ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Organometallic Chemistry 677 (2003) 53–56

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Cationic methallylnickel(II) complexes with α-diimine ligands: synthesis and X-ray structure

Ali Mechria [a], Claude Bavoux [b], Faouzi Bouachir [a,*]

[a] *Laboratoire de Chimie de Coordination, Faculté des Sciences de Monastir, 5000 Monastir, Tunisia*

[b] *Université Claude Bernard Lyon 1, CNRS UMR 5078, Laboratoire de Crystallographie, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

Received 9 October 2002; received in revised form 8 April 2003; accepted 22 April 2003

Abstract

The α-diimine ligands Ar–N=C(R)C(R)=N–Ar react with Ni(COD)$_2$ (**2**) in the presence of methallyloxyphosphonium hexafluorophosphate $[CH_2{=}C(Me)CH_2{-}O{-}P(NMe_2)_3]^+\cdot PF_6^-$ (**3**) to give new cationic methallyl complexes of nickel(II) with α-diimine ligands **4a** and **4b**. The same complexes **4a**–**d** can also be generated in high yields by reacting [α-diimine] NiBr$_2$ with zinc and methallyloxyphosphonium salt **3**. Molecular structure of **4a** was determined by a single-crystal X-ray diffraction.

Keywords: Nickel; Chemical reduction; Cationic methallyl complexes; α-Diimine; Methallyloxyphosphonium salt

Cationic allylnickel complexes with non-chelating ligands are known to catalyze the oligomerisation of ethylene [1,2]. A few examples of cationic η^3-allylnickel compounds with chelating ligands have been reported [3]. However, the synthesis of cationic η^3-allylnickel(II) complexes with α-diimine ligands is almost unknown and their catalytic properties have not been reported.

In this note, we report the synthesis of new cationic η^3-methallylnickel(II) complexes with bulky aryl-substituted α-diimine ligands.

According to the literature, [4] cationic η^3-methallylnickel complexes with chelating ligands **1a** and **1b** have been prepared by the reaction of bis[μ-bromo(η^3-methallyl)nickel] (**1**) with these ligands followed by the bromo ligand abstraction via metathetical exchange with tetrafluoroborate by adding TlBF$_4$ (Scheme 1).

Recently, we have described the development of a new class of cationic methallylpalladium complexes with aryl-substituted α-diimines [5]. This method has been successfully applied in the case of Ni(II) complexes. In fact, the oxidative addition of methallyloxyphosphonium hexafluorophosphate **3** to the zerovalent compound Ni(COD)$_2$ [6] in the presence of bulky aryl-substituted α-diimine ligands led to an exclusive formation, in high yields, of cationic η^3-methallylnickel(II) complexes with bidentate nitrogen ligands $[(\eta^3\text{-}C_4H_7)Ni(N^\wedge N)]^+\cdot PF_6^-$ (Scheme 2).

One thing to be noticed is that the preparation of the Ni(COD)$_2$ complex involves significant synthetic effort and that it is an air-sensitive product. This reagent must, therefore, be stored and handled under strictly controlled conditions. In order to use more simple and stable reagents, we have investigated the possibility of in situ generation of low-coordinated Ni^0(α-diimine) species. A convenient method for the in situ generation of these complexes results from the chemical reduction of divalent nickel(II) complexes containing aryl-substituted α-diimine ligands with zinc. Indeed, the reduction of the (α-diimine) NiBr$_2$ [7–9] complexes with zinc in the presence of the salt **3** in dichloromethane generates the cationic η^3-methallylnickel complexes with α-diimine ligands $[(\eta^3\text{-}C_4H_7)Ni(N^\wedge N)]^+\cdot PF_6^-$ (Scheme 3):

