II$^-$**: ^1H NMR ($CDCl_3$): δ 1.08 (d, $J_{H,H}$ = 6.9 Hz, 12H, ^{i}Pr), 3.01 (sept, $J_{H,H}$ = 6.9 Hz, 2H, ^{i}Pr)), 6.29 (dd, $J_{8,9}$ = 3.3, $J_{8,7}$ = 2.2 Hz, 1H, H^8), 6.65 (dd, $J_{7,8}$ = 3.3, $J_{7,9}$ = 1.0 Hz, 1H, H^7), 6.91 (broad s, 1H, H^9), 7.11 (overlapped m, 3H, $H^{3,4}$), 7.91 (s, 1H, H^5).

4.4. Identification of [(1–3-η)cycloocta-2-en-1-yl]{2-[N-(2,6-dimethylphenyl)imino-κN-methyl]pyrrolide-κN}nickel (*3*)

Compound **3** was prepared in an NMR-scale experiment. [$Ni(COD)_2$] (10 mg, 36.3 μmol) and iminopyrrole **IH** (7.2 mg, 36.3 μmol) were weighed in a dry-box and combined with C_6D_6 (0.8 mL) at room temperature. The solution was transferred to an NMR tube with PTFE valve, the tube was sealed, and the ^1H NMR spectrum of the sample was recorded soon after. This spectrum showed peaks corresponding to the unreacted starting materials. The tube was then immersed in an oil bath at 120 °C for 30 min and the spectrum was recorded again. The initial yellow solution turned dark orange during heating, and the new spectrum indicated the total consumption of **IH** and [$Ni(COD)_2$] and the presence of free 1,5-COD and a new complex characterised as compound **3**. ^1H NMR (C_6D_6): δ 1.0–1.2 (m, 4H, CH_2), 1.3–1.6 (m, 4H, CH_2), 1.6–1.7 (m, 2H, CH_2), 2.20 (s, 12H, Me), 2.44 (broad s, free COD), 2.79 (dt, $^3J_{H,Hcentral}$ = 8.0, $^3J_{H,H}$ = 8.0 Hz, 1H, allyl-H), 3.73 (dt, $^3J_{H,Hcentral}$ = 8.0, $^3J_{H,H}$ = 8.0 Hz, 1H, allyl-H), 5.05 (broad s, 1H, H^9), 5.09 (t, $^3J_{H,Hsyn}$, $^3J_{H,Hsyn}$ = 8.0 Hz, 1H, allyl-$H_{central}$), 5.57 (broad s, free COD), 5.98 (dd, $J_{8,7}$ = 3.8, $J_{8,9}$ = 1.8 Hz, 1H, H^8), 6.06 (s, 1H, H^5), 6.55 (dd, $J_{7,8}$ = 3.8, $J_{7,9}$ = 0.9 Hz, 1H, H^7), 6.8–7.0 (overlapped m, 3H, $H^{3,4}$).

4.5. X-ray crystallographic studies

Suitable single crystals of **1** were obtained by cooling a concentrated solution in acetonitrile to −20 °C overnight. A summary of crystal data and data collection and refinement parameters for the structural analysis is given in Table 3.

A red crystal of suitable size was glued to a glass fibre using an inert polyfluorinated oil and mounted in the N_2 stream of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit; data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were collected at 200 K, with an exposure time of 6 s per frame [6sets; 568frames; phi and omega scan (1.3° scan width)] and were corrected for Lorenz and polarisation effects in the usual manner. No extinction or absorption corrections were made. The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares procedures on F^2 (SHELXL-97) [17]. Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Some of the hydrogen atoms were located in the Fourier map and refined isotropically; the remainder were

Table 3
Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{26}H_{26}N_4Ni$
Formula weight	453.22
Color	Red
Temperature (K)	200.0(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	
a (Å)	11.1326(3)
b (Å)	8.4240(7)
c (Å)	24.529(3)
Volume (Å^3)	2300.4(3)
Z, Calculated density (g/cm^3)	4, 1.309
Absorption coefficient mm^{-1}	0.863
F(000)	952
Crystal size (mm^3)	0.35 × 0.25 × 0.25
θ range (°)	3.03–27.54
Limiting indices	$-14 \leq h \leq 14$, $-10 \leq k \leq 10$, $-31 \leq l \leq 31$
Reflections collected/unique [$R_{(int)}$]	46074/5277 [0.1302]
Completeness to $\theta = 27.54°$	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5277/0/308
Goodness of fit on F^2	0.912
Final R^a indices [$I > 2\sigma(I)$]	$R_1 = 0.0439$, $wR_2 = 0.0823$
R indices (all data)	$R_1 = 0.0846$, $wR_2 = 0.0908$
Absolute structure parameter	−0.015(15)
Largest difference peak and hole (e/Å^3)	0.434 and −0.322

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\sum \omega(F_o^2 - F_c^2)]/[\sum \omega(F_o^2)^2]^{1/2}$.

included from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system [18].

Supplementary material

CCDC 694280 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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