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Preparation of Five-Membered Nickelacycles with Anionic C−N−N′ Terdentate Ligands. X-ray Crystal Structure of [NiCl{2-($CH{=}NCH_2CH_2NMe_2$)-3-ClC_6H_3}]

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The five-membered metallacycles [Ni(C−N−N′)X] have been prepared by oxidative addition of *o*-halo-substituted imines derived from *N*,*N*-dimethylethylenediamine, $C_6R_nH_{5-n}CH{=}NCH_2CH_2NMe_2$ to [Ni(COD)$_2$]. The molecular structure of [NiCl{2-($CH{=}NCH_2CH_2NMe_2$)-3-ClC_6H_3}] has been determined by a single-crystal X-ray crystallographic study. Some ionic compounds [Ni(C−N−N′)L]BF_4 (L = NCMe, heterocyclic amines) were also obtained. The Ni−C bond of these complexes is inert toward insertion reactions of ethylene or PhC≡CPh. The action of [Ni(COD)$_2$] on the diamines $C_6R_nH_{5-n}CH_2N(Me)CH_2CH_2NMe_2$ affords highly insoluble organonickel derivatives, which by reaction with aromatic amines (L) in the presence of $TlBF_4$ lead to the ionic derivatives [Ni(C−N−N′)L]BF_4. The stabilization of organometallic Ni(III) compounds using $CuCl_2$ as oxidant was not achieved. Coordination compounds [NiClBr(N′−N)], where N−N′ = 2-$ClC_6H_4CH_2N(Me)CH_2CH_2NMe_2$, were formed probably by reductive elimination of Ni(III) species followed by reoxidation to Ni(II).

Introduction

In recent years, many multidentate ligands have been developed to obtain new organometallic complexes. The study of nickel complexes with polydentate ligands is especially interesting because of their reactivity and their catalytic activity. Bidentate nickel compounds with anionic P−O ligands have been widely studied, and they have been found to be highly active and selective catalysts in the oligomerization of ethylene to linear α-olefins.[1] Some nickelacycles containing bidentate anionic N−C ligands have also been described.[2] The study of organonickel compounds containing terdentate N-donor ligands is somewhat restricted. van Koten *et al.* have reported the synthesis and reactivity of nickel(II) complexes which contain the monoanionic, potentially *trans*-terdentate ligand $C_6H_3(CH_2NMe_2)_2$.[3] This N−C−N ligand has permitted the synthesis of stable organonickel(III) species[4] and a nickel complex which is an effective catalyst in the Karasch addition.[5] The same author describes the synthesis of a series of iridium, rhodium, ruthenium, palladium, and platinum complexes based on the monoanionic, potentially *cis*-terdentate ligand $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$.[6] Recently, Richmond *et al.* have described the oxidative addition of an *ortho* C−F bond of the Schiff base 2-$NMe_2C_6H_4N{=}CHC_6F_5$ to [Ni(COD)$_2$].[7]

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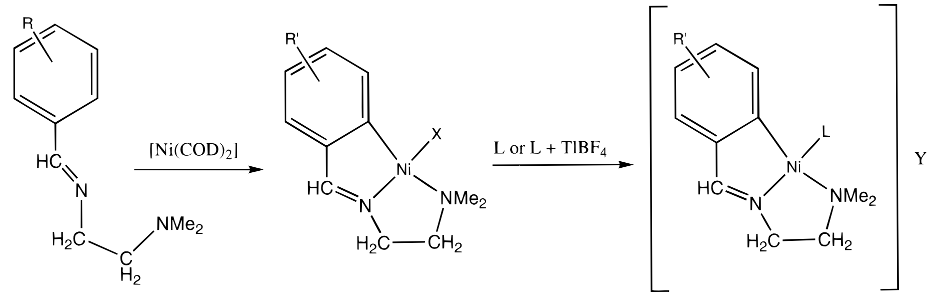
Scheme 1



R = 2-Br, **1a**
R = 2-Cl, **1b**
R = 2,6-Cl$_2$, **1c**
R = 2,3,6-Cl$_3$, **1d**
R = 2,3,5-Cl$_3$, **1e**

R' = H, X = Br, **2a**
R' = H, X = Cl, **2b**
R' = 3-Cl, X = Cl, **2c**
R' = 3,4-Cl$_2$, X = Cl, **2d**
R' = 4,6-Cl$_2$, X = Cl, **2e**

R' = H, L = NCMe, Y = BF$_4$, **3a**
R' = H, L = 2,4-lut, Y = BF$_4$, **4a**
R' = H, L = 2,4-lut, Y = Br, **5a**
R' = H, L = 2-pic, Y = Br, **6a**

Following our studies on C−N[8] and C−P[9] nickelacycles, we report here the reaction of [Ni(COD)$_2$] and *o*-halo-substituted diamines or imines derived from *N,N*-dimethylethylenediamine. This reaction allows the synthesis of the corresponding metallacycles containing anionic *cis*-C−N−N′ ligands in good yields. The potential stability of the Ni(III) species and the use of the imine complexes as precursors in the oligomerization of olefins have also been tested.