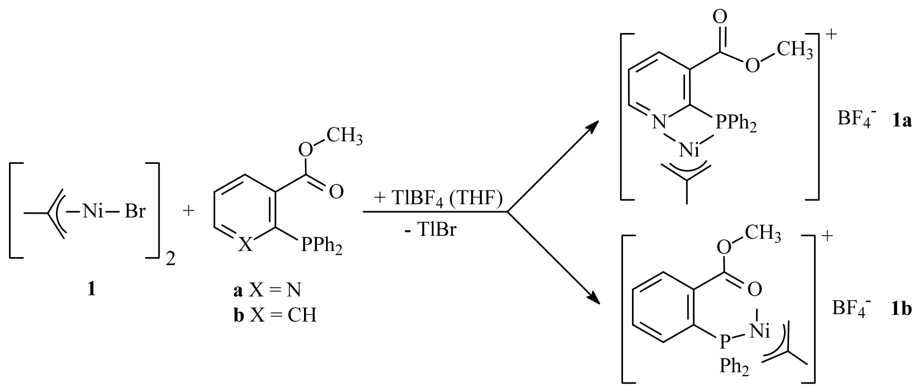
The new complexes exhibit spectroscopic data in accord with the proposed structures. The formation of the allyl complexes **4a**–**d** is clear from the observed *syn*- and *anti*-proton signals in the ^{1}H-NMR spectra. The complex **4a** presents equivalent signals of the *syn*- and *anti*-protons on one end of the allyl moiety as indicated

---

* Corresponding author. Fax: +216-73-500-278.

E-mail address: faouzi.bouachir@fsm.rnu.tn (F. Bouachir).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00345-0



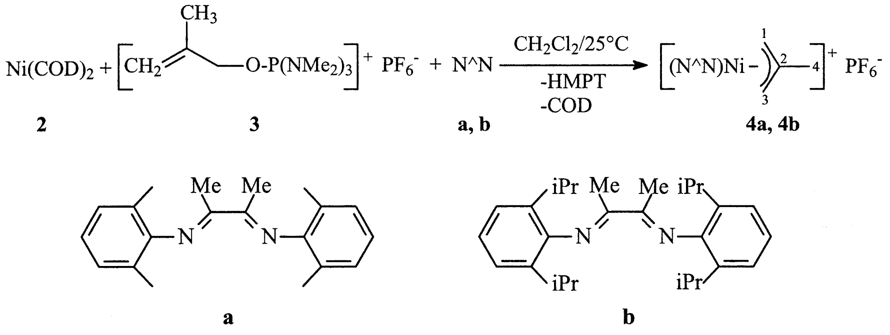
Scheme 1.

by analysis of the HMQC spectral data in which cross-peak was observed between δ_H 2.28 ($H_{syn,anti}$) and δ_C 61.9 ($C_{1,3}$). The ^{1}H-NMR spectra of complexes **4b** and **4c** are characterized by the *syn*- and *anti*-allylic protons; thus, the two resonances are at 2.34 ppm (H_{anti}); 2.45 ppm (H_{syn}) for **4b** and at 2.61 ppm (H_{anti}); 2.76 ppm (H_{syn}) for **4c**. In the ^{13}C-NMR spectra, the allylic carbons C_1 and C_3 appear at 61.9, 62.5, 61.8 and 60.9 for **4a**, **4b**, **4c** and **4d**, respectively. The C=N carbon appears at 178.7, 178.4, 173.5 ppm for **4a**, **4b**, **4c** and at 185.0, 185.3 for **4d**. The IR spectra are also instructive. The complexes **4a**–**d** show in IR spectroscopy a C=N stretching frequency in the region 1590–1690 cm^{-1}, which is in agreement with those reported for other α-diimine complexes coordinated as an s-*cis* conformation [9,10]. The $\nu(PF_6^-)$ value is evident (843 cm^{-1}).

