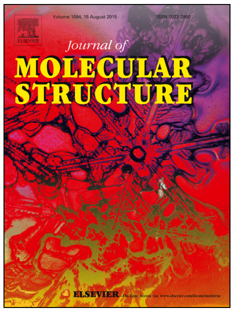

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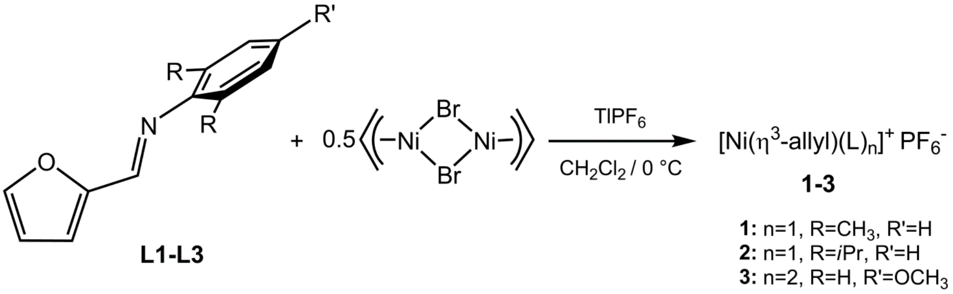
Graphical abstract

Three new cationic η^3-allyl Ni(II) complexes bearing 2-(N-arylformimino)furan N,O-donor ligands have been synthesised. The complexes have been characterised by FT-IR, NMR spectroscopy and elemental analysis. The structure of complex **2** has also been determined by single crystal X-ray diffraction.



Cationic allyl nickel complexes containing N,O-donor labile ligands: Synthesis and molecular characterisation

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Abstract:

Three 2-iminofuran ligands 2-(*N*-2,6-diisopropylphenylformimino)furan (**L1**), 2-(*N*-2,6-dimethylphenylformimino)furan (**L2**) and 2-(*N*-4-methoxyphenylformimino)furan (**L3**) were obtained by condensation reactions of the respective anilines with furfural.

The η^3-allyl Ni(II) cationic complexes **1-3** have been synthesised by reacting $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ with the corresponding ligands **L1-L3**, in the presence of $TlPF_6$. All complexes have been characterised by FT-IR, NMR spectroscopy and elemental analysis. The molecular structure of complex **2** has been determined by single crystal X-Ray diffraction. Complexes **1** and **2** have displayed a mono bidentate chelation mode of the respective ligand, while complex **3** showed a bis monodentate coordination framework. The respective complexes were studied by DFT calculations, showing a tendency to form the bis monodentate species, the formation of complex **3** being clearly the most favoured one.

Keywords: η^3-allyl complexes; cationic nickel(II) complexes; N,O-chelates; hemilabile ligands; DFT calculations

1. Introduction:

Most of the known bidentate complexes contain rather rigid ligand frameworks, which are intended to yield increased stabilities. On the other hand, a more flexible ligand backbone would allow a subtler interplay between lability and stability, which may be beneficial for some types of catalytic applications. Compounds containing N,O-donors can act as potentially bidentate type ligands, in general displaying high versatility in their design by the introduction of several kinds of steric and electronic features, each of the donor moieties exhibiting specific binding characteristics. N-donor ligands coordinate well to smaller transition metal ions such as V, Cr, Mn, Fe, Co, Ni, Cu and Zn. On the other hand, O-donor ligands tend to coordinate to metal ions such as the larger alkali, alkaline earth metal ions and large post transition metal ions [1-4].

Schiff base complexes derived from heterocyclic compounds have found an increased interest in the context of bioinorganic chemistry, where complexes having simultaneously nitrogen and oxygen donor atoms have been reported by several research groups [5–8], in addition to their applications in the fields of luminescence [9,10] and catalysis [11, 12]. Nickel(II) complexes bearing S,S, S,O, and O,O chelating ligands have also been applied in catalysis, demonstrating high catalytic activity for olefin oligomerisation. However, the product distribution was difficult to control and commercialisation could not be achieved. In contrast, the introduction of a nitrogen group into the bidentate O containing chelate Ni systems allowed the steric properties to be varied and resulted in almost 100% selectivity for linear hexenes with a high proportion (60-80%) being α-olefins [13]. The furan ring, as an important part of the ligand, has been studied and attracted great attention for a long time, significant progress being made in understanding the structure of its complexes [14–16]. Complexes of some transition metals with Schiff bases derived from furan-2-carboxaldehyde and *o*-phenylenediamine [17–19], hydrazine hydrate [20], 3,3'-diaminobenzidene [21], 3-aminodibenzofuran [22] and *o*-toluidine [23] were studied. Furfural Schiff bases were found to show selectivity towards anions, allowing them to act as anion-sensitive membrane electrodes [24], and also display nitrification inhibitory properties [25].

