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# Synthesis and structure of new cationic methallyl molybdenum(II) complexes supported by $\alpha$ -diimine ligands

ABSTRACT

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#### 1. Introduction

Molybdenum(II) complexes of the type  $[Mo(\eta^3-C_3H_4)(CO)_2-(NCMe)_2X]$  (X = halide or pseudohalide) have been used extensively over several decades as synthetic precursors for a wide variety of Mo(II)-allyl derivatives containing the  $12e-[Mo(CO)_2-(\eta^3-allyl)]^+$  fragment which are formed by substitution of the labile nitrile ligands and/or the anion X [1]. It has been recently found that the pseudooctahedral  $[MoX(CO)_2(\eta^3-allyl)(N-N)]$  (N–N = 2,2'-bipyridine, bipy; 1,10-phenanthroline, phen) complexes react with organolithium or organomagnesium reagents and with sodium alkoxides to afford new alkyl [2], alkynyl [3] and alkoxo [4] complexes by selective halide substitution. The same reaction with NaCN has provided access to the complexes  $[Mo(CN)(\eta^3-allyl)(CO)_2(N-N)]$  [5].

The well known allyl complex  $[Mo(\eta^3-C_3H_4)(CO)_2(NCMe)_2X]$  has been shown as a useful precursor to prepare mononuclear derivatives, used both as catalysts for polymerisation of certain dienes [6] and in organic synthesis for allylic alkylations [7]. Their cationic anologues, having the two nitriles replaced by a L–L ligand, for instance, always show a fac arrangement of the  $\eta^3-C_3H_4$  and the two CO ligands and exhibit two isomers, B (equatorial) with  $C_s$  symmetry and A (axial) without symmetry (Scheme 1).

An increased interest in the chemistry of  $\alpha$ -diimine ligands and their complexes [8–12] was stimulated by the recent discovery by Brookhart and co-workers of Ni(II) and Pd(II)  $\alpha$ -olefin polymerization catalyst containing bulky  $\alpha$ -diimine ligands [13–16].

In the last few years, several new cationic allyl complexes of palladium and nickel with  $\alpha$ -diimine ligands have been synthesized by our group [17]. We wish therefore to report new cationic Mo(II) allyl complexes of general formula [Mo( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2)(CO)<sub>3</sub>(N-N)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> with N-N as an  $\alpha$ -diimine ligands. The solid state structure of the cation **4** (N-N = 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-N=C(Me)-C(Me)=N-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>) was determined at room temperature, allowing the observation of the allyl geometry in great detail.

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#### 2. Results and discussion

Cationic complexes  $[Mo(\eta^3-C_3H_4-Me-2)(N-N)(CO)_3]^+PF_6^-$ ,  $\{N-N = bipy (2); DAD (Ar-N=C(Me)-C(Me$ 

 $C(Me) = N-Ar: Ar = o-Me-C_6H_4$  (3), 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> (4); Ar-BIAN (Ar = o-Me-C<sub>6</sub>H<sub>4</sub> (5), Ar = iPr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> (6));

were synthesized by treating the compound Mo(CO)<sub>3</sub>(p-xylene) with the allyloxyphosphonium salt

in situ in presence of diimine ligand. Complex **4** was characterized by single crystal X-ray diffraction. The solid state structure of the complexes revealed a preference for the more unsymmetrical axial isomer.

Allyl complexes of the type  $[Mo(\eta^3-C_3H_4-Me-2)(CO)_3-(N-N)]^+PF_6^-$  (**2**-**6**) (N-N = bipy, Ar-BIAN [18], DAD [19]) can be obtained successfully in high yields by an oxidative addition of methallyloxyphosphonium [20] to the zerovalent compound Mo-(CO)<sub>3</sub>(p-xylene) in tetrahydrofuran to produce the axial isomer  $[Mo(\eta^3-C_3H_4-Me-2)(CO)_3(THF)_2]^+PF_6^-$  (**1**) whereas "equatorial" isomers are found for halide analogues [21]. The reaction in situ of compound **1** with the  $\alpha$ -diimine ligand in methylene chloride at room temperature offered the cationic  $\eta^3$ -methallyl molybdenum complexes (**2–6**) supported by the  $\alpha$ -diimine ligands (Scheme 2).