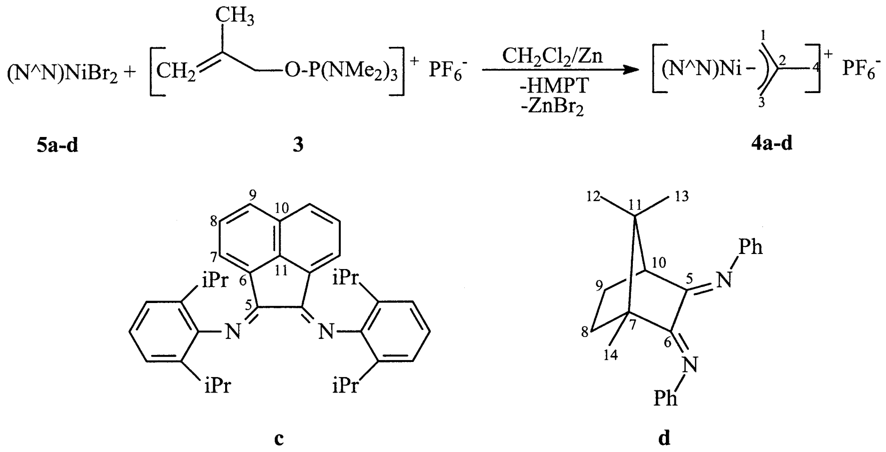
The single-crystal X-ray diffraction study of complex **4a** reveals a structure consisting of loosely associated $[(\eta^3\text{-}C_4H_7)Ni(N^\wedge N)]^+$ cations and octahedral PF_6^- counteranions without direct interactions as appears from the large distance between the metal and the nearest fluorine atom (Ni–F2 = 4.755(3) Å). The ORTEP diagram of **4a** is shown in Fig. 1. The ligand **a** was coordinated with an s-*cis* conformation as seen in Fig. 1, with Ni–N(sp^2) bond lengths of 1.922(7) and 1.923(7) Å which are very close to those reported for other nickel–imino–nitrogen bonds [11].

The N(1)–Ni–N(2) angle of 82.1(3)° reflects a slightly distorted square-planar coordination sphere. The metal-chelate ring (Ni–N1–C5–C6–N2) in complex **4a** is almost flat as indicated by the torsion angles of −2.9(3), 1.2(6) and 3.1(8)° for N(1)–C(5)–C(6)–N(2), Ni–N(2)–C(6)–C(5), and Ni–N(1)–C(5)–C(6), respectively. The methyl on the allyl group is slightly tilted out of the allyl plane by approximately 15° as indicated by the torsion angle of 165.4(8) for C(4)–C(2)–C(3)–C(1). The allyl plane makes an angle of 107.7(3)° with the nickel coordinative plane which is normal for η^3-2-methylallyl complexes of nickel [4]. 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 −87.8(6), 90.4(8), 92.3(7), and −91.1(4)° for C(5)–N(1)–C(9)–C(10), C(5)–N(1)–C(9)–C(14), C(6)–N(2)–C(17)–C(18) and C(6)–N(2)–C(17)–C(22), respectively.

In conclusion, a novel synthetic procedure for cationic methallylnickel(II) complexes with α-diimine ligands was described. This procedure offers the possibility to exchange the PF_6^- counteranion against more bulky and



Scheme 2.



Scheme 3.

very weakly coordinating anions. Our ongoing efforts in this way will be reported.

1. Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk tube techniques. Dichloromethane and diethylether were distilled under argon from P_2O_5 and sodium benzophenone ketyl, respectively, and stored under argon. The complexes $Ni(COD)_2$ [6] and (α-diimine) $NiBr_2$ [7–9] were synthesized following established procedures. NMR spectra were recorded on a Bruker AMX 300 spectrometer and infrared spectra on a BioRad FTS-6000 spectrophotometer.