The common methodology for the preparation of allyl-nickel complexes consists in opening the dimeric structure of $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ through the addition of the appropriate ligands, which leads to neutral complexes. The halide is then abstracted by thallium salts, giving rise to cationic η^3-allyl nickel(II) complexes having a non-coordinating anion. Recently, we employed this methodology to attempt the synthesis of Ni(II) complexes bearing chelating N,S-thienylimine ligands. The reactions of $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ with either one or two equivalents of the appropriate ligand L, in the presence of $TlPF_6$, in dichloromethane, afforded always the corresponding complexes $[Ni(\eta^3\text{-allyl})L_2][PF_6]$, containing two monodentate thienylimine ligands coordinated to Ni exclusively through the imine nitrogen atoms [26], a result explained by the soft character of the sulphur donor towards the hard nature of the nickel ion.

Following these results, we decided to apply this methodology to the preparation of η^3-allyl Ni(II) cationic complexes containing N,O-donor ligands. Herein, we report the synthesis and characterisation of new cationic allyl nickel(II) complexes bearing one chelating or two monodentate 2-(*N*-arylformimino)furan N,O-donor ligands and the molecular structure of one of the nickel(II) complexes containing a chelating ligand, as determined by X-ray diffraction.

2. Experimental

2.1. General Considerations

All experiments dealing with air and moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by Air Liquide and purified by passage through 4 Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g., Acrös, Aldrich,) and used without further purification. All solvents to be used under inert atmosphere were thoroughly dehydrated over a suitable drying agent (sodium for *n*-hexane, and CaH_2 for dichloromethane) and refluxed under nitrogen before use. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae.

The deuterated solvent CD_2Cl_2 used was dried by storage over 4 Å molecular sieves and degassed by the freeze-pump-thaw method, and stored under nitrogen. NMR spectra were recorded on a Bruker Avance III 300 spectrometer (^1H, 300.130 MHz; ^{13}C, 75.468 MHz), being referenced internally to the residual ^1H solvent resonances (^1H) and the solvent resonance (^{13}C) relative to tetramethylsilane (δ=0); ^{19}F, and ^{31}P were referenced externally using $CFCl_3$ (δ=0) and H_3PO_4 85% (δ=0), respectively. Infrared spectra were recorded using KBr pellets on a Jasco FT/IR 430. Elemental analyses were obtained from the Laboratório de Análises do IST (Fisons Instrument 1108).

2.2. General procedure for the synthesis of ligands ***L1-L3***

The synthesis of the ligands was adapted from a previously reported method [27]. Stoichiometric amounts of furan-2-carboxaldehyde, the respective aniline (52.07 mmol) and a catalytic amount of formic acid were combined in ethanol and the mixture was reacted for 4 h, at room temperature. The yellow-orange precipitates obtained were filtered, washed with cold 2-propanol and dried under vacuum. Recrystallisation of the respective solids from cold 2-propanol afforded the title ligands.

2.2.1. Synthesis of ligand **L1**

Ligand **L1** was prepared as described in the general procedure above using furan-2-carboxaldehyde (5 g, 52.07 mmol) and 2,6-dimethylaniline (6.30 g, 52.07 mmol).
Yield: (6.42 g, 62%). IR [ν(cm^{-1})]; 1634 (C=N).^{1}H NMR ($CDCl_3$): δ 2.17 (s, 6H, CH_3), 6.57-6.95 (m, 3H, H_{arom}), 7.07-7.63 (m, 3H, H_{furan}), 8.01 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.71, 111.47, 114.81, 123.33, 127.53, 145.00, 150.37, 151.28.

