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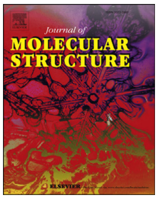

Cationic allylnickel(II) complexes bearing labile N,S-donor ligands: Synthesis, characterization and crystal structure

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The thienylimine ligands2,6-dimethyl-*N*-(thiophen-2-ylmethylene)aniline (**L1**), 2,6-diisoprop yl-*N*-(thiophen-2-ylmethylene)aniline (**L2**) and 4-methyl-*N*-(thiophen-2-ylmethylene)aniline (**L3**) were obtained by condensation reactions of 2-formyl thiophene with the corresponding anilines.

The reactions of bis(allyl)di-μ-bromodinickel with one or two equivalents of the ligands **L1**, **L2** and **L3**, in the presence of the thallium hexafluorophosphate $TlPF_6$, in dichloromethane, always afforded the corresponding complexes $[Ni(\eta^3\text{-allyl})L_2][PF_6]$ (L = **L1** (**1**), **L2** (**2**) or **L3**(**3**), containing two monodentate thienylimine ligands coordinated to Ni exclusively through the imine nitrogen atoms when the recrystallization was carried out in a non-coordinating solvent system such as dichloromethane/*n*-hexane. When complex **2** was recrystallized in dichloromethane/diethyl ether, one of the labile thienylimine ligands was substituted by a weekly coordinating diethyl ether solvent molecule giving rise to complex $[Ni(\eta^3\text{-allyl})(\mathbf{L2})(O(C_2H_5)_2)][PF_6]$ (**2′**). All new complexes **1** $[Ni(\eta^3\text{-allyl})$(2,6-dimethyl-*N*-(thiophen-2-ylmethylene)aniline$)_2][PF_6]$, **2** $[Ni(\eta^3\text{-allyl})$(2,6-diisopropyl-*N*-(thiophen-2-ylmethylene)aniline$)_2][PF_6]$, **3** $[Ni(\eta^3\text{-allyl})$(4-methyl-*N*-(thiophen-2-ylmethylene)aniline$)_2][PF_6]$, and **2’** $[Ni(\eta^3\text{-allyl})$(2,6-diisopropyl-*N*-(thiophen-2-ylmethylene)aniline$)(O(C_2H_5)_2)][PF_6]$ have been characterized by ^1H, ^{13}C,^{19}F,^{31}P NMR and FT-IR spectroscopies and by elemental analysis. The molecular structures in the solid state of complexes **2** and **2′** were determined by X-ray diffraction.

1. Introduction

The stabilization of a large number of metal complexes is easily achieved using bidentate ligands. Therefore, an increasing interest in the development of late transition metal complexes containing these type of ligands, especially those based on nitrogen, has been observed in the last two decades [1–3]. Those ligands are usually composed by Schiff bases and other neutral or monoanionic moieties, acting as good electron donors and displaying high versatility in their design, which facilitates the introduction of several kinds of steric and electronic features, as required for applications in the fields of biology, luminescence and catalysis [4–5,6,7,8,9,10]. Systems such as pyridine, pyrimidine, pyrazine, pyrrole, carbazole, furan and thiophene can be included in this class of neutral or monoanionic moieties [11–18]. However, although the nitrogen-containing heterocycles have been intensely studied, little attention has been paid to asymmetric heterocyclic derivatives containing sulfur [19–21].

To the best of our knowledge, only a limited number of imino-thiophene compounds have been reported in the literature [14,22–26], in particular, metal complexes containing these chelating ligands with hetero N,S donor atoms that are associated with interesting biological and catalytic studies [27–31]. Several bonding modes have been reported for imino-thiophene compounds, they acts as a monodentate N-donor in silver, palladium or platinum species [24,26,32–35], as cyclometallated [C,N] ligand [36–38] or as a bidentate [N,S] in copper chemistry [39]. Umani-Ronchi*et al.* reported the synthesis and structural characterization of $(\eta^3\text{-}C_3H_5)$\{(1R,2R)-*N*,*N*′-bis-[2,2’]bithiophenyl-5-

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ylmethylencyclo-hexanediamine}-palladium(II) tetrafluoroborate, [Pd(η^3-C_3H_5)(DIT2)][BF_4], revealing the presence of four conformers in the solid state [25]. The palladium center adopted a square planar geometry being coordinated by two nitrogen atoms of the DIT2 ligand and allylic carbons in the usual η^3 mode. Additionally, Kirchner et al. prepared a range of square-planar *trans*-dichloro palladium(II) complexes derived from 2-thiophenecarboxaldehyde as catalysts for the Suzuki cross-coupling of aryl bromides [26]. These complexes were found to be active as catalysts for Suzuki coupling reactions, being comparable to related α- and β-diimine systems. However, to the best of our knowledge, no reports on nickel systems containing this type of ligands were found in the literature.

We have been interested in the chemistry of cationic palladium and nickel complexes containing simultaneously α-diimine and methallyl ligands [40–43]. We reported the synthesis of new cationic allyl-palladium complexes bearing α-diimine ligands containing either DAD (DAD = *N,N′*-diaryl-1,4-diazabuta-1,3-diene) or BIAN (BIAN = *N,N′*-bis(aryl)acenaphthenequinonediimine) backbones from the oxidative addition of methylallyloxy-tris(dimethylamino)phosphonium hexafluorophophate to $Pd_2(dba)_3$ (tris(dibenzylideneacetone)-dipalladium), a zerovalent compound, in high yields [41], and we are able to extend this methodology to the preparation of analogous nickel(II) complexes [40]. More recently, we decided to apply this synthetic procedure to a related system, which consisted in the replacement of the previous DAD- or BIAN-ligands by a pyridinylimine moiety [42] or by a similar compound containing a *N,N*-donor bridging spacer [43]. The novel mono- and binuclear cationic methallyl palladium complexes were obtained in high yield, which attests the methodology's versatility.

These promising results prompted us to explore the possibility of replacing the pyridinyl ring by other heterocycles, such as the thiophene ring, and also to employ nickel as the metal center. In the present work, we report the synthesis and characterization of new cationic allylnickel(II) complexes bearing one and two monodentate thienylimine ligands. We also describe the molecular structures of two of such nickel(II) complexes as determined in the solid state by X-ray diffraction. In particular, these ligands allowed us to evaluate their weak coordination ability and easy displacement by weakly coordinating solvents such as diethyl ether.