Results and Discussion

Synthesis of [NiX{2-(CH=NCH$_2$CH$_2$NMe$_2$)C$_6$R′$_n$H$_{4-n}$}]. The five-membered metallacycles [Ni(C−N−N′)X] (**2a**−**e**), were prepared by reaction of [Ni(COD)$_2$] with the potentially terdentate N-donor ligands C$_6$R$_n$H$_{5-n}$CH=NCH$_2$CH$_2$NMe$_2$ by oxidative addition of one of the *ortho* C−X bonds (X = Cl or Br) in toluene or tetrahydrofuran (Scheme 1).

The new compounds obtained are slightly air-sensitive, bright orange solids which can be stored under nitrogen for several months. All these complexes were characterized by elemental analyses, infrared spectra, ^{1}H NMR in CDCl$_3$, C$_6$D$_6$, or CD$_3$COCD$_3$ under nitrogen, and a crystal structure determination of **2c** (see below). Mass spectra of selected compounds were also recorded. The proton NMR spectra (Table 1) are well-defined, indicating that there is no significant distortion of the square-planar geometry (the crystal structure determination of **2c** confirms this; see below), and permit the assignment of nearly all the signals. The methinic and NMe$_2$ protons appear as singlets, and their chemical shifts show the coordination of both nitrogen atoms to the metal.[6,8] The FAB spectra show signals corresponding to M and M−X and also some weak signals corresponding to M × 2 with a reasonable isotopic pattern. Nevertheless, the X-ray structure of **2c** shows the monomeric nature of these derivatives and, consequently, the signals assignable to M × 2 can be explained by dimerization produced in the ionization chamber, as has been described for analogous nickel derivatives.[9b,10]

The imine **1d** could afford two different five-membered metallacycles by activation of C−Cl bonds, but only the activation of the less hindered C−Cl bond was observed, leading to a metallacycle that does not contain any substituent on the carbon atom in the *ortho* position with relation to the metalated carbon. This result shows the importance of steric factors in the process. Nevertheless, it was possible to obtain the nickelacycle **2e**, which contains a chloro substituent in the carbon atom adjacent to the Ni−C bond, by reaction between [Ni(COD)$_2$] and the imine **1e**, in which the only C−Cl bond in an *ortho* position has an adjacent chloro substituent. The activation of the *ortho* C−H bond by [Ni(COD)$_2$] was not observed. Compound **2e** is clearly more unstable than the other nickelacycles derived from imines, which may be related to the reactivity of the metallacycle. It has been reported that cyclopalladated[11] and cycloplatinated[12] metallacycles, which contain a substituent adjacent to the M−C bond, are more reactive (the M−N bond is easily broken) than the corresponding metallacycles of nonsubstituted derivatives.

The addition of TlBF$_4$ and the Lewis base L (L = NCMe, 2,4-lutidine) to compounds **2**, [NiX(C−N−N′)], afforded the ionic derivatives **3a** and **4a**, [Ni(C−N−N′)L]BF$_4$, which were characterized by elemental analyses, infrared spectra, and conductivity measurements (see Experimental Section). The addition of aromatic amines L (2,4-lutidine and 2-picoline) to **2**, in the absence of the bulky counterion BF$_4^-$, only led to the ionic derivatives [Ni(C−N−N′)L]X (**5**, **6**) in the solid state when X = Br. The low values of their molar conductivities in acetone solution suggest an equilibrium in solution between the ionic ([Ni(C−N−N′)L]Br) and the neutral ([Ni(C−N−N′)Br]), complexes. When an excess of the aromatic amine L was added to these solutions, the conductivity increased, confirming the proposed equilibrium. Therefore, compound **4a** was also obtained by action of NH$_4$BF$_4$ and 2,4-lutidine on **2**, showing that the formation of the ionic compounds does

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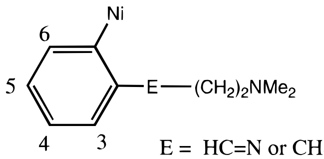
Table 1. Proton[a] NMR Data