Compounds **2–6**, crystallized as red crystals for complex **2**, blue-purple for complexes **3–4** and green for complexes **5–6** from  $CH_2Cl_2/n$ -hexane, and are soluble in methylene chloride, chloroform and acetonitrile but only sparingly soluble in diethylether. They are stable at room temperature under an inert atmosphere; however, significant decomposition can be observed at high temperature. These compounds have been characterized by various techniques including <sup>1</sup>H, <sup>13</sup>C, IR spectroscopy and the single crystal X-ray structure determinations of the complex **4**.





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Scheme	1
Scheme	



The variation of the steric and electronic proprieties of  $\alpha$ -diimine ligands is possible by changing the aromatic substituent on the imine N atom. The new complexes exhibit spectroscopic data in accord with the proposed structures. The formation of the allyl complexes 2-6 is clear from the observed syn and anti allylic proton signals in the <sup>1</sup>H NMR. These signals were attributed considering that in allyl complexes, the syn protons resonate at higher frequencies than the anti protons [21,22]. Thus, the two resonances are located, respectively, at 1.07, 1.72 and 1.97, 0.92 and 1.43 ppm for H<sub>anti</sub> and 1.23, 2.98, 2.58, 2.19 and 3.22 ppm for H<sub>syn</sub> for complexes **2–6**. In <sup>13</sup>C NMR spectroscopy, the two terminal allylic carbons C1 and C3 appear at 61.6, 67.0, 69.0, 63.2 and 70.6 ppm, respectively, for complexes 2-6. The C=N functions are shifted to high frequency when compared to free ligands and appear at 172.1, 171.0, 176.0 and 168.6, for complexes **3-6**, respectively. Two carbonyl carbon signals are shown in the <sup>13</sup>C NMR spectra.

The IR spectra are also instructive. The complexes **2–6** show in IR spectroscopy a C=N stretching frequency in the region 1606–1690 cm<sup>-1</sup>, which is in agreement with those reported for other  $\alpha$ -diimine complexes coordinated as an s-cis conformation [18,23]. Moreover, complexes **2–6** exhibit the frequency of the corresponding counteranion. The  $\nu(PF_6^-)$  value is evident (843 cm<sup>-1</sup>). The IR data for **2–6** show two strong carbonyl bands of equal intensity, consistent with cis-carbonyl groups in the [Mo(CO)<sub>2</sub>( $\eta^3$ -allyl] moiety.

A single crystal X-ray diffraction study confirms the identity of complex **4**. The molecular structure of **4** with the adopted number-

**Fig. 1.** ORTEP diagram of **4**.Thermal ellipsoids are drawn at the 50% probability level.  $PF_6^-$  anion and hydrogen atoms have been omitted for the sake of clarity.

ing Scheme is shown in Fig. 1 with details of the structure determination, including unit-cell data, summarized in Table 1 and relevant bond distances and angles in Table 2. The coordination environment of the molybdenum center is pseudooctahedral with two carbon atoms from the carbonyl groups and the centroid of the allyl ligand determining a fac stereochemistry. The structure of complex **4** consists of loosely associated  $[(\eta^3-C_3H_4-Me-2)Mo(CO)_3(N-N)]^+$  cation and octahedral PF<sub>6</sub><sup>-</sup> counteranion without direct interactions as appears from the large distance between the metal and the nearest fluorine atom (Mo-F4 = 4.369 Å) which is close to other cationic allyl complexes [17].

In complex **4** structure, the allyl ligand adopts the usual endo conformation in the solid or in the solution state, with the open side eclipsing the two carbonyls C26O2 and C27O3. The two nitrogen donors from the (N-N) fragment occupy an equatorial and an axial coordination position (B in Scheme 2) which is in agreement with those reported for other diimine complexes [21,22].