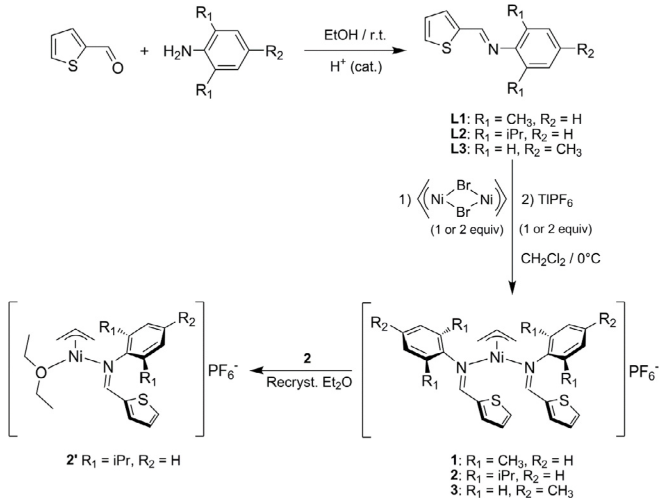
2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes employed in the syntheses of the ligands and their corresponding new cationic allylnickel(II) complexes is shown in Scheme 1.

The addition of a primary aromatic amine to the commercially available 2-thiophenecarboxaldehyde to afford the corresponding Schiff base ligand is a well-known route to N,S-donor ligands [44–47]. The reaction is an acid catalysed condensation, which can be conducted in alcohols. Variation of the amine therefore allows for the facile design of a family of ligands and subsequent metal complexes with different physical and chemical properties. The ligands were obtained as yellow crystalline solids, stable in air and soluble in the most common organic solvents.

Two routes have been attempted in the preparation of the corresponding cationic allylnickel(II) complexes:(a) oxidative addition of the allyloxytris(dimethylamino)phosphoni-um hexafluorophosphate salt ([$CH_2{=}CHCH_2{-}O{-}P(H)N(Me_2)_3$]$PF_6$) to the zerovalent $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) in the presence of thienylimine N,S-donor ligands [43]; and (b) metathetic halide exchange of bis[μ-bromo(η^3-allyl)nickel] with PF_6^- in the presence of thienylimine N,S-donor ligands (Scheme 1).



Scheme 1. Synthesis of new cationic allyl nickel complexes **1**–**3** and **2'**containing 2-(*N*-arylformimino)thiophene ligands.

The first route led to a complex mixture of unidentified products, all attempts to modify the reaction conditions (solvent, temperature, etc.) being unsuccessful. Route (b), where by a Ni starting material already containing a coordinated η^3-allyl ligand (bis[μ-bromo(η^3-allyl)nickel]) was employed, proved to be successful.

In fact, the new cationic η^3-allylnickel(II) complexes containing the potentially chelating thienylimine ligands **L1**-**L3** have been prepared by cleaving the dimeric structure of bis[μ-bromo(η^3-allyl) nickel] in the presence of the N,S-donor ligands, followed by the bromine abstraction via metathetical exchange with hexafluorophosphate by the addition of $TlPF_6$. Unfortunately, when less toxic salts like $NaPF_6$ and KPF_6 have been used, the reaction does not occur probably for insufficient solubility (Scheme 1).

However, in the attempts of using stoichiometric conditions of Ni and compounds **L1**-**L3**, using the non-coordinating CH_2Cl_2 as solvent and *n*-hexane as non-solvent in their double-layering recrystallization, these ligands were never able to coordinate in a bidentate fashion, rather acting in all cases as monodentate ligands towards nickel, coordinating exclusively through the imine nitrogen atom. This fact, Therefore, the major products obtained were complexes of the type $[Ni(\eta^3\text{-allyl})L_2]^+PF_6^-$ (L = **L1** (**1**), **L2** (**2**) or **L3** (**3**)), in which two of these monodentate ligands were present (Scheme 1). The reaction performed with 2 equivalents of **L1**-**L3** confirmed the same Ni compounds which were obtained in higher yields.

These new cationic allylnickel(II) complexes were isolated as red solids, soluble in dichloromethane, and reveal high sensitivity to air and moisture, rendering their analysis very difficult. All new complexes were characterized by elemental analysis(CHNS), FT-IR spectroscopy and, in two cases, by single crystal X-ray diffraction. The Schiff base ligands and their cationic allylnickel(II) complexes were analyzed by NMR.

The lability/poor thermodynamic stability of these complexes is exhibited when these compounds are recrystallized in CH_2Cl_2/diethyl ether. In the case of complex **2**, one of the thienylimine ligands is exchanged by the weakly coordinating Et_2O [48], giving rise to complex **2'** (Scheme 1), which was characterized by X-ray diffraction. This exchange reaction demonstrates well the weakness of the metal-ligand interaction.

In the IR spectral studies of ligands and metal complexes only the absorption frequencies related to groups involved in the complex formation, like azomethine υ(C=N), thiophene υ(C–S) and υ(M-N) are considered. The FT-IR spectra of the ligands presented a strong absorption band appeared at 1614 $cm^{-1}$for **L1**, 1621 cm^{-1} for **L2** and 1602 cm^{-1} for **L3**, typical of an imine functionality [49–52]. The relatively strong peak at 716 cm^{-1} has been assigned to the C–S stretching vibration [53–55]. From the IR spectra of both free ligands and complexes, it's clear that thienyl moiety is still intact and the formation of N,S-chelate ring, as expected, did not occur. For complexes **1**, **2** and **3**, The C–S stretching vibration bands still at about 720 cm^{-1}. However, coordination of the imine moiety to the nickel metal center is clear from the increase of υ(C=N) stretching frequencies after complexation [56–57] and the appearance of a peak at 596 cm^{-1} attribuated to stretching vibration υ(M-N). All IR spectra present the characteristic band of the PF_6^- counter-ion at around 830 cm^{-1} [58]. In addition, the presence of the non-coordinating PF_6^- counter-anion is evident from ^{31}P and ^{19}F NMR spectra.

The products formed in these reactions have low thermal stability in solution, at room temperature, and show broad signals in NMR spectra in CD_2Cl_2 that indicate a fluxional behavior. For example, the $^{13}C\{^1H\}$ resonances corresponding to the allylic CH_2 groups can be observed only at −20 °C at43.2 and 70.0 ppm and broaden to the baseline at room temperature. Although the thermal instability of the nickel complexes prevented us from observing the coalescence of these signals, this observation indicates a dynamic behavior of the η^3-allyl ligand [59].

