Pergamon

Tetrahedron Letters 43 (2002) 9463–9466

TETRAHEDRON
LETTERS

Synthesis and structure of cationic nickel allyl complexes supported by β-diimine ligands

Kamel Landolsi,[a] Mohamed Rzaigui[b] and Faouzi Bouachir[a,]*

[a] *Laboratoire de Chimie de Coordination, Faculté des Sciences de Monastir, 5000 Monastir, Tunisia*
[b] *Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia*

Received 12 July 2002; revised 28 September 2002; accepted 30 September 2002

Abstract—Reaction of (1,2-dimethoxyethane)$NiBr_2$ **a** with β-iminoamines ligands **c**–**f** is reported and produces a series of paramagnetic complexes (β-diimine)$NiBr_2$ **1c**–**f**. Reduction in situ of compounds **1c**–**f** in the presence of 2-methylallyloxyphosphonium salt **2** was found as a one-step synthesis of nickel allyl cationic complexes **3c**–**f** supported by β-diimine ligands. These compounds are diamagnetic, and have been characterized by NMR and IR spectroscopic data. The structure of cationic nickel complex **3d** was solved by X-ray diffraction methods. © 2002 Elsevier Science Ltd. All rights reserved.

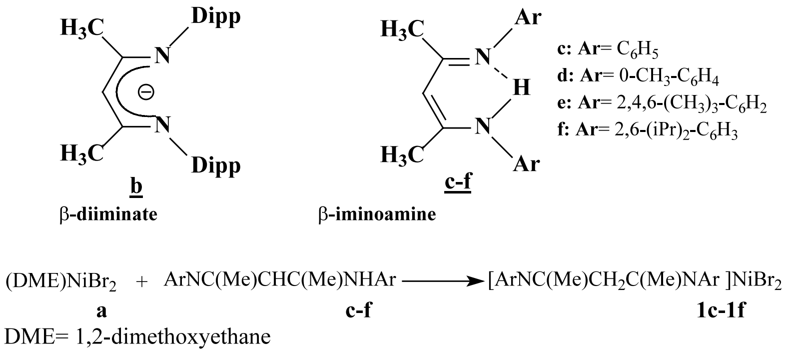
1. Introduction

Recent investigation of derivatives of the sterically encumbered β-diiminate ligand **b** $[HC(MeCDippN)_2]^-$ (Dipp = 2,6-$i$$Pr_2$-$C_6H_3$) have shown that it can stabilize a wide variety of species with unusual coordination numbers and bonding throughout the periodic table.[1–13]

However, coordination of this ligand in its neutral form (β-iminoamine) appears to be rare.[14] The discovery of a new class of Ni(II) and Pd(II) catalysts for the polymerization of ethylene and α-olefins using a β-iminoamine ligand **f** was reported recently by McLain and coworkers.[15]

Herein, we report on the use of a wide variety of bidentate β-iminoamine ligands **c**–**f** for the preparation of the cationic monomeric allyl nickel compounds. We have been particularly interested in using these chelate bidentate ligands in their neutral form (β-iminoamine) in the hope of generating unusual species. In the first step, we have prepared and isolated a (β-diimine)$NiBr_2$ complexes **1c**–**f** with a variety of sterically encumbered ligands. As a continuation of these studies, we have focused on exploring nickel chemistry further with this ligand.

Nickel dibromide compounds can be easily obtained by reaction of (DME)$NiBr_2$ **a** with 1 equiv. of β-imi-



Scheme 1. Synthesis of (β-diimine)$NiBr_2$.

Keywords: nickel; cationic allyl complexes; β-diimines; methylallyloxyphosphonium salt.

* Corresponding author. Fax: 216 73 500 278; e-mail: fbouachir@netscape.net

PII: S0040-4039(02)02187-1

noamine ligands **c**–**f** under mild conditions to afford (β-diimine)$NiBr_2$ **1c**–**f** in high yield (Scheme 1).