E = HC=N or CH$_2$-NMe

compd (solvent)	aromatic	others
2a (CDCl$_3$)	7.72 [d, *J*(HH) = 7.5, 1H, H^3] 7.07−6.60 (m, 3H)	7.93 (br s, 1H, HC=N) 3.62 [t, *J*(HH) = 6.2, 2H, N(CH$_2$)$_2$N] 2.77 [t, *J*(HH) = 6.2, 2H, N(CH$_2$)$_2$N] 2.64 [s, 6H, NMe$_2$]
2b (CD$_3$COCD$_3$)	7.51 [d, *J*(HH) = 7.5, 1H, H^3] 6.98−6.60 (m, 3H)	7.92 (s, 1H, HC=N) 3.64 [br t, 2H, N(CH$_2$)$_2$N] 2.81 [br t, 2H, N(CH$_2$)$_2$N] 2.63 [s, 6H, NMe$_2$]
2c (CDCl$_3$)	7.40 [d, *J*(HH) = 7.5, 1H, H^4] 6.98 [t, *J*(HH) = 7.5, 1H, H^5] 6.90 [d, *J*(HH) = 7.5, 1H, H^6]	8.26 (s, 1H, HC=N) 3.64 [t, *J*(HH) = 5.8, 2H, N(CH$_2$)$_2$N] 2.79 [t, *J*(HH) = 5.8, 2H, N(CH$_2$)$_2$N] 2.59 [s, 6H, NMe$_2$]
2d (C$_6$D$_6$)	8.03 [d, *J*(HH) = 7.7, 1H, H^5] 7.09 [d, *J*(HH) = 7.7, 1H, H^6]	7.53 (s, 1H, HC=N) 2.29 [br t, 2H, N(CH$_2$)$_2$N] 2.21 [s, 6H, NMe$_2$] 1.63 [br t, 2H, N(CH$_2$)$_2$N]
2e (CD$_3$COCD$_3$)	8.17 br s H^5 6.97 br s H^3	7.12 (s, 1H, HC=N) 3.72 [br t, 2H, N(CH$_2$)$_2$N] 2.75 [br t, 2H, N(CH$_2$)$_2$N] 2.44 [s, 6H, NMe$_2$]
7f (CDCl$_3$) (500 MHz)	7.12 (s, 1H, col.) 6.99 (s, 1H, col.) 6.87 [t, *J*(HH) = 7.5, 1H, H^4] 6.77 [d, *J*(HH) = 7.5, 1H, H^3] 6.53 [t, *J*(HH) = 7.5, 1H, H^5] 5.18 [d, *J*(HH) = 7.2, 1H, H^6]	4.51 (d, 1H, ArCH$_2$N) 3.98 (s, 3H, col) 3.52 (d, 1H, ArCH$_2$N) 3.47 [td, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 3.30 (s, 3H, col) 3.18 (td, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 2.93 (s, 3H, NMe) 2.68 (s, 3H, NMe$_2$) 2.55 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 2.50 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 2.30 (s, 3H, NMe$_2$) 2.06 (s, 3H, col)
8f (CD$_3$COCD$_3$)[b] (500 MHz)	8.90 [d, *J*(HH) = 6.0, 1H, lut] 7.56 (s, 1H, lut) 7.29 [d, *J*(HH) = 6.0, 1H, lut] 6.81 (m)[c] 6.50 (m)[c] 5.16 [d, *J*(HH) = 7.5, 1H, H^6]	4.51 (d, 1H, ArCH$_2$N) 3.84 (s, 3H, lut) 3.63 (d, 1H, ArCH$_2$N)[c] 3.59 [td, *J*(HH) = 14, 4.5, 1H, N(CH$_2$)$_2$N][c] 3.34 [td, *J*(HH) = 14, 4.5, 1H, N(CH$_2$)$_2$N] 3.09 (s, 3H, NMe) 3.03 (s, 3H, NMe$_2$) 2.69 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 2.62 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N][c] 2.44 (s, 3H, NMe$_2$) 2.07 (s, 3H, lut)
8f (CD$_3$COCD$_3$)[d] (500 MHz)	9.62 [d, *J*(HH) = 6.0, 1H, lut] 7.41 [d, *J*(HH) = 6.0, 1H, lut] 7.38 (s, 1H, lut) 6.81 (m)[c] 6.50 (m)[c] 5.13 [d, *J*(HH) = 7.5, 1H, H^6]	4.74 (d, 1H, ArCH$_2$N) 3.75 [td, *J*(HH) = 14, 4, 1H, N(CH$_2$)$_2$N] 3.59 (d, 1H, ArCH$_2$N)[c] 3.28 [td, 1H, (HH) = 14, 4, N(CH$_2$)$_2$N] 3.17 (s, 3H, NMe) 2.94 (s, 3H, NMe$_2$) 2.63 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N][c] 2.61 [dd, 1H, *J*(HH) = 14, 4, N(CH$_2$)$_2$N] 2.43 (s, 3H, lut) 2.31 (s, 3H, NMe$_2$) 2.06 (s, 3H, lut)

[a] Chemical shifts in ppm with respect to internal SiMe$_4$; coupling constants in Hz. Numbering is given in the diagram at the top of the table. Abbreviations: col, 2,4,6-collidine; lut, 2,4-lutidine. [b] Major isomer. [c] Overlapping resonances of protons of the two isomers; see Results. [d] Minor isomer.

not require the abstraction of the bromide ion by formation of an insoluble salt.