The ^1H, ^{19}F and ^{31}P NMR spectra were obtained despite the instability of the complexes. Analysis of the cationic nickel complexes **2** and **3** by ^1H NMR reveals changes in chemical shifts compared to free ligands. For example, the sharp singlet and doublet signals from the *ortho*-isopropyl and *para*-methyl groups of the free ligands **L2** and **L3**, at 1.20 and 2.38 ppm, respectively, split into broad singlets in complexes **2** and **3**. The ^1H NMR spectra of complexes **1**–**3** show similar trends and present, in all cases, proton resonances assigned to the ligand –C*H*=N around 8.5–8.9 ppm, which were downfield shifted in relation to the free ligand (8.30 ppm) after complexation to nickel. The ^{19}F and ^{31}P NMR spectra are consistent with the cationic allylnickel(II) complexes formulation.

2.2. X-ray diffraction studies

Suitable prismatic orange single crystals of complex **2** were obtained by crystallization from CH_2Cl_2/*n*-hexane, at −20 °C. This complex crystallizes in the orthorhombic *Pbca* space group (Table 1). The corresponding ORTEP diagram is shown in Fig. 1 confirms the identity of complex **2**, its structure consisting of an organometallic cation and a $[PF_6^-]$ counter-anion.

Selected bond lengths and angles are listed in Table 2. The $[Ni(\eta^3\text{-}C_3H_5)(\mathbf{L2})_2]^+$ cation adopts the usual slightly distorted square planar arrangement, taking into account the imine nitrogen atoms N1 and N2 of each of the thienylimine ligands and the two terminal carbon atoms of the allyl group (C36 and C38), showing that the thiophene moieties are not coordinated to Ni [60].

Complex**2** reveals a structure consisting of a loosely associated $[\text{allyl Ni}(\mathbf{L2})_2]^+$ cation and octahedral PF_6^- counter-anion without direct interactions because of the large distance between the metal and the nearest fluorine atom (Ni···F1 = 4.922 Å). Another aspect of the relatively weak cation–anion attraction is the presence of C–H···F hydrogen bonding with ranging distances between 2.365 and 3.944 Å [61].

The nitrogen-nickel bonds of 1.992(3) Å and 1.958(3) Å are slightly longer than those reported in diamine nickel(II) systems [40,62] and a slightly shorter than iniminopyridine nickel complexes [63,64]. The imine C6–N1 and C23–N2 distances of 1.298(5) and 1.306(5) Å are in the range of reported carbon-nitrogen double bonds [65–67]. The allyl ligand is bonded asymmetrically to the nickel center with Ni–C(36) = 2.001(4) Å and Ni–C(38) = 2.027(4) Å. A relatively large N1–Ni–N2 angle of 101.4(1)° is observed likely because of steric repulsion between the two bulky thienylimine ligands. The bond angles around the Ni atom, which sum to 360.04°, are consistent with a planar geometry [68].

The coordination plane Ni–N1–C36–C38–N2 in **2** is almost flat as indicated by the torsion angles of −1.6(5)°, −1.1(7)° and −2.2(0)° for Ni–N1–C36–C38, Ni–N2–C38–C36 and C38–C36–N1–N2, respectively. The imines are *cis* to one another and the thiophene rings lie almost perpendicular. The plane of one of the thiophene rings C5–S1–C2 makes an angle of 70.39° with the nickel coordination plane, while the other thiophene plane C19–S2–C22 is almost coplanar with it.

In these syntheses, we avoided using the diethyl ether in order to try to coordinate the thiophene ring sulfur atom, by using a mixture of CH_2Cl_2/*n*-hexane. However, **L2** acted as a monodentate ligand and we obtained two imines coordinated to the nickel center of complex **2**, despite of the use of a stoichiometric amount (1:1) [33,69]. As referred above, recrystallization of **2** from CH_2Cl_2/Et_2O led to complex **2'**.

The ORTEP diagram of complex **2′** is shown in Fig. 2. Suitable prismatic orange single crystals of **2′** were obtained. The complex **2′** crystallized in the orthorhombic $P22_12_1$ space group (Table 1). The ORTEP diagram of the molecular structure of the cationic moiety of **2′** is shown in Fig. 2, and selected bond lengths and angles are listed in Table 2.

The molecular structure confirms the identity of **2′**, as a cationic allyl nickel complex containing the 2-iminothiophene ligand coordinating through the imine nitrogen atom to the Ni metal center in a monodentate fashion. The soft thiophene ring sulfur is not coordinated to the metal while the oxygen atom of the diethyl ether is coordinated to the Nickel during the recrystallization [70].

The structure of complex **2′** consists of a loosely associated $[Ni(\eta^3\text{-}C_3H_5)(\mathbf{L2})\{O(C_2H_5)_2\}]^+$ cation and an octahedral $[PF_6^-]$ counter-anion (Fig. 2). The **2′** cation adopts the usual slightly distorted square planar arrangement as appears from the bond angles of 98.3(3)°, 94.1(2)°, 94.9(3)° and 72.4(4)° for N–Ni–C19, N–Ni–O, C21–Ni–O and C21–Ni–C19 bond angles, respectively. The sum of the bond angles around nickel in **C2′** is 359.79° indicating a nearly perfect square planar coordination geometry [71].

The diethyl ether ligand lie plane and perpendicular (89.64°) to the O Ni N plane, while 59.97° is the angle between the allyl and O Ni N planes. The 2,6-disubstituted phenyl ring is also almost perpendicular to the chelating plane with an angle of 88.13°.

The allyl ligand appears much more symmetrically arranged than in **2**, with Ni–C(21) = 2.008(9) Å, Ni–C(19) = 1.984(9) Å and with a shorter Ni–C(20) of 1.94(1) Å [72].

The Ni–O bond length is 1.986(5) Å, which is longer than Ni–N bond length of 1.945(5) Å compares well with the bonds lengths of [O,N] nickel complexes [73].

Because the coordination of the sulfur heteroatom to the nickel center was not observed, two possible explanations for this behavior were considered. First, the coordination ability of diethyl ether is too great in comparison to the sulfur in thiophene. Rieb et al. studied the reaction of bis(imino)thiophene ligands with $FeCl_2$ and no coordination of thiophene has been observed in this case [74], confirming that sulfur atom is also a poor donor in these systems. Second, an aromatic behavior of the thiophene moieties may thermodynamically exclude the coordination to the nickel [75].