Complexes **1c**–**f** form purple crystals, which are paramagnetic and display a contact-shifted ^1H NMR spectra with relatively narrow line widths at room temperature. The formation of **1f** was confirmed by an X-ray single-crystal analysis.[15]

Reduction of **1c**–**f** with zinc for 24 h in methylene chloride as solvent in the presence of $[CH_2{=}C(Me)CH_2\text{-}O\text{-}P(NMe_2)_3]^+PF_6^-$ salt[16–19] **2** afforded the first example of room temperature stable cationic monomeric allyl Ni(II) species $[H_2C(CMeNAr)_2Ni(\eta^3\text{-}C_4H_7)]^+PF_6^-$ **3c**–**f**. Yields ranged from 70 to 83% (Scheme 2).

Compounds **3c**–**f**, crystallized as yellow-brown crystals from CH_2Cl_2/*n*-hexane, are soluble in methylene chloride and acetonitrile but only sparingly soluble in diethyl ether and chloroform. 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 ^1H, ^{13}C NMR and IR spectroscopy. Single crystals of **3d**, suitable for X-ray analysis, were obtained from CH_2Cl_2/*n*-hexane at −30°C.

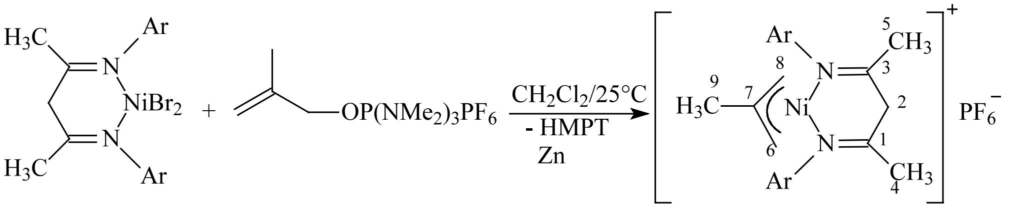
2. Results and discussion

The variation of the steric and electronic proprieties of β-iminoamine 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 ^1H NMR spectra of these compounds are characterized by the *syn* and *anti* allylic protons; thus, the two resonances are at 2.06, 2.02, 1.95 and 1.93 ppm (H_{anti}) and at 2.3, 2.42, 1.97 and 2.13 ppm (H_{syn}), respectively, for complexes **3c**–**f**.

In the ^{13}C NMR spectra, the allylic carbons C(6) and C(8) appear at 61.09 ppm (60.96 and 62.41 ppm) and 62.325 ppm (61.35 and 61.73 ppm), respectively, for complexes **3c**–**f**. The C=N carbon appears between 178.78 and 184.70 ppm.

The IR spectra of **3c**–**f** are also instructive, since the ν(C=N) stretching frequencies for **3c**–**f** are different from those of complexes **1c**–**f**. The absence of ν(H–N) stretching frequencies detected in β-iminoamine ligands **c**–**f** confirms that they are indeed β-diimine tautomers. The $\nu(PF_6^-)$ signal is evident (839–841 cm^{-1}).

A single-crystal X-ray diffraction study confirmed the identity of the complex.[20] An ORTEP diagram of **3d** is shown in Fig. 1. The β-iminoamine ligand is bound as the β-diimine tautomer, with Ni–N (sp^2) bond lengths of 1.92 Å, which are very close to those reported for other Ni–imino-nitrogen bonds.[15] Complex **3d** is a distorted square-planar structure and this distortion is illustrated



1c-1f **2** **3c-3f**

HMPT: hexamethylphosphotriamide

Scheme 2. Synthesis of $[H_2C(CMeNAr)_2Ni(\eta^3\text{-}C_4H_7)]^+PF_6^-$ complexes.