The proton NMR resonances in the spectra of the ionic compounds at room temperature are broad, suggesting that the position *trans* to the iminic nitrogen is very labile and that fast equilibria with Lewis bases present in solution such as the bromide ion, the amine L, water, or even the solvent are possible.

Molecular Structure of 2c. The crystal structure of **2c** has been determined (Figure 1). Crystallographic data and selected bond lengths and angles are listed in Tables 2and 3, respectively.

The crystal structure consists of discrete molecules separated by van der Waals distances. The nickel atom is in a slightly distorted square-planar environment, coordinated to carbon, chlorine, and the two nitrogen

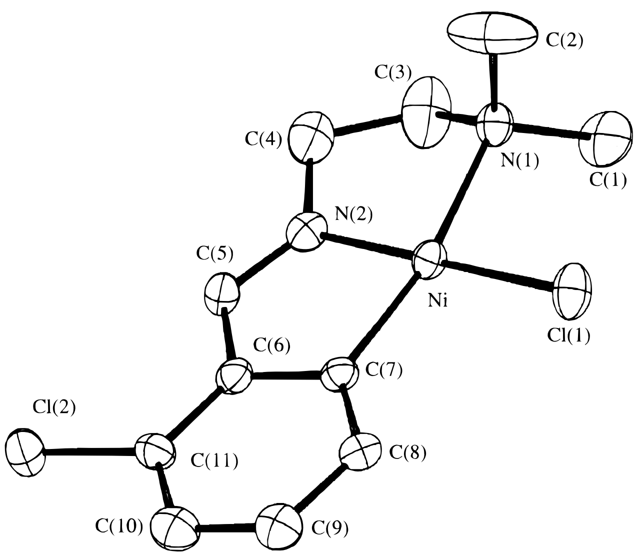


Figure 1. Ortep view of the structure of complex **2c**, [NiCl{2-(CH=NCH$_2$CH$_2$NMe$_2$)3-ClC$_6$H$_3$}], showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Crystallographic Data Collection for [NiCl{2-(CH=NCH$_2$CH$_2$NMe$_2$)-3-ClC$_6$H$_3$}] (2c)

formula	$C_{11}H_{14}Cl_2N_2Ni$
fw	303.85
cryst size (mm)	0.1 × 0.1 × 0.2
cryst syst	orthorhombic
space group	*Pcab*
a (Å)	15.953(3)
b (Å)	14.472(3)
c (Å)	11.022(2)
V (Å^3)	2544.7(8)
Z	8
D_c (g cm^{-3})	1.586
F(000)	1248
temp (K)	293(2)
wavelength (Å)	Mo Kα, 0.710 69
abs coeff	1.918
data collecn range (θ) (deg)	2.55–30.05
index ranges	$0 \leq h \leq 22$, $0 \leq k \leq 20$, $0 \leq l \leq 15$
no. of rflns collected	3716
no. of indep rflns	3716 ($R_{int} = 0.0000$)
data/restraints/params	2880/0/147
Goodness of fit on F^2	0.655
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0298, wR2 = 0.0723
R indices (all data)	R1 = 0.1058, wR2 = 0.2276
extinction coeff	0.0001(4)
largest diff peak and hole (e Å^{-3})	0.659 and −0.286

Table 3. Bond Lengths (Å) and Bond Angles (deg) for [NiCl{2-(CH=NCH$_2$CH$_2$NMe$_2$)-3-ClC$_6$H$_3$}] (2c)

Ni−N(2)	1.852(3)	Ni−N(1)	2.056(3)
Ni−C(7)	1.922(4)	Ni−Cl(1)	2.174(1)
N(1)−C(2)	1.427(6)	N(1)−C(1)	1.465(6)
N(1)−C(3)	1.509(6)	N(2)−C(5)	1.292(5)
N(2)−C(4)	1.454(5)	Cl(2)−C(11)	1.752(4)
C(3)−C(4)	1.459(6)	C(5)−C(6)	1.431(5)
C(6)−C(11)	1.394(5)	C(6)−C(7)	1.430(5)
C(7)−C(8)	1.406(5)	C(9)−C(10)	1.398(6)
C(8)−C(9)	1.402(6)	C(10)−C(11)	1.409(6)