Table 1
Crystal data for the complexes **2**and **2'**.

	2	2′
Chemical formula	$C_{37}H_{47}N_2NiS_2F_6P$	$C_{24}H_{35}F_6NNiOPS$
Crystal size (mm^3)	0.2 × 0.15 × 0.08	0.15 × 0.1 × 0.08
Formula weight	787.56	589.27
Crystal system	Orthorhombic	Orthorombic
Space group	P b c a	$P\,22_12_1$
a (Å)	21.2383(9)	11.1750(16)
b (Å)	18.6520(8)	17.820(3)
c (Å)	18.9158(9)	13.821(2)
β (°)	90.000	90.00
V ($Å^3$)	7493.2(6)	2752.29
Z	8	4
T (K)	150(2)	150(2)
ρ_{calc}(g cm $^{-3}$)	1.396	1.422
Total reflections	7154	5248
Unique reflections	3732	3638
Parameters	450	324
Flack parameter	−0.116(9)	−0.02(2)
θ_{max} (°)	51.604	51.498
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.731	0.897
F(000)	3296	1228
Goodness-of-fit	0.909	0.904
Final R indices [I > 2sigma(I)]	$R_1 = 0.0559$, $wR_2 = 0.1343$	$R_1 = 0.0572$, $wR_2 = 0.1445$

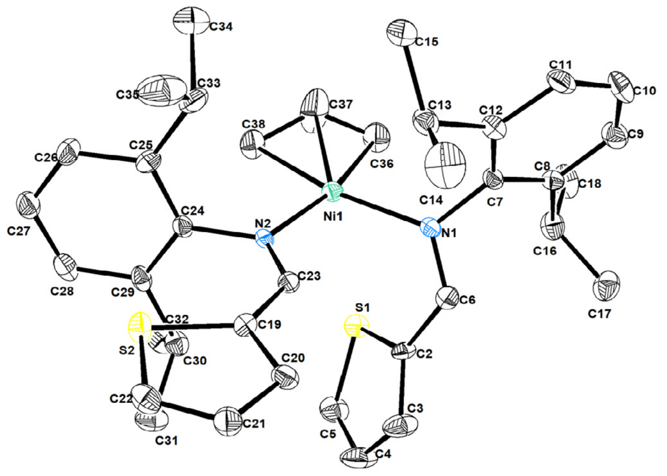


Fig. 1. ORTEP diagram of the X-ray molecular structure of the cationic allyl nickel moiety of complex **2**. Hydrogen atoms and the PF_6^- anion were omitted for clarity.

3. Experimental

3.1. Materials and methods

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 specialized companies (Air Liquide, etc.) 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 deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium for diethyl ether and *n*-hexane, and calcium hydride for dichloromethane. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannula.

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 Varian Unity 300 instrument and were referenced to the residual ^1H solvent resonances. 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).

3.2. Preparation of ligands

3.2.1. Synthesis of L1

The ligand was prepared by combined thiophene-2-carboxldehyde (5 g; 44.6 mmol), 2,6-dimethylaniline (5.4 g; 44.6 mmol) and 50 mL of ethanol in a 250 mL round flask and stirred at room temperature in presence of two drops of formic acid. After 4 h the yellow solution was dried under vaccum and then the residu was washed with cold isopropanol to afford 7.19 g of yellow cristals. Yield (75%).

Anal. Calc. for $C_{13}H_{13}NS$ (215.07): C, 72.52; H, 6.09; N, 6.51; S, 14.89. IR [ν(cm^{-1})]; 1614, 1591 (C=N). ^1H NMR (300 MHz, $CDCl_3$, 298 K, δ[ppm]): (2.185 (s, 6H, CH_3), 6.934–7.263 (m, $3H_{arom}$), 7.448–7.542 (m, 3H $_{thiophene}$), 8.73 (s, 1H, CH=N). RMN ^{13}C (75.5 MHz, $CDCl_3$, 298 K, δ[ppm]) 17.742, 123.332, 126.91, 127.12, 129.58, 131.156, 142.185, 150.063, 155.022.

3.2.2. Synthesis of L2

Ligand L2 was prepared in a similar manner to ligand L1. Thiophene-2-carboxldehyde (5 g; 44.6 mmol) added to 2,6-diisopropylaniline (7.9 g; 44.6 mmol) to afford 9.67 g of yellow solid (80%) yield.

Anal. Calc. for $C_{17}H_{21}NS$ (271.13): C, 75.23; H, 7.80; N, 5.16; S, 11.81. IR [ν(cm^{-1})]; 1621, (C=N). RMN ^1H (300 MHz, $CDCl_3$, 298 K, δ [ppm]): 1.20 (s, 12H, iPr-CH_3); 3.02 (sept, 2H, H_{iPr}); 7.14–7.17 (m, 2H, H_{arom}); 7.26–7.28 (m, 2H, $H_{thiophene}$) 7.45 (d, 1H H_{arom}); 7.55 (d, 1H $H_{thiophene}$); 8.92 (s, 1H, CH=N). RMN ^{13}C (75.5 MHz, $CDCl_3$, 298 K, δ [ppm]) 22.94; 27.52; 122.50; 123.76; 127.15; 129.65; 131.01; 137.41; 142.17; 148.13; 154.41.

3.2.3. Synthesis of L3

Ligand L3 was prepared in a similar manner to ligand L1.

Table 2
Selected bond distances (Å)and angles (°)for complexes [Ni(η^3-allyl)(**L2**)$_2$]$^+$PF$_6$ (**2**) and [Ni(η^3-allyl)(**L2**)(OEt$_2$)]$^+$PF$_6^-$ (**2′**).