In all complexes, the remaining equatorial position is taken by a carbonyl ligand. The  $\alpha$ -diimine ligand is coordinated in a symmetric fashion as seen in Fig. 1, with Mo–N bond lengths of 2.213(7) and 2.267(9) Å which are very close to those reported for other related complexes [21,22]. The N1–Mo–N2 angle of 70.8(3)° reflects a



Scheme 2.

Table 1

Summary of crystallographic data and X-ray experimental details for 4.

Empirical formula	C27H31F6MoN2O3P
Formula weight	672.45
Crystal system	monoclinic
Space group	P21/c
Ζ	4
a (Å)	9.459(3)
b (Å)	19.113(5)
c (Å)	16.234(7)
α (°)	90
β(°)	92.98(3)
γ (°)	90
V (Å <sup>3</sup> )	2931.0(17)
$ ho_{ m calc} ({ m g}{ m cm}^{-3})$	1.524
Crystal dimension (mm)	0.12  imes 0.19  imes 0.33
Temperature (K)	293(2)
Radiation, $\lambda$ (Å)	Mo, 0.71073
F(000)	1368
$2\theta$ range (°)	1.65–27.13
Limiting indices	$-12 \leqslant h \leqslant 12, \ -2 \leqslant k \leqslant 24, \ -20 \leqslant l \leqslant 2$
No. of scanned reflections	8879
No. of independent reflections	6422
No. of observed reflections	6422
No. of parameters varied	354
Absorption correction	empirical (DIFABS)
Data reductions programs	XCAD4
Programs used	shelx-97
$R_1(F_0), wR_2(F_0^2) (I > 2\sigma(I))$ (%)	8.80, 21.75
Goodness-of-fit on F <sup>2</sup>	0.960

#### Table 2

Bond lengths (Å) and angles (°) for 4.

Mo-N1	2.213(7)	Mo-N2	2.267(9)
Mo-C1	2.344(10)	Mo-C2	2.302(11)
Mo-C3	2.37(10)	N2-C6	1.289(11)
N1-C5	1.289(13)	N2-C13	1.468(11)
N1-C7	1.448(12)	Mo-C25	2.227(9)
Mo-C26	1.960(13)	Mo-C27	1.857(16)
N1-Mo-N2	70.8(13)		
N1-Mo-C1	147.1(4)	N2-Mo-C3	87.3(4)
N1-Mo-C3	152.2(4)	N2-Mo-C1	137.9(3)
N1-Mo-C2	165.6(4)	N2-Mo-C2	102.4(4)
C2-Mo-C3	34.0(5)	C1-Mo-C2	35.9(4)
C1-Mo-C3	60.1(4)		
C5-N1-C7	117.8(8)	C6-N2-C13	117.1(9)
C5-N1-Mo	119.9(6)	C6-N2-Mo	118.6(6)
C7-N1-Mo	122.2(6)	C13-N2-Mo	124.1(6)

slightly distorted pseudo-octahedral coordination sphere which is identical to known values in the literature for other molybdenum allyl complexes [21,22]. The metal chelate ring (Mo-N1-C5-C6-N2) in complex **4** is almost flat as indicated by the torsion angles of -2.7(16), 7.0(13) and -3.0(13)° for N1-C5-C6-N2, Mo-N2-C6-C5 and Mo-N1-C5-C6, respectively. The allyl ligand is bonded symmetrically to the molybdenum center (Mo-C1 = 2.344(10) Å and Mo–C3 = 2.369(10) Å). We note that the Mo–C(allyl) distances are reasonable for an allyl trans to a ligand of moderate trans influences. The methyl on the allyl group is in the same plane of the allyl ligand as indicated by the torsion angle of 178.1° for C4–C2–C3–C1. The geometric arrangement found for the studied complex can be easily characterized by  $\phi$ , which is the angle between the Mo– C25 with the line defined by the centroid of the allyl moiety and the molybdenum with Mo-C25. This  $\phi$  parameter gives the orientation of the allyl fragment relative to the monodentate ligand and determines unequivocally the position of the bidentate ligand in the metal coordination sphere. Thus, in complex 4, the  $\phi$  angle takes an approximate value of 90° and the chelating of the  $\alpha$ -diimine ligand occur via equatorial and axial sites.