N(2)−Ni−C(7)	83.6(1)	C(5)−N(2)−Ni	118.6(3)
N(2)−Ni−N(1)	84.3(1)	N(2)−C(5)−C(6)	113.9(3)
N(2)−Ni−Cl(1)	179.1(1)	C(6)−C(7)−Ni	110.9(3)
C(7)−Ni−Cl(1)	96.0(1)	C(4)−N(2)−Ni	118.0(3)
C(7)−Ni−N(1)	167.8(1)	C(4)−C(3)−N(1)	111.4(4)
N(1)−Ni−Cl(1)	96.05(9)	N(2)−C(4)−C(3)	108.0(4)
C(2)−N(1)−C(1)	110.3(4)	C(7)−C(6)−C(5)	113.0(3)
C(2)−N(1)−C(3)	114.7(5)	C(8)−C(7)−C(6)	118.0(3)
C(1)−N(1)−C(3)	101.7(4)	C(8)−C(7)−Ni	131.1(3)
C(2)−N(1)−Ni	109.6(3)	C(9)−C(8)−C(7)	120.7(4)
C(1)−N(1)−Ni	115.8(3)	C(10)−C(9)−C(8)	121.9(4)
C(3)−N(1)−Ni	104.6(3)	C(9)−C(10)−C(11)	117.2(4)
C(5)−N(2)−C(4)	123.4(3)	C(6)−C(11)−C(10)	122.3(4)
C(11)−C(6)−C(7)	119.9(3)	C(6)−C(11)−Cl(2)	119.6(3)
C(11)−C(6)−C(5)	127.1(4)	C(10)−C(11)−Cl(2)	118.1(3)

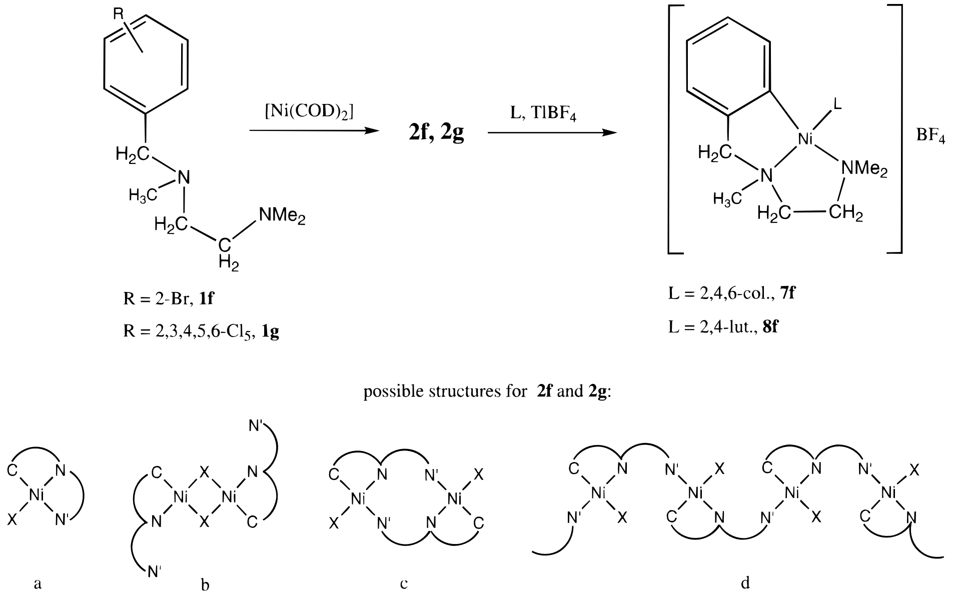
atoms, the deviations from the mean plane (plane 1) being as follows: Ni, −0.019 Å; Cl(1), −0.004 Å; N(1), 0.015 Å; N(2), −0.008 Å; C(7), 0.016 Å. The nitrogen atoms adopt a *cis* arrangement, and the NCH$_2$CH$_2$N group shows the characteristic staggered conformation. The angles between adjacent atoms in the coordination sphere lie in the range 96.1(9) (N(1)−Ni−Cl(1)) to 83.6-(14)° (C(7)−Ni−N(2)). The distances between nickel and the coordinated atoms are similar to those reported for other analogous compounds.[3b,c,8] The aromatic and the two fused five-membered rings are nearly coplanar, with deviations in the range ±0.002 Å for the corresponding atoms, excluding C(3), which is −0.502 Å from the mean plane defined by Ni, N(1), C(4), and N(2) (plane 2). The metalated phenyl ring C(6)-C(11) (plane 3), the ring containing the iminic moiety Ni, N(2), C(5), C(6), and C(7) (plane 4), and planes 1 and 2 show the following angles between normals: p1/p2, 1.10°; p1/p3, 3.38°; p1/p4, 0.91°; p2/p3, 4.41°; p2/p4, 1.93°; p3/p4, 2.49°.

The distance between the methinic proton and the *o*-chloro substituent can be estimated to be 2.828 Å, showing some interaction between these atoms. The low-field shift of the methinic proton in the NMR spectrum of **2c** confirms this interaction.

Synthesis of [NiL{2-(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-C$_6$R′$_n$H$_{4-n}$}]BF$_4$. The action of [Ni(COD)$_2$] on the diamines C$_6$R$_n$H$_{5-n}$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$ in toluene or THF affords the highly insoluble organonickel derivatives **2f**,**g** (Scheme 2).