2.2.2. Synthesis of ligand **L2**

Ligand **L2** was prepared as described in the general procedure above using furan-2-carboxaldehyde (5 g, 52.07 mmol) and 2,6-diisopropylaniline (9.22 g, 52.07 mmol).
Yield: (10.89 g, 82%). IR [ν(cm^{-1})]; 1627 (C=N). ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 12H, iPr-CH_3), 3.02 (sept, 2H, H_{iPr}), 6.58-6.99 (m, 6H, $H_{arom+furan}$), 7.99 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.07, 27.37, 111.50, 122.52, 124.03, 137.39, 145.06, 150.01, 151.25.

2.2.3. Synthesis of ligand **L3**

Ligand **L3** was prepared as described in the general procedure above using furan-2-carboxaldehyde (5 g, 52.07 mmol) and 4-methoxylaniline (6.40 g, 52.07 mmol).
Yield: (5.96 g, 57%). IR [ν(cm^{-1})]; 1622 (C=N).^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H, O-CH_3), 6.54 (s, 1H, H_3), 6.91 (s, 2H, H_{arom}), 6.93 (s, 1H, H_{furan}), 7.24 (d, 2H, H_{arom}), 7.59 (s, 1H, H_{furan}), 8.30 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 54.96, 114.94, 111.57, 113.93, 121.77, 143.75, 144.79, 145.24, 151.86, 157.99.

*2.3. General procedure for the synthesis of complexes **1-3***

A Schlenk tube was charged with $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ and the respective ligand and the mixture was dissolved in CH_2Cl_2 (*ca.* 20 mL) and cooled to 0 °C. $TlPF_6$ was added to the mixture, which was stirred at room temperature for 60 min. After the reaction, the solution was filtered through Celite® and the solvent removed under vacuum. The orange-red residue was washed with *n*-hexane (3×20 mL) and further recrystallised from a CH_2Cl_2/*n*-hexane (1:3

v/v) solution cooled to -20 ºC. The complexes were obtained as orange-red powders or crystals.

2.3.1. Synthesis of complex **1**

Complex **1** was prepared using the method described above using $[Ni(\eta^3-C_3H_5)(\mu-Br)]_2$ (0.088 g, 0.25 mmol), ligand **L1** (0.099 g, 0.5 mmol) and $TlPF_6$ (0.174 g, 0.5 mmol).
Yield: (0.37 g, 83%). Found (Calc.) for $(C_{16}H_{18}F_6NNiOP)_3.CH_2Cl_2$: C, 41.12 (41.54); H, 3.51 (3.98); N, 2.54 (2.97). IR [ν(cm^{-1})]; 1635 (C=N), 866 (PF_6). ^1H NMR (CD_2Cl_2): δ 2.32 (br, 6H, CH_3), 2.48 (br, 2H, η^3-allylCH_2, overlapping with CH_3), 3.06 (br, 2H, η^3-allyl CH_2), 5.77 (br, 1H, η^3-allyl CH), 6.41 (br, 1H, H_{furan}), 7.21 (br, 3H, $H_{aromatic+furan}$), 7.60 (br, 1H, H_{furan}), 8.2 (br, 1H, N=CH). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ -71.02 (d, PF_6^-). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -145.01 (h, PF_6^-).

2.3.2. Synthesis of complex **2**

Complex **2** was prepared using the method described above using $[Ni(\eta^3-C_3H_5)(\mu-Br)]_2$ (0.088 g, 0.25 mmol), ligand **L2** (0.099 g, 0.5 mmol) and $TlPF_6$ (0.174 g, 0.5 mmol). Single crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 solution double-layered with *n*-hexane (1:3 v/v), at -20 ºC.
Yield: (0.44 g, 89%). Found (Calc.) $(C_{20}H_{26}F_6N_2NiO_4P)_3.CH_2Cl_2$: C, 41.46 (41.36); H, 4.80 (4.55); N, 4.78 (4.74). IR [ν(cm^{-1})]; 1636 (C=N), 800 (PF_6). ^1H NMR (CD_2Cl_2): δ 1.30 (br, 12H, *i*Pr CH_3), 1.44 (br, 2H, η^3-allyl CH_2), 2.63 (br, 2H, *i*Pr CH), 3.06 (m, 2H, η^3-allyl CH_2), 3.27 (br, 2H, *i*Pr CH), 6.05 (m, 1H, η^3-allyl CH), 6.94 (br, 1H, H_{furan}), 7.25-7.40 (m, 6H, $H_{aromatic}$), 7.57 (br, 1H, H_{furan}), 7.86 (br, 1H, H_{furan}), 8.12 (br, 1H, N=CH). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ -71.34 (d, PF_6^-).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -144.68 (h, PF_6^-).