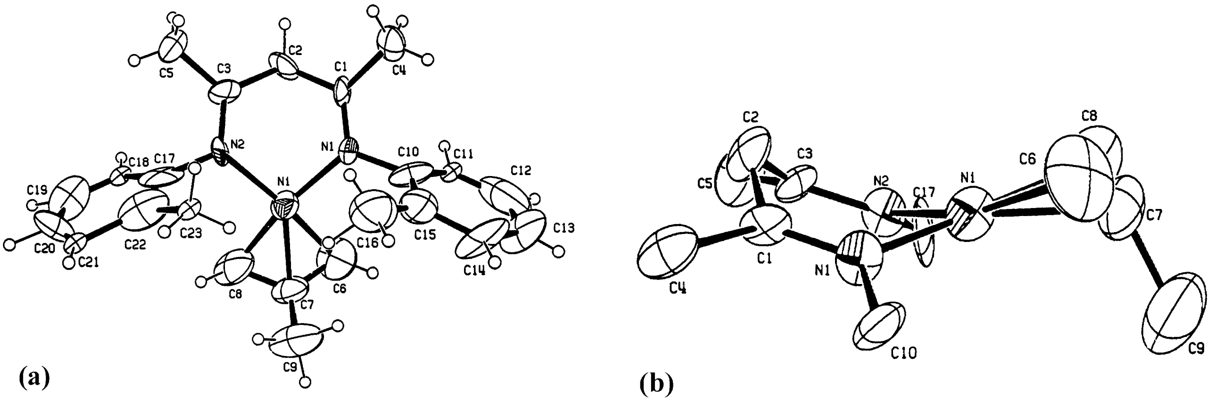


Figure 1. (a) ORTEP diagram of **3d**. Thermal ellipsoids are at 50% probability. PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–N1 = 1.92, Ni–N2 = 1.92, Ni–C8 = 2.06, Ni–C6 = 2.05, Ni–C7 = 1.95, N1–C1 = 1.29, N2–C3 = 1.3, N2–C17 = 1.49, N1–C10 = 1.44, C2–C1 = 1.52, C2–C3 = 1.5; N1–Ni–N2 = 93.6(7), N1–Ni–C6 = 96.1(8), N2–Ni–C8 = 95.8(8), Ni–N1–C1 = 122.7(4), Ni–N2–C3 = 122.16. (b) View of the chelate ring in **3d**. The aromatic rings and hydrogen atoms are omitted for clarity.

by the N(1)–Ni–N(2) bond angle of 93.6(7)°. Bond distances within the six-membered chelate ring are consistent with the localized diimine structure drawn in Scheme 2; the ring itself adopts a boat conformation, as indicated in Fig. 1(b).

The methyl on the allyl group is slightly tilted out of the allyl plane by about 12° as indicated by the torsion angle of 168.5(3)° for C(7)–C(6)–C(8)–C(9). The aryl plane makes an angle of 95(2)° with the nickel coordinative plane. The aryl rings are tilted out of the N(1)=C(1)–C(3)=N(2) plane by about 67°, as indicated by torsion angles of 113(2), −78(2), 75(2) and −112(2)° for C(3)–N(2)–C(17)–C(22), C(3)–N(2)–C(17)–C(18), C(1)–N(1)–C(10)–C(11) and C(1)–N(1)–C(10)–C(15), respectively.

In conclusion, the synthesis of new cationic allyl complexes of Ni with β-iminoamine ligands are described and fully characterized. The synthetic procedure for preparing **3c**–**f** offers great versatility for the generation of cationic β-diimine allyl complexes of possible catalytic interest.

3. Experimental

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethylether was distilled from sodium benzophenone. Methylene chloride and hexane were distilled over P_2O_5.

NMR spectra were recorded on a Bruker AC-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent resonance relative to TMS. Melting points are uncorrected. IR spectra were recorded on a Bruker Victor or a Biorad FTS6000 spectrometer in KBr pellets. (DME)$NiBr_2$[21] and β-iminoamine ligands[22–24] were prepared according to literature methods.