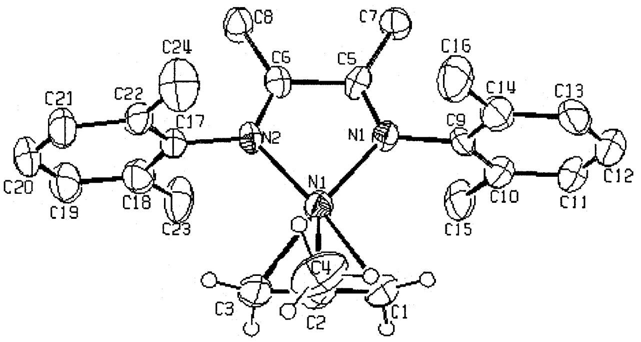


Fig. 1. ORTEP diagram of **4a**·CH_2Cl_2. Thermal ellipsoids are at 40% probability. Methylene chloride of crystallization and PF_6^- anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–N1 = 1.922(7), Ni–N2 = 1.923(7), Ni–C1 = 2.010(10), Ni–C2 = 1.977(10), Ni–C3 = 2.003(10), N1–C5 = 1.268(10), N1–C9 = 1.450(10), N2–C6 = 1.290(11), N2–C17 = 1.447(10), C1–C2 = 1.388(14), C2–C3 = 1.38(2); N1–Ni–N2 = 82.1(3), N1–Ni–C1 = 103.6(4), N2–Ni–C3 = 102.7(4), Ni–N1–C5 = 115.7(6), Ni–N2–C6 = 115.3(5).

*1.1. Preparation of **4a***

1.1.1. Method A

To 20 ml of CH_2Cl_2 solution of $Ni(COD)_2$ (140 mg, 0.5 mmol) was added 193 mg of salt **3** (0.5 mmol) and DAB **a** (150 mg, 0.5 mmol) at ambient temperature. After 24 h of stirring, the red solution was filtered through a celite filter and the residue was washed with CH_2Cl_2 (2 × 5 ml). The combined filtrates were evaporated to dryness and the product was washed with diethylether (3 × 10 ml) and dried in vacuo yielding 240 mg of **4a** as a red solid (87%).

1.1.2. Method B

To a mixture of [diacetyl-bis(2,6-dimethylphenylimine)]$NiBr_2$ (340 mg, 0.66 mmol) in dichloromethane (20 ml) was added 252 mg of salt **3** (0.66 mmol) and Zn powder (65 mg, 1 mmol). After 48 h of stirring at ambient temperature, the mixture was filtered through a celite filter to remove zinc bromide formed and the residue was washed with dichloromethane (2 × 5 ml). The combined filtrates were evaporated to dryness and the product was washed with diethyl ether (3 × 15 ml) to remove HMPT and dried in vacuo yielding 280 mg of **4a** as a red solid (78%).

Decomposition: 210 °C. IR [ν cm^{-1}] (KBr): 841 (PF_6^-); 1591; 1629 (C=N). ^1H-NMR (300 MHz, CD_2Cl_2): δ 2.03 (s, 3H, H_4); 2.06 (s, 6H, *o*-CH_3); 2.13 (s, 6H, *o*-CH_3); 2.28 (s, 4H, $H_{anti,syn}$); 2.31 (s, 6H, CH_3); 7.08–7.20 (m, 6H, H_{arom}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): δ 18.4, 18.5 (*o*-CH_3); 19.0 (CH_3); 24.2 (C_4); 61.9 ($C_{1,3}$); 127.8–135.7 ($C_{ar}+C_2$); 146.5 (C_{ipso}); 178.7 (C_{imin}). Anal. Calc. for **4a**·CH_2Cl_2($C_{24}H_{31}N_2NiPF_6$·CH_2Cl_2): C, 47.20; H, 5.22; N, 4.40%. Found: C, 46.82, H, 5.11; N, 4.45%.

1.2. Preparation of **4b**

The complex **4b** was obtained from Ni(COD)$_2$ (170 mg; 0.62 mmol), 250 mg of **b** (0.62 mmol) and 235 mg of salt **3** (0.62 mmol) in 88% yield by the same procedure (method A) as an orange–red solid.