Compounds **2f**,**g** are respectively pale orange and pale pink solids, highly insoluble in the common organic solvents. The analytical data agree with the stoichiometry [Ni(C−N−N′)X], and the IR spectra show the bands of the coordinated diamine. The FAB spectra show the signals corresponding to M and M−X and also some weak signals corresponding to M × 2. It was not possible to record ^{1}H NMR spectra of **2f**,**g** due to their insolubility, but when an excess of pyridine-d_5 was added to an CDCl$_3$ suspension of **2f**, a clear yellow solution was formed immediately. The ^{1}H NMR data for this solution agree with the formation, in solution, of the ionic complex [Ni(C−N−N′)(py-d_5)]X. van Koten *et al.* have recently prepared an analogous palladium derivative with the same diamine ligand.[6a] This result prompted us to study the action of aromatic amines on **2f**. The addition of 2,4,6-collidine or 2,4-lutidine to **2f**, in the presence of TlBF$_4$, led to the ionic derivatives [Ni-(C−N−N′)L]BF$_4$ (**7f**, **8f**). These complexes have been characterized by elemental analyses, IR spectra, conductivity measurements, and ^{1}H NMR spectra. The presence of a well-defined AB pattern of the benzylic CH$_2$ group and the presence of three distinct resonances for the NMe groups show the lack of a symmetry plane in these complexes and that the bond between the nickel and the nitrogen atom of the CH$_2$N(Me)CH$_2$ group is stable in solution; consequently, this nitrogen atom is chiral. In the spectrum of **7f**, the two *o*-methyl groups and the two aromatic hydrogen atoms of the collidine

Scheme 2



are nonequivalent, confirming the lack of a symmetry plane. The aromatic protons of the diamine, as well as the aromatic protons of the heterocyclic amines, are shifted to high field, showing the *cis* arrangement of both ligands. The *o*-methyl groups of the heterocyclic amines are shifted to low field. This shift can be explained by the paramagnetic anisotropy of the metal[13] and shows that these groups occupy the axial positions of the metal atom, as has been found by the X-ray structure determination of a closely related nickel C–N derivative.[8]

The ^{1}H NMR spectrum of the 2,4-lutidine derivative **8f** contains two sets of signals, in the ratio 3/1, in accord with the presence of two isomers in solution. In these complexes, the different arrangement of the NMe group and the *o*-methyl of the lutidine, which occupies an axial position in the coordination sphere of the metal, leads to *syn* and *anti* isomers. These isomers are present in different relative amounts, and we assume that the major complex is the less hindered *anti* isomer.

Scheme 2 shows the possible structures of **2f** and **2g**. The different color and solubility of these complexes in comparison with the mononuclear imine derivatives rules out the mononuclear structure a. Furthermore, the MS FAB spectra suggest a dinuclear structure, although dimerization can take place in the ionization chamber (see above). When the oxidative addition of [Ni(COD)$_2$] to C–X bonds of *o*-halo-substituted imines $C_6R_nH_{5-n}CH{=}NR'$ or amines $C_6R_nH_{5-n}CH_2NR'$ was performed in the absence of a Lewis base L (L = aromatic amine, PMe$_2$Ph), no organometallic compound was obtained.[8] This result shows the low stability of dinuclear halo-bridged organonickel compounds and rules out the dinuclear structure b, with halo-bridged ligands for **2f**,**g**. Consequently a dinuclear or polynuclear diamine-bridged structure (c or d) can be proposed for these complexes.

It is worth noting the different reactivities with regard to [Ni(COD)$_2$] of *o*-halo-substituted imines, which permit the synthesis of mononuclear species, and *o*-halo-substituted diamines, which lead to polynuclear nickel derivatives. The planarity of the imine moiety (see the X-ray structure of **2c**) and the sp^2 hybridization of the methinic nitrogen atom in imine derivatives favors the coordination of the nitrogen atoms of the CH=NCH$_2$ and NMe$_2$ groups to the same nickel atom; consequently, mononuclear complexes are formed with imines. In contrast, the sp^3 hybridization of both nitrogen atoms in the diamine ligands probably allows the coordination of the NMe$_2$ group to a second nickel atom and dinuclear complexes, with folded coordination planes, are formed.

Insertion Reactions. Bearing in mind that nickel compounds with N-donor ligands have been used successfully as precursors of catalytic species in different processes,[14] the action of ethylene and diphenylacetylene on the new nickelacycles prepared has been studied. When a THF solution of the ionic compound **3a** was treated with ethylene at 35 bar and 75 °C, the starting compound was recovered unchanged. Gas chromatographic analysis of the solutions did not show any decomposition compounds coming from an insertion of ethylene into the Ni–C bond followed by β-elimination. Furthermore, when **2c** was treated with diphenylacetylene, in the ratio 1/1.5, in refluxing THF for a period of 3 h, the starting complex was recovered unaltered. These results show that the Ni–C bonds in the tridentate C–N–N′ imine derivatives are surprisingly inert to insertion reactions. Since these insertion reactions were observed in Ni–C–P[15] and Ni–C–N[2a] compounds, the difference can be attributed to an unfavorable transition-state geometry for the insertion process.