The N1–C5, N2–C6 and C5–C6 bond distances of 1.289(13), 1.289(11) and 1.502(13)Å, respectively, confirm the conjugated

nature of this ligand [24]. The o,o'-dimethylphenyl groups make an angle of approximately 90° to the plane of the C=N bonds, due to the presence of the o-methyl substituents, as appears from the torsion angles of -82.5(13), 98.5(11), 100.2(12) and -80.4(13)for C6-N2-C13-C18, C6-N2-C13-C14, C5-N1-C7-C12 and C5-N1-C7-C8, respectively.

#### 3. Conclusion

π-Allyldicarbonyl complexes of molybdenum and tungsten formulated as [M(η<sup>3</sup>-allyl)X(CO)<sub>2</sub>L<sub>2</sub>] (M = Mo, W; X = halogen; L = 2-electron donating molecule) have been extensively explored [25], since [M(η<sup>3</sup>-allyl)(CO)<sub>2</sub>] fragment often plays a role of the key in the catalytic organic transformations [26]. From this point of view, much effort has been made on the synthesis and reaction of these compounds bearing various monodendate (2-electron donor) and bidentate (4-electron donor) ligands [27].The nitrile complexes [Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)X(CO)<sub>2</sub>(NCMe)<sub>2</sub>] (X = halide) have been shown to act as precursors in the ring-opening metathesis polymerization of norbornene [28] and polymerization of terminal acetylenes as well as catalyze the oligomerization of *n*Ph(CC)*n*Ph, (*n* = 1, 2) [29]. Following these results, we prepared and characterized new complexes of the type [Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>-Me-2)-(N-N)(CO)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (N-N = α-diimine).

The X-ray structure of the complexes studied showed the presence of the equatorial-axial isomer, B in Scheme 1.

The synthetic procedure for preparing **2–6** complexes offers great versatility for the generation of other  $\alpha$ -diimine allyl complexes of possible catalytic interest. The application of these compounds in catalytic reaction such as polymerisation of alkenes (ethylene, styrene, etc.), functional alkenes (methyl acrylate) and ring opening metathesis polymerisation of norbornene is currently under study.

#### 4. Experimental

#### 4.1. General

All manipulations were carried out under an atmosphere of dry argon using standard schlenk techniques. Diethyl ether was distilled from sodium benzopheneone; methylene chloride and hexane was distilled over  $P_2O_5$ . 2-Methylaniline, 2,6-diisopropylaniline were distilled from potassium hydroxide prior to use. Bipyridine (Bipy) and acenaphtenquinone were used as received from commercial sources. p-xylene was purified via column on alumna.  $\alpha$ -diimine ligands were prepared according to literature methods [18,19]. NMR spectra were recorded on a Bruker AMX 300 spectrometer. H and C chemical shifts were given in ppm and referenced to the residual solvent resonance relative to TMS; H<sub>syn</sub> and H<sub>anti</sub> designate the syn- and the anti-H atoms, respectively, of the allyl ligand. The atom labelling scheme for the allyl complexes was shown below.