2		2′	
Bond distances		*Bond distances*	
Ni–N1	1.958(3)	Ni–O1	1.986(5)
Ni–N2	1.992(3)	Ni–N1	1.945(5)
Ni–C36	2.001(4)	Ni–C21	2.007(9)
Ni–C37	1.957(5)	Ni–C20	1.936(10)
Ni–C38	2.027(4)	Ni–C19	1.984(8)
N1–C6	1.298(5)	S1–C2	1.730(8)
N1–C7	1.443(5)	S1–C5	1.691(8)
N2–C23	1.306(5)	O1–C24	1.463(9)
N2–C24	1.449(5)	O1–C23	1.445(9)
		N1–C7	1.457(9)
		N1–C6	1.290(9)
Bond angles		*Bond angles*	
N1–Ni–N2	101.38(13)	O1–Ni–N1	94.1(2)
N1–Ni–C36	90.79(17)	O1–Ni–C21	94.9(3)
N1–Ni–C37	125.9(2)	O1–Ni–C20	130.0(4)
N1–Ni–C38	163.17(16)	O1–Ni–C19	166.7(3)
N2–Ni–C36	167.79(17)	N1–Ni–C21	170.4(3)
N2–Ni–C37	129.7(2)	N1–Ni–C20	133.9(4)
N2–Ni–C38	95.38(16)	N1–Ni–C19	98.3(3)
C36–Ni–C37	38.5(2)	C21–Ni–C20	38.5(5)
C36–Ni–C38	72.49(19)	C21–Ni–C19	72.4(4)
C37–Ni–C38	39.1(2)	C20–Ni–C19	39.7(4)
Ni1–N–C6	121.9(3)	C2–S1–C5	91.5(4)
Ni1–N–C7	123.4(3)	Ni1–O1–C24	117.6(5)
C23–N2–C24	116.4(3)	Ni1–O1–C23	119.7(5)

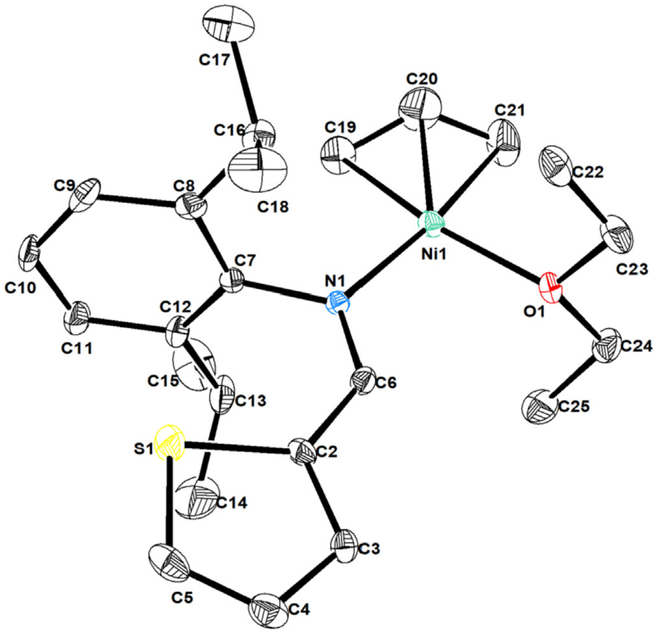


Fig. 2. ORTEP diagram of the X-ray molecular structure of cationic allyl nickel moiety of complex **2'**. Hydrogen atoms and the PF$_6^-$ anion were omitted for clarity.

Thiophene-2-carboxldehyde (5 g; 44.6 mmol) added to 4-methylaniline (4.77 g; 44.6 mmol) to afford 7.08 g of yellow solid (79%) yield.

Anal. Calc. for $C_{12}H_{11}NS$ (201.06): C, 71.60; H, 5.51; N, 6.96; S, 15.93. IR [ν(cm^{-1})]; 1602, (C═N). RMN ^{1}H (300 MHz, CDCl$_3$, 298 K, δ [ppm]): 2.38 (s, 3H, CH$_3$); 7.12 (dd, 1H, H$_{\text{thiophene}}$); 7.17–7.26 (m, 4H, H$_{\text{arom}}$); 7.48 (m, 2H, H$_{\text{thiophene}}$), 8.58 (s, 1H, CH═N). RMN ^{13}C (75,5 MHz, CDCl$_3$, 298 K, δ[ppm]) 20.52; 120.44; 127.47; 129.28; 129.57; 131.42; 135.43; 142.51; 148.33; 151.76.

3.3. Synthesis of cationic allylnickel(II) complexes

0.25 mmol of bis(allyl-μ-bromonickel), [Ni(η^3-CH$_2$CHCH$_2$)Br]$_2$, were added to 0.5 mmol of ligand (thiophene derivatives), at 0 °C, in 30 mL of anhydrous dichloromethane, under nitrogen, and then 0.5 mmol of TlPF$_6$ was added to the solution. After 1 h of stirring at room temperature, red solutions containing a white precipitate (TlBr) were obtained. The mixture was filtred to another Schlenk, using Celite® under nitrogen, and the resulting red solution evaporated to dryness. The resulting powder was washed with *n*-hexane (2 × 30 mL). The recrystallization of the complexes was made by making a double layer of a solution in dichloromethane and *n*-hexane (1:4), at −20 °C. After two days, orange crystals of the complex**2**were obtained (Scheme 1).

3.3.1. Synthesis of complex**1**

Bis(allyl-μ-bromonickel) (0.088 g, 0.25 mmol), the iminothiophene ligand **L1** (0.107 g, 0.5 mmol) and CH$_2$Cl$_2$ (20 mL) were combined in a Schlenk tube at 0 °C, followed by the addition of TlPF$_6$ (0.174 g, 0.5 mmol), and the mixture was stirred at room temperature. After 60 min, the dichloromethane solution was filtered through a filter cannula containing Celite®to another Schlenk tube and the solvent removed under vacuum. The orange-red residue was washed with *n*-hexane (3 × 20 mL). Yield: 76 mg (45%).

Anal. Calc. for $(C_{29}H_{31}F_6N_2NiPS_2)_2(CH_2Cl_2)_{1/2}C_6H_{14}$ (M = 888.31): C, 45.97; H, 4.76; N, 3.15; S, 7.22. Found: C, 45.55; H, 4.81; N, 3.08; S, 7.12.

IR [υ(cm^{-1})]: 1623, 1600 (C═N); 836 (PF$_6^-$).^{1}H NMR (CD$_2$Cl$_2$): δ 2.28 (broad s, 6H, CH$_3$), δ 2.46 (broad s, 6H, CH$_3$), 2.9 (broad s, 1H, CH$_{2\text{allyl}}$), 3.16 (broad s, 1, CH$_{2\text{allyl}}$), 5.86 (broad m, H, CH$_{\text{allyl}}$), 7.07 (broad m, 12H, H$_{\text{Ar+thiophene}}$), 8.55 (broad s, H, N═C*H*), 8.96 (broad s, H, N═C*H*), 2 H allyl resonances missing. ^{19}F NMR (CD$_2$Cl$_2$): δ −72.26 (d, PF$_6$)·^{31}P NMR (CD$_2$Cl$_2$): δ −144.654 (Sept, PF$_6^-$).