Redox Behavior of Organonickel(II) Complexes. The symmetrical 2,6-bis[(dimethylamino)methyl]phenyl ligand allows the stabilization of well-defined Ni(III) species, in pentacoordinate[4a] or hexacoordinate[4c] aryl complexes. The reaction between the imine derivative **2c** and CuCl$_2$ in THF gave undefined decomposition

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compounds, but when this reaction was performed with the amine derivative **2f**, a dark red solution was initially formed which in few minutes turned green; finally, a green solid was obtained. The analytical data for this product were reproducible and agree with a stoichiometry corresponding to $[NiBrCl_2(2\text{-}C_6H_4CH_2N(Me)CH_2CH_2NMe_2]$, but the magnetic moment observed ($\mu_{eff} = 2.95\ \mu_B$ at 23 °C) indicates the presence of two unpaired electrons. The mass spectra of this compound, obtained either in the solid state (FAB) or from its solutions (GC-coupled), showed fragments of the bidentate amine $2\text{-}ClC_6H_4CH_2N(Me)CH_2CH_2NMe_2$. All these results indicate that the green product is the Ni(II) tetrahedral compound $[NiBrCl(2\text{-}ClC_6H_4CH_2N(Me)CH_2CH_2NMe_2)_2]$, probably formed by reductive elimination from a Ni(III) species followed by reoxidation to the Ni(II) coordination compound. The terminal position of the Ni−C bond in the C−N−N′ compound, which probably facilitates the decomposition of the organometallic compound by reductive elimination, explains its lower stability in relation to analogous derivatives with the symmetrical N−C−N ligand.

We have tested THF solutions of the soluble imine complexes by cyclic voltammetry. For example, the results obtained from a 1.2×10^{-3} M solution of **2c** in THF, with Bu_4NBF_4 (0.1 M) as supporting electrolyte, showed a quasi-reversible Ni(II)/Ni(III) oxidation reduction couple with $E_{pa} = +0.85$ V. This value is higher than the oxidation potentials reported by van Koten et al.[4a] (+0.24 to +0.57 V in acetone) for similar complexes with symmetrical terdentate ligands [Ni(N−C−N)Cl], indicating that the oxidation of the Ni(II) complexes is much more difficult with the unsymmetrical ligand C−N−N′.

Experimental Section

^1H NMR spectra were obtained using a Varian Gemini-200 (200 MHz) spectrometer. Solvents used were $CDCl_3$, $[^2H_6]$ acetone, and C_6D_6. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and by the Serveis Científico-Tècnics de la Universitat de Barcelona. Mass spectra were recorded on a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzyl alcohol for FAB analysis and then subjected to bombardment with cesium atoms. Conductivity measurements were taken with a Radiometer CDM3 instrument in 10^{-3} M acetone solutions at 20 °C.

Materials and Synthesis. All manipulations of the organonickel compounds were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and toluene were distilled over sodium−benzophenone, under nitrogen, before use. Pyridines and $TlBF_4$ were obtained commercially. Diamines,[6a] imines,[16] and $[Ni(COD)_2]$[17] were prepared according to procedures described elsewhere.

$[NiX\{2\text{-}(CH{=}NCH_2CH_2NMe_2)C_6R'_nH_{4-n}\}]$ (X = Br, R′ = H, 2a; X = Cl, R′ = H, 2b; X = Cl, R′ = 3-Cl, 2c; X = Cl, R′ = 3,4-Cl$_2$, 2d; X = Cl, R′ = 4,6-Cl$_2$, 2e). To a suspension of $[Ni(COD)_2]$ (0.65 g, 2.40 mmol) in THF (30 cm^3) at −78 °C was added the corresponding imine (2.40 mmol). The reaction mixture was warmed to room temperature and maintained for 2 h under these conditions. The solvent was partially removed under vacuum, and ether was added. Compounds **2** were precipitated and recrystallized in toluene−ether. Data for **2a:** 0.52 g, 70%. Anal. Found: C, 42.1; H, 4.9; N, 9.0. Calcd for $C_{11}H_{15}BrN_2Ni$ (M_r = 314): C, 42.09; H, 4.78; N, 8.92. MS: *m/z* 314 (M). Data for **2b:** 0.35 g, 55%. Anal. Found: C, 49.2; H, 5.8; N, 10.3. Calcd for $C_{11}H_{15}ClN_2Ni$ (M_r = 269): C, 49.04; H, 5.62; N, 10.39. MS: *m/z* 269 (M), 234 (M − Cl). Data for **2c:** 0.45 g, 60%. Anal. Found: C, 44.7; H, 4.9; N, 9.2. Calcd for $C_{11}H_{14}Cl_2N_2Ni$ (M_r = 304): C, 43.46; H, 4.61; N, 9.22. MS: *m/z* = 304 (M). Data for **2d:** 0.41 g, 50%. Anal. Found: C, 38.1; H, 3.9; N, 8.0. Calcd for $C_{11}H_{13}Cl_3N_2Ni$ (M_r = 338): C, 39.06; H, 3.87; N, 8.28. Data for **2e:** 0.55 g, 67%. Anal. Found: C, 39.0; H, 3.9; N, 8.1. Calcd for $C_{11}H_{13}Cl_3N_2Ni$ (M_r = 338): C, 39.06; H, 3.87; N, 8.28.