4.2. General procedure for the preparation of  $[(\alpha - diimine)Mo(CO)_3 (\eta^3-C_3H_4-Me-2)]^+PF_6^-$  complexes

In an inert atmosphere,  $Mo(CO)_6$  compound (1 equiv.) was dissolved in small amount of p-xylene and refluxed for 2 h. Methallyloxyphosphonium  $[C_4H_7OP^+(NMe_2)_3PF_6^-]$  was added to the cold solution previously prepared in tetrahydrofuran. The yellow solution was stirred at room temperature for 24 h. The solvent was removed under vacuum to afford an oil compound which was dissolved in anhydrous  $CH_2Cl_2$  and a  $\alpha$ -diimine ligand was added. The solution was stirred at room temperature for 24 h. The supernatant was separated by filtration through a Celite filter, and the solvent was removed under vacuum to afford the oil complex. This was washed with n-hexane (3 × 15 ml) and dried in vacuum. The solid was crystallized from methylene chloride/ n-hexane solution at room temperature. Yields ranged from 83% to 94%.

#### 4.2.1. Synthesis of $[(Bipy)Mo(CO)_3(\eta^3-C_3H_4-Me-2)]^+PF_6^-(\mathbf{2})$

Following the general procedure, from  $Mo(CO)_6$  (0.080 g, 0.3 mmol), p-xylene (5 ml), THF (15 ml), 2-methylallyloxyphosphonium (0.1 g, 0.26 mmol) and Bipy. (0.049 mg, 0.31 mmol) was obtained 0.188 g of **2** as a red solid after crystallization from a mixture (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>: 9/1).

Yield 91%: IR [ $\nu$  cm<sup>-1</sup>] (KBr): 1606 (C=N); 1937, 1840 (CO); 848 (PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$  [ppm]): 1.02 (s, 3H, H<sub>4</sub>);

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 1.02 (s, 3H, H<sub>4</sub>); 1.05–1.07 (d, 2H, H<sub>anti</sub>,  $J_{HH}$  = 6 Hz), 1,23 (s, 2H, H<sub>syn</sub>); 7.50–8.80 (m, 8H, bipy).

 $^{13}\text{C}$  NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$  [ppm]): 19.7 (C<sub>4</sub>); 61.6 (C<sub>1,3</sub>), 81.9 (C<sub>2</sub>); 124.7, 126.9, 141.4, 151.3, 154.3 (bipy); 205, 208 (CO).

## 4.2.2. Synthesis of $[(o-CH_3-C_6H_4N=C(Me)-C(Me)=N-C_6H_4-o-CH_3) Mo(CO)_3 (\eta^3-C_3H_4-Me-2)]^+PF_6^- (3)$

Following the general procedure, from Mo(CO)<sub>6</sub> (0.080 g, 0.3 mmol), p-xylene (5 ml), THF (15 ml), 2-methylallyloxyphosphonium (0.1 g, 0.26 mmol) and (o- $CH_3$ - $C_6H_4$ N=C(Me)-C(Me)=N- $C_6H_4$ -o- $CH_3$ ) (0.079 mg, 0.3 mmol) was obtained 0.180 g of **3** as a blue-purple solid after crystallization from a mixture (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>: 8/2).

Yield 93%. IR [v cm<sup>-1</sup>] (KBr): 1608 (C=N); 1949, 1860 (CO); 846 (PF<sub>6</sub><sup>-</sup>).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 1.18 (s, 6H, o-CH<sub>3</sub>); 1.57 (s, 3H, H<sub>4</sub>); 1.72 (s, 2H, H<sub>anti</sub>); 2.14 (s, 3H, CH<sub>3</sub>-C=N); 2.31 (s, 3H, CH<sub>3</sub>-C=N); 2.98 (s, 2H, H<sub>syn</sub>); 7.01–7.38 (m, 8H, H<sub>ar</sub>).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 18.1 (o,o-CH<sub>3</sub>), 20.4 (o',o'-CH<sub>3</sub>); 21.5, 26.9 (CH<sub>3</sub>-C=N); 30.1 (C<sub>4</sub>); 67.0 (C<sub>1,3</sub>); 71.0 (C<sub>2</sub>); 104 (C<sub>ortho'</sub>); 121.1 (C<sub>para</sub>); 127.9 (C<sub>ortho</sub>); 128.1 (C<sub>meta'</sub>); 131.8 (C<sub>meta</sub>); 149.8 (C<sub>ipso</sub>); 172.1 (C=N); 204, 205 (CO).