3.1. General procedure for the preparation of [(β-diimine)Ni(η^3-C_4H_7)]$^+$$PF_6^-$ complexes

In an inert atmosphere, (β-diimine)$NiBr_2$ complex (1 equiv.) was dissolved in anhydrous CH_2Cl_2. 2-Methylallylloxyphosphonium salt ($C_4H_7OP(NMe_2)_3PF_6$) was added (0.90 equiv.). Zinc was then added (5 equiv.) as a reducing agent. The deep purple solution was stirred at room temperature for 24 h. The supernatant was separated by filtration, and the solvent was removed under vacuum to afford the oily compound. This was precipitated out of a CH_2Cl_2/diethylether mixture. The pure compound was isolated as a yellow-brown solid by crystallization from methylene chloride/hexane solution at −30°C. Yields ranged from 70 to 83%.

3.2. Synthesis of [(PhNC(Me)CH_2C(Me)NPh)Ni(η^3-C_4H_7)]$^+$$PF_6^-$ (3c)

Following the general procedure, from (PhNC(Me)CH_2C(Me)NPh)$NiBr_2$ (0.32 mmol, 0.15 g), zinc (0.1 g, 1.8 mmol) and 2-methylallyloxyphosphonium (0.30 mmol, 0.11 g) was obtained **3c** (0.135 g, yield 83%) as a yellow solid after crystallization from a mixture of *n*-hexane/CH_2Cl_2 (10/1); mp = 228°C (dec.); IR ($\nu_{C=N}$ = 1654 cm^{-1}); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 1.97 (s, 3H, Me (allyl)), 2.06 (s, 2H, H^6_{anti} and H^8_{anti}), 2.16 (s, 6H, ligand-Me), 2.3 (s, 2H, H^6_{syn} and H^8_{syn}), 3.96 (dd, 2H, J = 17.16 Hz, ligand-CH_2), 7.00–7.03 (d, 4H, J = 7.41 Hz, *o*-ArH), 7.28–7.30 (t, 2H, J = 7.44 Hz, *p*-ArH), 7.43–7.48 (dd, 4H, J = 7.95 Hz, J = 7.68 Hz, *m*-ArH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 22.96 (Me (allyl)), 24.79 (Me on ligand), 49.33 (CH_2 on ligand), 61.09 (C(6) and C(8), CH_2 (allyl)), 121.36 (*o*-C on C_6H_5), 127.27 (*p*-C on C_6H_5), 130.01 (*m*-C on C_6H_5), 131.86 (C(7)-allyl), 150.21 (C–N on C_6H_5), 178.78 (C=N on ligand).

Yields, physical and spectral data of compounds **3d**–**f** are reported below.

3.3. [(*o*-CH_3-C_6H_4NC(Me)CH_2C(Me)NC_6H_4-*o*-CH_3)Ni(η^3-C_4H_7)]$^+$$PF_6^-$ (3d)

Yield = 80%; mp = 230°C (dec.); IR ($\nu_{C=N}$ = 1656 and 1629 cm^{-1}); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 1.95 (s, 3H, Me (allyl)), 2.02 (s, 2H, H^6_{anti} and H^8_{anti}), 2.08 (m, 12H, H_1, H_5 and H_g, Me on ligand and *o*-CH_3 on C_6H_5), 2.42 (s, 2H, H^6_{syn} and H^8_{syn}), 3.99 (dd, 2H, J = 18.21 Hz, ligand-CH_2), 6.80–7.28 (m, 8H, ArH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 17.824 (Me (allyl)), 18.849 (Me on allyl), 23.385 (Me on ligand), 25.153 and 25.590 (*o*-C on C_6H_4), 45.668 and 49.448 (CH_2 on ligand), 60.957 and 62.402 (C(6) and C(8), CH_2 (allyl)), 121.556 (*p*-C on C_6H_4), 122.387 (*o′*-C on C_6H_4), 127.686 and 128.084 (*m*-C on C_6H_4), 129.816 (*m′*-C on C_6H_4), 131.875 and 132.082 (*o*-C on C_6H_4), 135.063 (C(7)-allyl), 144.975 and 150.118 (C–N on C_6H_4), 179.39 (C=N on ligand).