2.3.3. Synthesis of complex **3**

Complex **3** was prepared using the method described above using $[Ni(\eta^3-C_3H_5)(\mu-Br)]_2$ (0.088 g, 0.25 mmol), ligand **L3** (0.092 g, 0.5 mmol) and $TlPF_6$ (0.174 g, 0.5 mmol).Yield: (0.27 g, 42%). Found (Calc.) for $(C_{27}H_{30}F_6N_2NiO_4P)_3.CH_2Cl_2$: C 48.79 (48.38); H, 3.83 (4.56); N, 4.01 (4.13). IR [ν(cm^{-1})]; 1622 (C=N), 837 (PF_6). ^1H NMR (CD_2Cl_2): δ 2.68 (m, 2H, η^3-allyl CH_2), 3.48 (br, 2H, η^3-allyl CH_2), 3.74 (s, 6H, OCH_3), 6.08 (m, 1H, η^3-allyl CH), 6.63 (br, 2H, H_{furan}), 6.75-6.79 (d, 4H, $H_{aromatic}$), 7.00-7.10 (m, 6H, $H_{aromatic+furan}$) 7.84 (m, 4H, H_{furan} + N=CH). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ -72.31 (d, PF_6^-). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -144.17 (h, PF_6^-).

2.4. X-ray crystallography

Crystals of complex **2** were selected under an inert atmosphere, covered with polyfluoroether oil, and mounted on a nylon loop. Crystallographic data for compound **2** was collected using graphite monochromated Mo-Kα radiation (λ=0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat at 150 K. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS [28], structure solution and refinement were performed using direct methods with the programs SIR2014 [29], included in the package of programs WINGX-Version 2014.1 [30] and SHELXL [31]. All hydrogen atoms were inserted in idealised positions and allowed to refine riding on the parent carbon atoms. Data was deposited in the CCDC under deposit no. 1585090 for compound **2**.

Table 1. Crystal data and structure refinement for complex **2**.

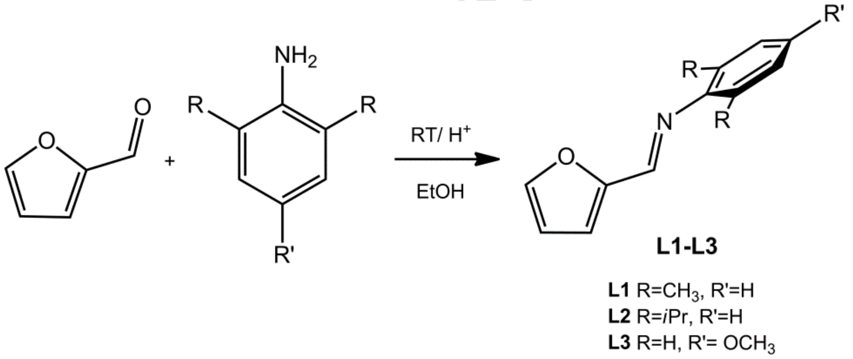
Chemical formula	$C_{41}H_{54}Cl_2F_{12}N_2Ni_2O_2P_2$
Crystal size (mm^3)	0.1×0.1×0.2
Formula weight	1085.12
Crystal system	Monoclinic
Space group	C2/c
a (Å)	27.0269(18)
b (Å)	10.3375(7)
c (Å)	17.5800(12)
α (º)	90
β (°)	105.467(3)
γ (º)	90
V (Å^3)	4733.8(6)
Z	8
T (K)	150
ρ_{calc} (g cm^{-3})	1.523
Total reflections	34954
Unique reflections	3429
R_{int}	0.0501
$2\theta_{max}$ (°)	51.316
λ (Å)	0.71073
μ (mm^{-1})	1.060
h,k,l_{max}	32,12,21
θ_{max}	25.680
F(000)	2232
Goodness-of-fit	1.102
R (reflections)	0.0682
wR_2 (reflections)	0.1987
Dq_{max}, eÅ^3	1.412
Dq_{min}, eÅ^3	-0.921