3.3.2. *Synthesis of complex **2***

The analogous complex **2** was prepared from bis(allyl-μ-bromonickel) (0.088 g, 0.25 mmol), ligand **L2** (0.13 g, 0.5 mmol) and $TlPF_6$ salt (0.174 g, 0.5 mmol) following the method described above. Single crystals suitable for X-ray analysis were obtained by the recrystallization of **2** in dichloromethane double-layered with n-hexane. Yield: 95 mg (48%).

Complex **2**′ was obtained by the recrystallization of **2** in dichloromethane double-layered with diethyl ether. Single crystals suitable for X-ray analysis were obtained. Yield: 126 mg (42%).

*Complex **2***:Anal. Calc. $C_{37}H_{47}F_6N_2NiPS_2$ (M = 787.57):C, 56.42; H, 6.01; N, 3.55; S, 8.14. Found: C, 57.06; H, 5.81; N, 3.18; S, 7.92. IR [υ(cm^{-1})]: 1625 (C=N); 839 (PF_6^-).^{1}H NMR (CD_2Cl_2): δ 1.15 (d, 24H, CH_3–iPr), 2.22 (broad, 2H, CH–iPr), 2.79 (broad, 4H, $CH_{2\ allyl}$), 5.68 (broad q, 1H, CH_{allyl}), 7.14–7.93 (m, 12H, $H_{Ar+thiophene}$), 8.26 (broad, 2H, N=C*H*)· ^{19}F NMR (CD_2Cl_2): δ −71.94 (d, PF_6^-). ^{31}P NMR (CD_2Cl_2): δ −143.54 (sept, PF_6^-).

*Complex **2’***: Anal. Calc. $C_{24}H_{36}F_6NNiOPS$ (M = 589.15): C, 48.83; H, 6.15; N, 2.37; Ni, 9.94; S, 5.43. Found: C, 48.30; H, 5.93; N, 2.14; S, 5.14. IR [υ(cm^{-1})]: 1627 (C=N); 837 (PF_6^-). ^{1}H NMR (CD_2Cl_2): δ 1.19 (6 H, CH_3–ether), 1.39 (12 H, CH_3–iPr), 2.91 (broad d, 2H, CH_{2allyl}), 3.084 (broad, 2H, CH–iPr), 3.26 (broad, $CH_{2\ allyl}$), 3.57 (broad, 2H, CH_2-ether), 5.93 (broad q, 1H, CH_{allyl}), 7.11–7.86 (m, 12H, $H_{Ar+thiophene}$), 8.48 (broad, 1H, N=C*H*), ^{19}F NMR (CD_2Cl_2): δ −72.54 (d, PF_6^-).^{31}P NMR (CD_2Cl_2): δ-149.37 (sept, PF_6^-).

3.3.3. *Synthesis of complex **3***

The analogous complex **3** was prepared from bis(allyl-μ-bromonickel) (0.088 g, 0.25 mmol), ligand **L3** (0.1 g, 0.5 mmol) and $TlPF_6$ salt (0.174 g, 0.5 mmol) following the method described above. Yield: 66 mg (41%).

Anal. Calc. for $C_{27}H_{27}F_6N_2NiPS_2 \cdot CH_2Cl_2$ (M = 732.24): C, 45.93; H, 3.99; N, 3.83; S, 8.76. Found: C, 46.63; H, 4.05; N, 3.74; S, 8.26.

IR [υ(cm^{-1})]: 1610 (C=N); 837 (PF_6^-). ^{1}H NMR (CD_2Cl_2): δ 3.78 (s, 6H, CH_3), 3.52 (broad, 2H, CH_{2allyl}), 2.73 (broad, 2H, CH_{2allyl}), 6.11 (q, 1H, CH_{allyl}), 6.67–7.11 (m, 8H, H_{Ar}), 7.84 (s, 2H, N=C*H*), ^{19}F NMR (CD_2Cl_2): δ −72.31 (d, PF_6^-).^{31}P NMR (CD_2Cl_2): δ −144.42 (sept, PF_6^-).

3.4. *Crystal structure determination and refinement*

Crystals of air- and moisture-sensitive compounds were selected under an inert atmosphere, covered with polyfluoroether oil, and mounted on a nylon loop. Data were collected using a Bruker SMART CCD diffractometer at 150 K. Crystallographic data for compounds **2** and **2**′ were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXSKAPPA 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 [76]. For all the complexes, structure solution and refinement were performed using direct methods with the programs SHELXTL v6.12 [77], SIR2004 [78], and SIR2011 [79] included in the package of programs WINGX-Version 2014.1 [80] and SHELXL [80]. All hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atoms.

4. Conclusion

The reaction of bis(allyl)di-μ-bromodinickel with thienylimine ligands **L1**–**L3** followed by metathetical exchange of bromine with hexafluorophosphate gives novel monometallic cationic allyl nickel(II) complexes **1**–**3** in which the ligands coordinate only via the imine nitrogen atoms. The thiophene moiety sulfur atom is too soft to coordinate nickel and the thienylimine ligand can be easily moved by a weak coordinate solvent such diethyl ether during recrystallization to afford the complex **2’**. The coordination geometry around the Ni(II) center in both cationic complexes **2** and **2**′ is slightly distorted square planar with an angle N1–Ni–N2 of **2** greater than N–Ni–O of **2**′ due to steric repulsion between the two bulky thienylimine ligands.

Supplementary material

CCDC 1585088 and CCDC 1585089 contain the crystallographic data for the structural analysis of C**2** and C**2’**. Copies 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 Center, 12 Union Road, CambridgeCB2 1EZ; United Kingdom; Fax: +44 (0)1223 336033.

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References

[1] L. Guo, W. Liu, C. Chen, Mater. Chem. Front 1 (2017) 2487–2494.

[2] B.P. Carrow, K. Nozaki, Macromolecules 47 (8) (2014) 2541–2555.

[3] A. Togni, L.M. Venanzi, Angew. Chem. Int. Ed. 33 (5) (1994) 497–526.