3.4. [(2,4,6-$(CH_3)_3$-C_6H_2NC(Me)CH_2C(Me)NC_6H_2-2,4,6-$(CH_3)_3$)Ni(η^3-C_4H_7)]$^+$$PF_6^-$ (3e)

Yield = 76%; mp = 236°C (dec.); IR ($\nu_{C=N}$ = 1637 and 1591 cm^{-1}); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 1.95 (s, 3H, Me (allyl)), 1.84 (s, 6H, *o*-CH_3), 1.95 (s, 2H, H^i_{anti} and H^j_{anti}), 1.97 (s, 2H, H^6_{syn} and H^8_{syn}), 2.04 (s, 6H, Me on ligand), 2.14 (s, 6H, *o′*-CH_3), 2.29 (s, 6H, *p*-CH_3), 3.95 (dd, 2H, J = 21 Hz, CH_2 on ligand), 6.4 (s, 4H, *m*-ArH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 18.71 (Me (allyl)), 18.93 (*p*-Me on C_6H_2), 23.215 (*o′*-Me on C_6H_2), 23.876 (Me on ligand), 48.14 (CH_2 on ligand), 62.32 (C(6) and C(8), CH_2 (allyl)), 127.39 (*p*-C on C_6H_2), 127.87 (*o*-C on C_6H_2), 130.120 (*o′*-C on C_6H_2), 132.65 (C(7)-allyl), 136.92 (*m*-C on C_6H_2), 148.4 (C–N on C_6H_2), 179.88 (C=N on ligand).

3.5. [(2,6-$(iPr)_2$-C_6H_3NC(Me)CH_2C(Me)NC_6H_3-2,6-$(iPr)_2$)Ni(η^3-C_4H_7)]$^+$$PF_6^-$ (3f)

Yield = 70%; mp = 230°C (dec.); IR ($\nu_{C=N}$ = 1657 and 1632 cm^{-1}); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, δ [ppm]): δ = 1.057 (d, 6H, J_{HH} = 6.9 Hz, $CHMe_2$), 1.154

(d, 6H, $J_{HH}=6.9$ Hz, $CHMe_2$), 1.256 (d, 6H, $J_{HH}=6.9$ Hz, $CHMe_2$), 1.404 (d, 6H, $J_{HH}=6.9$ Hz, $CHMe_2$), 1.493 (s, 3H, Me-allyl), 1.936 (s, 2H, H^6_{anti} and H^8_{anti}), 1.976 (s, 6H, CH_3 on ligand), 2.132 (s, 2H, H^6_{syn} and H^8_{syn}), 2.634 (m, 1H, CH–CH_3, $J=6.6$ Hz), 3.276 (sept., 1H, CH–CH_3, $J_{HH}=6.3$ Hz), 3.829 (sept., 1H, CHMe, $J_{HH}=6.9$ Hz), 4.256 (sept., 1H, CHMe, $J_{HH}=6.6$ Hz), 2.68 (d, 2H, $J=13.5$ Hz, CH_2 on ligand), 7.156–7.288 (m, 6H, H_{arom}, aromatic H of Ar group); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25°C, δ [ppm]): $\delta=$ 20.07 (Me-allyl), 20.10 (Me-allyl), 20.65–22.94 (Me on ligand), 23.11–23.70 (Me on *i*Pr group), 24.025 (Me on *i*Pr group), 24.99 (Me on *i*Pr group), 25.66 (Me on *i*Pr group), 26.66 (CH on *i*Pr group), 26.73 (CH on *i*Pr group), 28.63 (CH on *i*Pr group), 29 (CH on *i*Pr group), 45.35 (CH_2 on ligand), 47.143 (CH_2 on ligand), 60.73 and 61.35 (C(6) and C(8), CH_2 (allyl)), 184.70 and 183.85 (C=N on ligand).

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