2.5. DFT calculations

All calculations were performed using the Gaussian 09 software package [32] and the PBE1PBE functional [33]. The geometry optimisations were accomplished without symmetry constraints using a standard 6-31G** basis set [34] for all atoms except for nickel, that used a LanL2DZ basis set [35] with a f-polarisation function [36]. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. The electronic energies obtained were converted to free energies at 298.15 K and 1 atm by using zero-point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

3. Results and discussion

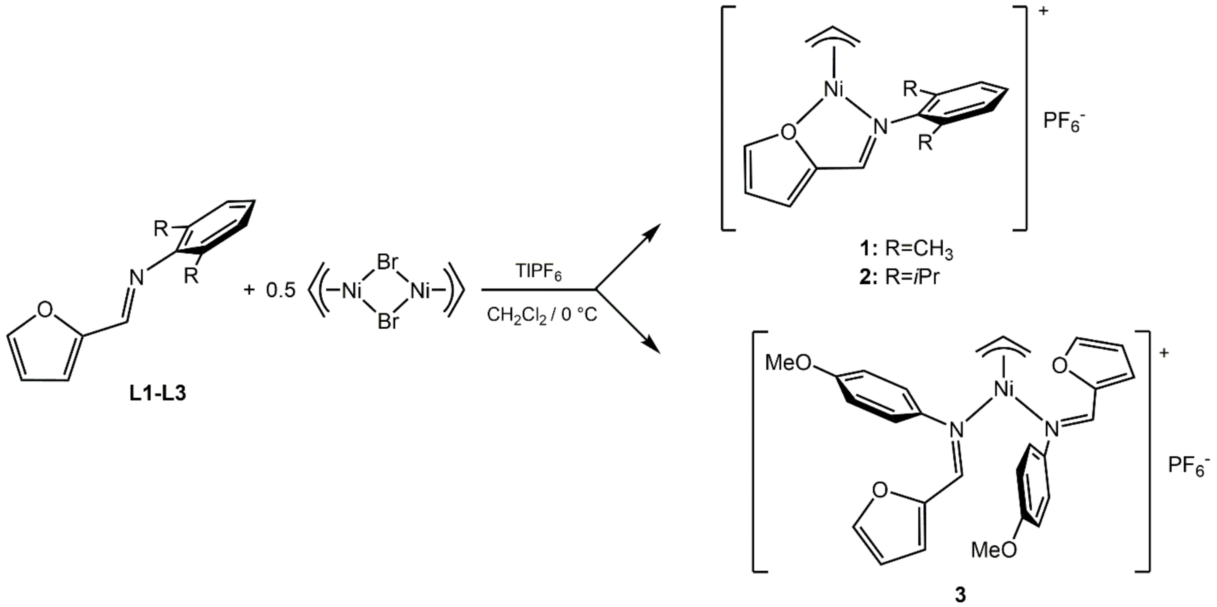
The ligands were synthesized from the condensation reaction of furan-2-carboxaldehyde and the respective anilines in the presence of a catalytic amount of formic acid, in ethanol for 4 h, at room temperature (Scheme 1). Variations in the amine allowed the facile design of ligands with different physical and chemical properties [37,38].



Scheme 1. Synthesis of the ligands **L1-L3**.

The new cationic η^3-allyl Ni(II) complexes **1-3** were prepared via the metathetic exchange reaction of [Ni(η^3-C_3H_5)(μ-Br)]$_2$ with $TlPF_6$, in the presence of the respective ligands **L1-L3**, in CH_2Cl_2 at 0 °C, in moderate yields (Scheme 2). The new Ni(II) complexes **1-3** were isolated as red solids, which are soluble in soluble in CH_2Cl_2.