[4] H. Yu, W. Zhang, Q. Yu, F.-P. Huang, H.-D. Bian, H. Liang, Molecules 22 (2017) 1772.

[5] W.H. Sun, L.L. Wu, L. Ye, Y. Xin, Y. Zhang, H. Liu, K.W. Lv, C.N. Shang, Z. You, W. Li, Inorg. Nano-Met. Chem. 47 (10) (2017) 1385–1391.

[6] K. Mashima, H. Tsurugi, J. Organomet. Chem. 690 (2005) 4414–4423.

[7] S.C. Marker, S.N. MacMillan, W.R. Zipfel, Z. Li, P.C. Ford, J.J. Wilson, Inorg. Chem. 57 (3) (2018) 1311–1331.

[8] J.A. Zuleta, M.S. Burberry, R. Eisenberg, Coord. Chem. Rev. 97 (1990) 47–64.

[9] L. Li, P.S. Lopes, C.A. Figueira, C.S.B. Gomes, M.T. Duarte, V. Rosa, C. Fliedel, T. Avilés, P.T. Gomes, Eur. J. Inorg. Chem. (2013) 1404–1417.

[10] C.S.B. Gomes, A.F.G. Ribeiro, A.C. Fernandes, A. Bento, M.R. Ribeiro, G. Kociok-Köhn, S.I. Pascu, M.T. Duarte, P.T. Gomes, Catal. Sci. Technol. 7 (2017) 3128–3142.

[11] K. Tenza, M.J. Hanton, A.M.Z. Slawin, Organometallics 28 (16) (2009) 4852–4867.

[12] J.L.S. Milani, A.C.A. Casagrande, P.R. Livotto, O.L. Casagrande Jr., Appl. Catal. Gen. 523 (2016) 247–254.

[13] B.-Y. Su, J.-X. Wang, X. Liu, Q.-D. Li, Acta Crystallogr. C69 (2013) 1073.

[14] Y. Jiang, Y. Guo, X. Zhu, D. Song, Y. Wang, X. Song, F. Verpoort, X. Chang, Inorg. Chim. Acta. 376 (2011) 144–151.

[15] (a) R.M. Bellabarba, P.T. Gomes, S.I. Pascu, Dalton Trans. 23 (2003) 4431–4436;
(b) D. Suresh, C.S.B. Gomes, P.S. Lopes, C.A. Figueira, B. Ferreira, P.T. Gomes, R.E. Di Paolo, A.L. Maçanita, M.T. Duarte, A. Charas, J. Morgado, D. Vila-Viçosa, M.J. Calhorda, Chem. Eur J. 21 (2015) 9133–9149.

[16] L. Beaufort, F. Benvenuti, A.F. Noels, J. Mol. Catal. Chem. 260 (1–2) (2006) 215–220.

[17] E.M. Cheprakova, E.V. Verbitskiy, M.A. Kiskin, G.G. Aleksandrov, P.A. Slepukhin, A.A. Sidorov, D.V. Starichenko, Y.N. Shvachko, I.L. Eremenko, G.L. Rusinov, V.N. Charushin, Polyhedron 100 (2015) 89–99.

[18] A.M. Hollas, W. Gu, N. Bhuvanesh, O.V. Ozerov, Inorg. Chem. 50 (2011) 3673–3679.

[19] F.M. Elantabli, M.P. Radebe, W.M. Motswainyana, B.O. Owaga, S.M. El-Medani, E. Ekengard, M. Haukka, E. Nordlander, M.O. Onani, J. Organomet. Chem. 843 (2017) 40–47.

[20] Z. Yin, H. Qian, Q. Wang, H. Dong, S. Yan, C. Zhang, J. Li, Aust. J. Chem. 66 (2013) 218–226.

[21] F.J. Barros-Garcıa, A. Bernalte-Garcıa, A.M. Lozano-Vila, F. Luna-Giles, E. Vinuelas-Zahınos, Polyhedron 24 (2005) 129–136.

[22] L. Cuesta, D. Prat, T. Soler, R. Navarro, E.P. Urriolabeitia, Inorg. Chem. 50 (17) (2011) 8598–8607.

[23] D. Yuan, H.V. Huynh, Molecules 17 (3) (2012) 2491–2517.

[24] J.F. Modder, J.M. Ernsting, K. Vrieze, M. De Wit, C.H. Stam, G. Van Koten, Inorg. Chem. 30 (1991) 1208–1214.

[25] V.G. Albano, M. Bandini, M. Monari, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, Inorg. Chim. Acta. 360 (2007) 1000–1008.

[26] J. Wiedermann, K. Mereiter, K. Kirchner, J. Molec. Catal. A Chem. 257 (2006) 67–72.

[27] P. Sengupta, R. Dinda, S. Ghosh, W.S. Sheldrick, Polyhedron 22 (3) (2003)