### 4.2.3. Synthesis of $[(2,6-(CH_3)_2-C_6H_3N=C(Me)-C(Me)=N-C_6H_3-2,6-(CH_3)_2)Mo(CO)_3 (\eta^3-C_3H_4-Me-2)]^*PF_6^{-}(4)$

Following the general procedure, from Mo(CO)<sub>6</sub> (0.080 g, 0.3 mmol), p-xylene (5 ml), THF (15 ml), 2-methylallyloxyphosphonium (0.1 g, 0.26 mmol) and  $(2,6-(CH_3)_2-C_6H_3N=C(Me)-C(Me)=N-C_6H_3-2,6-(CH_3)_2)$  (0.087 mg, 0.3 mmol) was obtained 0.190 g of **4** as a blue-purple solid after crystallization from a mixture (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>: 8/2).

Yield 94%. IR [ $\nu$  cm<sup>-1</sup>] (KBr): 1622 (C=N); 1940, 1857 (CO); 843 (PF<sub>6</sub><sup>-</sup>).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 1.25 (s, 6H, o,o'-CH<sub>3</sub>); 1.73 (s, 3H, H<sub>4</sub>); 1.97 (s, 2H, H<sub>anti</sub>); 2.18 (s, 6H, o,o'-CH<sub>3</sub>); 2.24 (s, 6H, CH<sub>3</sub>-C=N); 2.58 (s, 2H, H<sub>syn</sub>); 7.00–7.26 (m, 6H, H<sub>ar</sub>).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 17.5 (0,0-CH<sub>3</sub>), 18.6 (0',0'-CH<sub>3</sub>); 20.2, 23.4 (CH<sub>3</sub>-C=N); 24.1 (C<sub>4</sub>); 69.0 (C<sub>1,3</sub>); 86.0 (C<sub>2</sub>);

127.2 (C<sub>orthovortho'</sub>); 128.7 (C<sub>para</sub>); 129.0 (C<sub>meta</sub>); 149.8 (C<sub>ipso</sub>); 171 (C=N); 200, 207 (CO).

#### 4.2.4. Synthesis of [(o-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-BIAN)Mo(CO)<sub>3</sub>

 $(\eta^{3}-C_{3}H_{4}-Me-2)]^{+}PF_{6}^{-}(5)$ 

Following the general procedure, from  $Mo(CO)_6$  (0.080 g, 0.3 mmol), p-xylene (5 ml), THF (15 ml), 2-methylallyloxyphosphonium (0.1 g, 0.26 mmol) and (*o*-*CH*<sub>3</sub>-*C*<sub>6</sub>*H*<sub>4</sub>-*BIAN*) (0.108 g, 0.3 mmol) was obtained 0.185 g of **5** as a green solid after crystallization from a mixture (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>: 8/2).

Yield 91%. IR [ $\nu$  cm<sup>-1</sup>] (KBr): 1638, 1690 (C=N); 1948, 1854 (CO); 840 (PF<sub>6</sub><sup>-</sup>).

<sup>1</sup>H NMR (300 MHz, MeOD, 25 °C, δ [ppm]): 0.92 (s, 2H, H<sub>anti</sub>); 1.29 (s, 3H, H<sub>4</sub>); 2.19 (s, 2H, H<sub>syn</sub>); 2.39(s, 3H, o,o'-CH<sub>3</sub>); 2.69 (s, 3H, o,o'-CH<sub>3</sub>); 7.15–7.29 (m, 14H, 8H<sub>ar</sub> + 6 H<sub>7,8,9</sub>).