Both the ligands and the complexes were characterised in the solid state by FT-IR spectroscopy, their spectra being shown in Figures S1-S6 of the Supplementary Material. The IR spectra of the complexes were assigned by comparison with the IR spectra of the ligands, the complexes exhibiting a typical ν(C=N) band between 1622 to 1634 cm^{-1} [39]. The absorption wavenumbers do not change significantly upon coordination, meaning that π-back bonding from the metal to the ligands is not significant possibly due to low chelating strength. A strong absorption band is exhibited at approximately 800-866 cm^{-1}, for all three complexes, corresponding to the characteristic fingerprint stretching vibration of the non-coordinated PF_6^- counter-ion [40]. For complex **2**, weak bands are observed at 596 cm^{-1} (ν(Ni-N)) [41] and at 414 cm^{-1} (ν(Ni-O)) [42].



Scheme 2. Synthesis of the complexes **1-3.**

The three complexes were characterised in solution by NMR spectroscopy, the respective spectra being consistent with their formulation. In general, the ^{1}H NMR spectra of the complexes (Figures S13-S15 of the Supplementary Material) are somewhat broad. Although the compounds were analytically pure, they showed a relatively thermally unstable behaviour in solution, leading to a slight degree of decomposition, possibly giving rise to paramagnetic Ni impurities, which may a reason for the slightly broad features of the resonances. The thermally instability is likely justified by the overall low donor ability and hemilability of the potentially bidentate ligands. Contrarily to the observed with the analogous N,S thienylimine ligands [26], which behave exclusively as monodentate ligands coordinated through the N-atom to nickel, complexes **1** and **2** exhibit the expected Ni:ligand ratio of 1:1 for a species containing a chelating N,O 2-iminofuran ligand. Conversely, a 1:2 ratio was found for complex **3**. The ^{1}H NMR of **1** and **2** reveal changes in the chemical shifts of C*H*=N, which were only slightly downfield shifted in relation to the free ligands by 0.1 ppm [43], whereas the C*H*=N of **3** is upfield shifted from 8.30 to 7.84 ppm after complexation to nickel. In all complexes, the iminic proton resonance was observed at 8.20 and 8.12 for complexes **1** and **2**, respectively, and 7.84 for complex **3**. The presence of the non-coordinated PF_6^- counter-ions in complexes **1-3** was also confirmed by the respective $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra.

Because of the harder nature of the O-atom of the ligands employed in this work, in relation to the S-atom of the previously reported thienylimine ligands [26], its affinity for nickel is higher and the bulkier N,O-ligand precursors **L1** and **L2** behave as bidentate towards the metal. However, the expected higher electron density at the N-atom in ligand precursor **L3** (which has a *para*-substituted methoxy donor group), the lower stereochemical protection of this ligand and a possibly weak/labile chelation of its furan moiety are likely sufficient to thermodynamically favour the coordination of two N-monodentate 2-(N-4-methoxyphenylformimino)furan (**L3**) ligands, leading to the formation of complex **3**. In summary, depending on their stereochemical and electronic natures, these ligands can coordinate with 1:1 or 1:2 metal to ligand ratios with or without oxygen-to-metal bonding [44].

In particular, the bidentate chelation mode of the ligands in complex **2** was unambiguously confirmed by single crystal X-ray diffraction. Crystals of complex **2** suitable for X-ray diffraction were grown from a CH_2Cl_2/*n*-hexane solution at -20 °C. The crystallographic data for complex **2** is presented in Table 1 (see Experimental Section). Complex **2** crystallised in the monoclinic system, within the C2/c space group. The molecular structure of complex **2** is depicted in Figure 1, selected bond lengths and angles being shown in Table 2.

Complex **2** reveals a structure consisting of a cationic nickel centre containing iminofuran, η^3-allyl moieties and an octahedral PF_6^- counter anion, without any direct interactions, as depicted from the large distance between the metal and the nearest fluorine atom (Ni···F3 = 4.431(7) Å). Although classic hydrogen bonds were not found, four non-classic hydrogen bonds can be observed, consistent with the distances C(6)–H(6)···F(3) of 2.48 Å [C(6)···F(3) 3.303(6) Å, C(6)–H(6)···F(3) 144º], C(13)–H(13)···N(1) of 2.39 Å [C(13)···N(1) 2.881(6) Å, C(13)–H(13)···N(1) 109º], C(16)–H(16)···N(1) of 2.40 Å [C(16)···N(1) 2.905(6) Å, C(16)–H(16)···N(1) 111º], and C(19)–H(19B)···F(5) of 2.51 Å [C(19)···F(5) 3.231(12) Å, C(19)–H(19B)···F(5) 130º]. The geometry around the cationic nickel centre in complex **2** can be described as square planar, when considering the plane formed by the atoms C19 and C21, the allyl group and the atoms O1 and N1 of the ligand. The relatively small N1-Ni-O bite