447−453.
[28] H.V. Huynh, Y.X. Chew, Inorg. Chim. Acta. 363 (2010) 1979−1983.
[29] B. Machura, R. Kruszynski, J. Kusz, Polyhedron 26 (2007) 2543−2549.
[30] S.O. Ojwach, M.G. Tshivhase, I.A. Guzei, J. Darkwa, S.F. Mapolie, Can. J. Chem. 83 (2005) 843−853.
[31] S.A. da Silva, C.Q.F. Leite, F.R. Pavan, N. Masciocchi, A. Cuin, Polyhedron 79 (2014) 170−177.
[32] E.C. Constable, L.R. Sousa, J. Organomet. Chem. 427 (1992) 125.
[33] W.S. Hwang, J.H. Lai, D.L. Wang, M.Y. Chiang, J. Chin. Chem. Soc. 46 (4) (1999) 529−533.
[34] B. Machura, R. Kruszynski, J. Kusz, Polyhedron 26 (2007) 2543−2549.
[35] M. Barwiolek, M. Babinska, A. Kozakiewicz, A. Wojtczak, A. Kaczmarek-Kedziera, E. Szlyk, Polyhedron 124 (2017) 12.
[36] C. Anderson, M. Crespo, M. Font-Bardia, A. Klein, X. Solans, J. Organomet. Chem. 601 (2000) 22.
[37] M. Maestri, D. Sandrini, V. Balzani, A. von Zelewsky, P. Jolliet, Helv. Chim. Acta 71 (1988) 135.
[38] D. Wang, D. Cui, W. Miao, S. Lia, B. Huanga, Dalton Trans. (2007) 4576.
[39] A.B. Gündüzalp, İ. Özsen, H. Alyar, S. Alyar, N. Özbek, J. Mol. Struct. 1120 (2016) 259.
[40] A. Mechria, C. Bavoux, F. Bouachir, J. Organomet. Chem. 677 (2003) 53−56.
[41] A. Mechria, M. Rzaigui, F. Bouachir, Tetrahedron Lett. 41 (2000) 7199−7202.
[42] S. Dridi, A. Mechria, M. Msaddek, J. Organomet. Chem. 772−773 (2014) 217−221.
[43] S. Dridi, A. Mechria, P. Sgarbossa, R. Bertani, M. Msaddek, J. Organomet. Chem. 819 (2016) 255−259.
[44] A.M. Abu-Dief, I.M.A. Mohamed, Beni-Suef Univ. J. Basic Appl. Sci. 4 (2) (2015) 119−133.
[45] O. Sebastian, A. Thapa, J. Chem. Pharmaceut. Res. 7 (10) (2015) 953−963.
[46] R.C. Maurya, B.A. Malik, J.M. Mir, P.K. Vishwakarma, D.K. Rajak, N. Jain, J. Coord. Chem. 68 (16) (2015) 2902−2922.
[47] A.B. Powell, J.R. Brown, K.V. Vasudevan, A.H. Cowley, Dalton Trans. (2009) 2521−2527.
[48] Y. Sarazin, D.L. Hughes, N. Kaltsoyannis, J.A. Wright, M. Bochmann, J. Am. Chem. Soc. 129 (2007) 881−894.
[49] W. Zhang, W.-H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Cheng, P. Hao, J. Organomet. Chem. 691 (2006) 4759.
[50] G. Smith, R. Chen, S. Mapolie, J. Organomet. Chem. 673 (2003) 111.
[51] P. Singh, S. Das, R. Dhakarey, J. Chem. 6 (2009) 99.
[52] Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu, Y. Hu, J. Mol. Catal. Chem. 230 (2005) 1.
[53] J. Coates, Interpretation of Infrared Spectra of Organic Structures, John Wiley, New York, 2000.
[54] A.A. Dehghani-Firouzabadi, S. Firouzmandi, J. Braz. Chem. Soc. 28 (2017) 768−774.
[55] Y. Harinath, D. Harikishore, K. Reddy, B.N. Kumar, Ch Apparao, K. Seshaiah, Spectrochim. Acta Mol. Biomol. Spectrosc. 101 (2013) 264.
[56] A. Arrais, E. Diana, D. Marabello, G. Gervasio, P.L. Stanghellini, J. Organomet. Chem. 696 (2011) 2299.
[57] A. Arrais, E. Diana, G. Gervasio, R. Gobetto, D. Marabello, P.L. Stanghellini, Eur. J. Inorg. Chem. 7 (2004) 1505.
[58] A.M. Bünzli, H.J. Bolink, E.C. Constable, C.E. Housecroft, J.M.J. Hernández, M.E. Neubur Ortí, A. Pertegás, J.J. Serrano-Pérez, D. Torderab, J.A. Zampesea, Dalton Trans. 43 (2014) 738−750.
[59] J. Cámpora, L.O. de la Tabla, P. Palma, E. Álvarez, F. Lahoz, K. Mereiter, Organometallics 25 (14) (2006) 3314−3361.
[60] T.S. Lobana, P. Kumari, R. Sharma, A. Castineiras, R.J. Butcher, T. Akitsu, Y. Aritake, Dalton Trans. 40 (2011) 3219−3228.
[61] G. Elbaze, F. Dahan, M. Dartiguenave, Y. Dartiguenave, Inorg. Chim. Acta. 87 (1984) 91−97.
[62] K. Landolsi, M. Rzaigui, F. Bouachir, Tetrahedron Lett. 43 (51) (2002) 9463−9466.
[63] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112−124.
[64] G.J.P. Britovsek, S.P.D. Baugh, O. Hoarau, V.C. Gibson, D.F. Wass, A.J.P. White, D.J. Williams, Inorg. Chim. Acta. 345 (2003) 279−291.
[65] P. Pérez-Puente, E. de Jesús, J.C. Flores, P. Gómez-Sal, J. Organomet. Chem. 693 (2008) 3902−3906.
[66] J. Li, H. Song, C. Cui, Appl. Organomet. Chem. 24 (2010) 82−85.
[67] Y.D.M. Champouret, J.-D. Maréchal, R.K. Chaggar, J. Fawcett, K. Singh, F. Maseras, G.A. Solan, New J. Chem. 31 (2007) 75−85.
[68] M. Mikuriya, M. Hara, D. Yoshioka, Anal. Sci. X-Ray Struct. Anal. 33 (2017) 59−61. Online.
[69] W.S. Hwang, D.L. Wang, S.T. Hsu, L.K. Liu, J. Chin. Chem. Soc. 45 (2) (1998) 269−275.
[70] W.L. Green, E.R. Sirianni, G.P.A. Yap, C.G. Riordan, Acta Crystallogr. C 72 (2016) 791−796.
[71] J.A. Celaje, M.K. Pennington-Boggio, R.W. Flaig, M.G. Richmond, T.J. Williams, Organometallics 33 (8) (2014) 2019−2026.
[72] M.J. Tenorio, M.C. Puerta, I. Salcedo, P. Valerga, I. de losrios, K. Mereiter, Dalton Trans. 10 (2009) 1842−1852.
[73] S. Pandey, P.P. Das, A.K. Singh, R. Mukherjee, Dalton Trans. 40 (2011) 10758−10768.
[74] J. Rieb, R. Andreas, S. Haslinger, K. Manuel, P. Alexander, C. Mirza, J.M. Basset, F.E. Kuhn, Inorg. Chem. 53 (18) (2014) 9598−9606.
[75] R. Mishra, K.K. Jha, S. Kumar, I. Tomer, Der Pharma Chem. 3 (4) (2011) 38−54.
[76] G.M. Sheldrick, Acta Crystallogr. C 71 (1996) 3−8.
[77] (a) G.M. Sheldrick, Acta Crystallogr. C: Struct. Chem. 71 (2015) 3−8;
(b) C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 44 (2011) 1281−1284.
[78] SIR2004, M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381−388.
[79] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, J. Appl. Crystallogr. 45 (2012) 351−356.
[80] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849−854.