1.2.1. Method B

The complex **4b** was synthesized in 79% yield following the procedure for **4a** (method B) from [diacetyl-bis(2,6-diisopropylphenylimine)]NiBr$_2$.

Decomposition: 203 °C. IR [ν cm^{-1}] (KBr): 844 (PF_6^-); 1590; 1625 (C=N). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.10 (d, $J_{HH} = 7.13$ Hz, 6H, CH$_3$–^{i}Pr); 1.23 (d, 6H, $J_{HH} = 7.43$Hz, CH$_3$–^{i}Pr); 1.32 (d, $J_{HH} = 6.98$ Hz, 12H, CH$_3$–^{i}Pr); 2.03 (s, 3H, H$_4$); 2.18 (s, 6H, CH$_3$); 2.34 (s, 2H, H^1_{anti}, H^3_{anti}); 2.45 (s, 2H, H^1_{syn}, H^3_{syn}); 2.90 (m, 2H, CH–^{i}Pr); 3.17 (m, 2H, CH–^{i}Pr); 7.26 (m, 6H, H$_{ar}$). ^{13}C-NMR (75.47 MHz): δ 20.5 (CH$_3$); 23.4 (C$_4$); 23.7, 24.2, 24.4 (CH$_3$–^{i}Pr); 29.9, 30.1 (CH–^{i}Pr); 62.5 (C$_{1,3}$); 125.2–137.4 (C$_{ar}$+C$_2$); 143.9 (C$_{ipso}$); 178.4 (C$_{i\text{-}min}$).

1.3. Preparation of **4c**

The complex **4c** was synthesized from [2,6-^{i}Pr$_2$C$_6$H$_3$-BIAN]NiBr$_2$ following the procedure for **4a** (method B), in 72% yield as an orange–red solid.

Decomposition: 237 °C. IR [ν cm^{-1}] (KBr): 844 (PF_6^-); 1600; 1635 (C=N). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 0.91 (d, $J_{HH} = 6.23$ Hz, 6H, CH$_3$–^{i}Pr); 1.05 (d, $J_{HH} = 6.47$ Hz, 6H, CH$_3$–^{i}Pr); 1.40 (d, $J_{HH} = 6.73$ Hz, 12H, CH$_3$–^{i}Pr); 2.19 (s, 3H, CH$_3$-allyl); 2.61 (s, 2H, H^1_{anti}, H^3_{anti}); 2.76 (s, 2H, H^1_{syn}, H^3_{syn}); 3.15 (m, 2H, CH–^{i}Pr); 3.43 (m, 2H, CH–^{i}Pr); 6.63 (d, $J_{HH} = 7.29$ Hz, 2H, H$_3$); 7.36 (m, 4H, H$_{10,12}$); 7.43 (m, 2H, H$_{11}$); 7.53 (pst, 2H, H$_4$); 8.23 (d, $J = 8.35$ Hz, 2H, H$_5$). ^{13}C-NMR (75.47 MHz): δ 23.3, 23.5 (CH$_3$–^{i}Pr); 24.1 (C$_4$); 24.4 (CH$_3$–^{i}Pr); 30.0 (CH–^{i}Pr); 61.8 (C$_{1,3}$); 124.4 (C$_7$); 125.2, 125.4 (C$_{m,m'}$); 126.2 (C$_p$); 129.6 (C$_8$); 129.9 (C$_6$); 132.1 (C$_9$); 134.3 (C$_{10}$); 135.6 (C$_{o,o'}$); 138.5 (C$_{11}$); 143.0 (C$_2$); 147.8 (C$_{12}$); 173.5 (C$_5$).