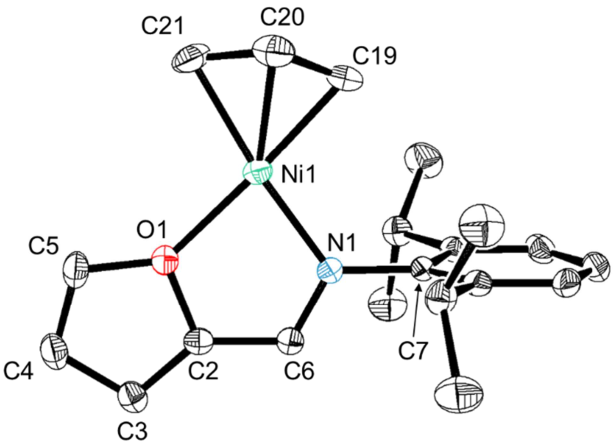


Figure 1. Molecular of the cation of complex **2**, determined by X-ray diffraction, showing 50% probability ellipsoids. Hydrogen atoms, the PF_6^- anion and a CH_2Cl_2 molecule were omitted for clarity.

angle in complex **2** of 88.22(13)º, is a result of chelating ligand steric constraints. The bond angles around the Ni atom sum *c.a.* 360°, being consistent with a square planar geometry. The metal chelation ring (formed by the atoms Ni1-N1-C6-C2-O1) in complex **2** is almost flat. The allyl carbons (C19, C20 and C21) give rise to an angle of 61.7(6)° with the plan of metal-chelate ring. The Ni-O bond length in complex **2** is equal to 1.982(3) Å, being longer than the Ni-N length, of 1.921(3) Å. This feature has been analogously reported [45,46], but still shorter than those reported for both nickel(II)furan [41] or nickel(II) iminopyridine [47-49] complexes. The Ni-C_{allyl} bond lengths in complex **2** lie between 1.963(5) and 2.013(5) Å and compare well with the Ni-C distances observed in other related Ni(II) η^3-allyl complexes [50,51].

The η^3-allyl, phenyl and furan planes give rise to angles of 61.7(6)°, 91.56(15)° and 1.52(14)° with the nickel coordination plane, respectively.

Table 2. Selected bond lengths (Å) and angles (º) of complex **2**.

Bond lengths	
Ni1-N1	1.921(3)
Ni1-O1	1.982(3)
Ni1-C19	1.963(5)
Ni1-C20	1.986(6)
Ni1-C21	2.013(5)
N1-C6	1.281(6)
N1-C7	1.447(5)
O1-C2	1.397(5)
O1-C5	1.373(5)
Bond angles	
N1-Ni1-O1	82.2(1)
N1-Ni1-C19	100.9(2)
N1-Ni1-C20	135.7(2)
N1-Ni1-C21	173.3(2)
O1-Ni1-C20	137.4(2)
O1-Ni1-C21	103.4(2)
C19-Ni1-C21	73.4(2)
Ni1-N1-C6	115.3(3)
C6-N1-C7	119.2(3)
Ni1-O1-C2	111.9(2)
Ni1-O1-C5	142.1(3)