<sup>13</sup>C NMR (75.5 MHz, MeOD, 25 °C, δ [ppm]): 14.2 (o,o'-CH<sub>3</sub>); 22.7 (C<sub>4</sub>); 63.2 (C<sub>1,3</sub>); 71.6 (C<sub>2</sub>); 113.1 (C<sub>ortho'</sub>); 123.6 (C<sub>7</sub>); 127.1 (C<sub>para</sub>); 127.2 (C<sub>ortho</sub>); 127.6 (C<sub>meta'</sub>); 128.9 (C<sub>8</sub>); 129.7(C<sub>9</sub>); 129.9 (C<sub>10</sub>); 130.3 (C<sub>meta</sub>); 131.5 (C<sub>6</sub>); 139.2 (C<sub>11</sub>); 148.1 (C<sub>ipso</sub>); 176 (C=N); 203, 205 (CO).

### 4.2.5. Synthesis of $[(2,6-(iPr)_2-C_6H_3-BIAN)Mo(CO)_3 (\eta^3-C_3H_4-Me-2)]^*PF_6^-(\mathbf{6})$

Following the general procedure, from  $Mo(CO)_6$  (0.080 g, 0.3 mmol), p-xylene (5 ml), THF (15 ml), 2-methylallyloxyphosphonium (0.1 g, 0.26 mmol) and (2,6-(*iPr*)<sub>2</sub>-*C*<sub>6</sub>H<sub>3</sub>-*BIAN*) (0.142 g, 0.3 mmol) was obtained 0.226 g of **6** as a green solid after crystallization from a mixture (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>:8/2).

Yield 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$  [ppm]): 0.77–0.79 (d, 12 H,  $J_{HH}$  = 6.6 Hz, CH<sub>3</sub>–iPr); 1.05–1.03 (d, 12H,  $J_{HH}$  = 6.9 Hz, CH<sub>3</sub>–iPr); 1.25 (s, 3H, H<sub>4</sub>); 1.43 (s, 2H, H<sub>anti</sub>); 2.81–2.86 (sept, 4H,  $J_{HH}$  = 6.6 Hz, CH–iPr); 3.22 (s, 2H, H<sub>syn</sub>); 6.43–6.45 (d, 2H,  $J_{HH}$  = 7.2 Hz, H<sub>7</sub>); 7.07–7.37 (m, 6H, H<sub>ar</sub>), 7.67–7.70 (d, 2H, H<sub>9</sub>, J = 8.1 Hz).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C, δ [ppm]): 14.1 (C<sub>4</sub>); 23.7, 24.3, 25.0, 25.3, 25.7, 26.5 (CH<sub>3</sub>-iPr); 28.0, 28.5, 29.4, 29.7 (CH-iPr); 70.6 (C<sub>1,3</sub>); 75.1 (C2); 125.0 (C<sub>7</sub>); 125.3 (C<sub>meta</sub>); 125.7 (C<sub>para</sub>); 127.5 (C<sub>8</sub>); 128.1(C<sub>9</sub>); 128.6 (C<sub>6</sub>); 130.3 (C<sub>10</sub>); 139.5 (C<sub>ortho</sub>); 141.0(C<sub>11</sub>); 147.7 (C<sub>ipso</sub>); 168.6 (C=N); 203, 205 (CO).

#### 4.3. X-ray crystallographic study

The X-ray crystallographic study of complex **4** is carried out on a MACH3 Enraf Nonius diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293 K. Accurate unit cell parameters and orientation matrix are determined from 25 reflections in the range 13–15°. Intensity data are collected by using the  $\omega$ –2 $\theta$ scan mode with a range of  $2 < \theta < 27^{\circ}$ . All the intensity data are corrected for Lorentz and polarization effects. The crystal structure solution carried out with direct methods from the SHELXS-97 permitted the location of all non-hydrogen atoms. After anisotropic leastsquares refinement, hydrogen atoms are placed at their geometrically calculated positions and refined riding on the corresponding atoms with isotropic thermal parameters. Final refinement based on the reflections  $[I > 2\sigma(I)]$  converged at  $R_1 = 0.0880$ ,  $wR_2 = 0.2175$  and GoF = 0.960. The experimental conditions of data collection, strategy followed for the structure determination, and final results are given in Table 1.

#### Appendix A. Supplementary data

CCDC 276931 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.050.

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