1.4. Preparation of **4d**

The complex **4d** was obtained from [Ph–BIC]NiBr$_2$ following the procedure for **4c**, in 83% yield as a red solid. Decomposition: 220 °C. IR [ν cm^{-1}] (KBr): 843 (PF_6^-); 1595; 1650; 1689 (C=N). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 0.59 (s, 3H, H$_{12}$); 0.95 (s, 3H, H$_{14}$); 1.05 (s, 3H, H$_{13}$); 1.74–2.12 (m, 4H, H$_{8,9}$); 2.19 (s, 3H, H$_4$); 2.55–2.70 (m, 5H, 2H$_{anti}$+2H$_{syn}$+H$_{10}$); 7.18 (d, $J_{HH} = 7.29$ Hz, 4H, H$_{o,o'}$); 7.40–7.51 (m, 6H, H$_{m,m',p}$). ^{13}C-NMR (75.47 MHz): δ 11.4, 17.5, 22.1 (C$_{12,13,14}$); 24.6 (C$_4$); 24.0, 33.1 (C$_{8,9}$); 50.8 (C$_7$); 51.4(C$_{10}$); 57.9 (C$_{11}$); 60.9 (C$_{1,3}$); 121.4, 122.3 (C$_{o,o'}$); 128.4, 129.0 (C$_p$); 130.0, 130.4 (C$_{m,m'}$); 133.5 (C$_{allyl}$); 147.4, 147.5 (C$_{ipso}$); 185.0, 185.3 (C$_{5,6}$). Anal. Calc. for **4d**·CH$_2$Cl$_2$(C$_{26}$H$_{31}$N$_2$NiPF$_6$·CH$_2$Cl$_2$): C, 49.12; H, 5.03; N, 4.24%. Found: C, 49.05, H, 5.44; N, 4.10%.

1.5. Crystallographic data for **4a**

$C_{24}H_{31}N_2PF_6Ni \cdot CH_2Cl_2$; f.w. = 636.12; monoclinic; $P2(1)$; $Z = 2$; $a = 10.952(2)$ Å; $b = 10.759(2)$ Å; $c = 13.191(3)$ Å; $\beta = 110.41(3)°$; $V = 1456.7(5)$ Å^3; $D_{calc} = 1.453$ g cm^{-3}; $R = 0.0703$; $R_w = 0.1730$; $-14 \le h \le 14$; $-13 \le k \le 12$; $-17 \le 1 \le 17$; Mo ($R_w = 0.7107$ Å); $T = 223$ (2) K.

Atomic coordinates and anisotropic temperature factors have been deposited at the Cambridge Crystallographic Data Center, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ (CCDC 176884).

References

[1] R.B.A. Pardy, I. Tkatchenko, J. Chem. Soc. Chem. Comm. (1981) 49.

[2] R. Ceder, G. Muller, J. Sales, J. Vidal, D. Neibecker, I. Tkatchenko, J. Mol. Catal. 68 (1991) 23.

[3] A. Ecke, W. Keim, F. Dahan, M.C. Bonnet, I. Tkatchenko, Organometallics 14 (1995) 5302.

[4] M.C. Bonnet, F. Dahan, A. Ecke, W. Keim, R.P. Schultz, I. Tkatchenko, J. Chem. Soc. Chem. Comm. (1994) 615.

[5] A. Mechria, M. Rzaigui, F. Bouachir, Tetrahedron Lett. 41 (2000) 7199.

[6] B. Bogdanovic, M. Kroner, G. Wilke, Annalen 1 (1966) 699.

[7] R. van Asselt, E. Rijnberg, C. Elsevier, J. Organometallics 13 (1994) 706.

[8] R. van Asselt, E.E.C.G. Gielens, R.E. Rülke, K. Vrieze, C.J. Elsevier, J. Am. Chem. Soc. 116 (1994) 977.

[9] R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, R. Benedix, Recl. Trav. Chim. Pays-Bas 113 (1994) 88.

[10] M. Svoboda, H. tom Dieck, J. Organomet. Chem. 191 (1980) 321.

[11] J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, Organometallics 16 (1997) 1514.