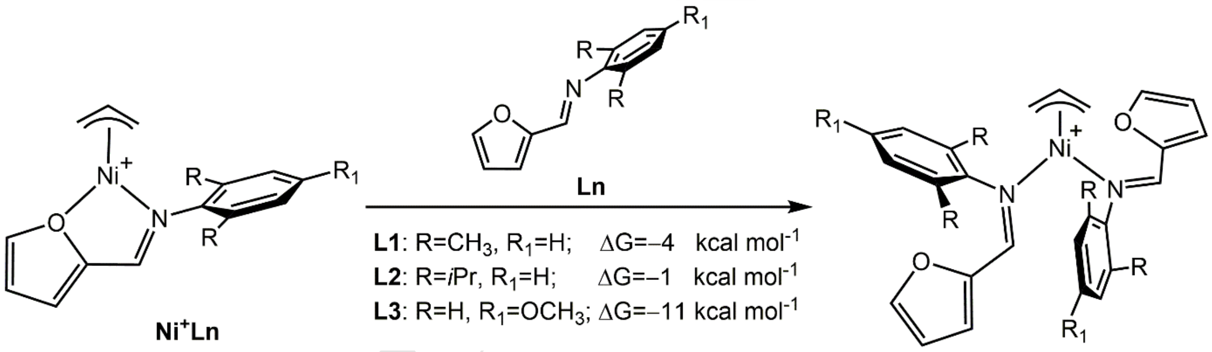
In order to rationalise the observations made related to the formation of the three complexes of this study, some DFT calculations were performed. To that effect, geometry optimisations on the cations of the mono chelated complexes of the type **Ni^+Ln**, on the cations of the bis chelated complexes of the type **Ni^+Ln_2**, and on the respective ligands, **Ln**, with n=1, 2 and 3, were carried out (see the atomic coordinates for the optimised species in the respective xyz files of the Supplementary Material). In the case of complex **2**, the one that was characterised in the solid state by single-crystal X-ray diffraction, it can be seen that its experimental and theoretical structures are similar (see Table S1 of the Supplementary Material).

We also utilised the frequencies calculations obtained for the cations of complexes **1**-**3**, using the same functional, in order to simulate their C=N stretching vibrations. The comparison of the experimental and calculated IR stretching vibrations is presented in Table

S2 of the Supplementary Material and, as can be observed, they are well comparable albeit theoretically overestimated, mainly owing to the overestimation of the respective force constants [52].

The consistency in the bond parameters of complex **2** in both the X-ray diffraction, as well as its DFT optimised structure indicates that the theoretical methods used are suitable for the present system. Therefore, we proceeded to a more detailed thermodynamic analysis of the system.

Subsequently, the free energy balances of the reactions of conversion of **Ni^+Ln** into **Ni^+Ln_2** were determined (Scheme 3). From these results it is possible to observe that, thermodynamically, the **Ni^+Ln_2** products are favoured in all of the considered structures, with the reaction involving ligands **L1** and **L2** virtually representing a chemical equilibrium (ΔG being equal to –4 and –1 kcal mol^{-1}, respectively). However, the reaction corresponding to the formation of complex **3**, which was, in fact, the isolated product, is clearly the most favoured one, reinforcing the rational made above concerning its formation.



Scheme 3. Energy balances (kcal mol^{-1}) determined by DFT calculations for the formation of bis(*N*-monodentate iminofuran) allyl nickel(II) complexes from the addition of an iminofuran ligand to mono(*N*,*O*-chelating iminofuran) allyl nickel(II) complexes.

4. Conclusions

We have described, in the present work, a convenient synthetic procedure for the preparation of new cationic allylnickel complexes supported by 2-(*N*-arylformimino)furan ligands with [PF_6^-] as the counter anion (**1**-**3**).

The chemistry of N,O ligands **L1**-**L3**, used in this work, has led to different coordination modes. In the three newly prepared η^3-allyl Ni(II) cationic complexes **1**-**3** it was observed that the 2-iminofuran derivatives displayed both bidentate and monodentate coordination modes, respectively, in complexes **1**-**2** and **3**.

DFT studies on all complexes indicated that the formation of the bis chelated monodentate complex **3** is clearly the most favoured outcome of all the reported synthetic procedures.

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6. Supplementary material

CCDC 1585090 contains the crystallographic data for the structural analysis of **2**. Copy of this information can be obtained free of charge via http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx or from the Cambridge Crystallographic Data Centre, 12 Union Road, CambridgeCB2 1EZ; United Kingdom; Fax: +44 (0)1223 336033.

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Highlights

- Synthesis of η^3-allyl Ni(II) cationic complexes containing N,O-donor ligands
- Characterisation by elemental analysis, IR and NMR
- Single crystal X-ray diffraction structure of one of the complexes has been determined