2f,g. To a suspension of $[Ni(COD)_2]$ (0.65 g, 2.40 mmol) in toluene (30 cm^3) at −78 °C was added the corresponding diamine (2.40 mmol). The reaction mixture was warmed to room temperature and maintained for 3 h under these conditions. The insoluble solid formed (pale orange, **2f**; pale pink, **2g**) was washed with hexane and ether. Data for **2f:** 0.65 g, 82%. Anal. Found: C, 41.9; H, 5.5; N, 7.9. Calcd for $C_{12}H_{19}BrN_2Ni$: C, 43.70; H, 5.76; N, 8.49. Data for **2g:** 0.80 g, 78%. Anal. Found: C, 35.3; H, 3.6; N, 6.4. Calcd for $C_{12}H_{15}Cl_5N_2Ni$: C, 34.05; H, 3.57; N, 6.62.

$[Ni\{2\text{-}(CH{=}NCH_2CH_2NMe_2)C_6R'_nH_{4-n}\}L]X'$ (R′ = H, L = NCMe, X′ = BF$_4$, 3a; R′ = H, L = 2,4-Me$_2$(C$_5$H$_3$N), X′ = BF$_4$, 4a). $TlBF_4$ (0.58 g, 2.0 mmol) was added to a suspension of **2a** (0.63 g, 2.00 mmol) in THF (40 cm^3) containing acetonitrile or 2,4-lutidine (2.4 mmol). After the mixture was stirred at room temperature for 4 h, the precipitate of thallium bromide formed was filtered off. The solvent was partially removed *in vacuo*, and the yellow solids obtained were filtered off and washed with ether. Data for **3a:** 0.45 g, 62%. Molar conductivity $\Lambda_M = 107$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 43.4; H, 5.0; N, 11.3. Calcd for $C_{13}H_{18}BF_4N_3Ni$ (M_r = 362): C, 43.16; H, 5.01; N, 11.61. Data for **4a:** 0.60 g, 70%. Molar conductivity $\Lambda_M = 130$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 50.0; H, 5.4; N, 10.0. Calcd for $C_{18}H_{24}BF_4N_3Ni$ (M_r = 428): C, 50.52; H, 5.65; N, 9.82. MS: *m/z* = 340 (M − BF$_4$).

$[Ni\{2\text{-}(CH{=}NCH_2CH_2NMe_2)C_6H_4\}L]X'$ (L = 2,4-Me$_2$(C$_5$H$_3$N), X′ = Br, 5a; L = 2-Me(C$_5$H$_4$N), X′ = Br, 6a. To a suspension of **2a** (0.63 g, 2.00 mmol) in THF (50 cm^3) was added 2.50 mmol of 2,4-lutidine or 2-picoline. After the mixture was stirred for 2 h, the solvent was removed and ether was added. The yellow compounds so obtained were filtered. Data for **5a:** 0.59 g, 70%. Molar conductivity $\Lambda_M = 80$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 49.3; H, 5.8; N, 9.9. Calcd for $C_{18}H_{24}BrN_3Ni$ (M_r = 421): C, 51.35; H, 5.74; N, 9.98. MS: *m/z* = 340 (M − BF$_4$). Data for **6a:** 0.60 g, 74%. Molar conductivity $\Lambda_M = 20$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 49.7; H, 5.2; N, 10.0. Calcd for $C_{17}H_{22}BrN_3Ni$ (M_r = 407): C, 50.17; H, 5.44; N, 10.32.

$[Ni\{2\text{-}(CH_2N(Me)CH_2CH_2NMe_2)C_6H_4\}L]X'$ (L = 2,4,6-Me$_3$(C$_5$H$_2$N), X′ = BF$_4$, 7f; L = 2,4-Me$_2$(C$_5$H$_3$N), X′ = BF$_4$, 8f). To a suspension of **2f** (0.5 g, 1.5 mmol) in acetone (30 cm^3) at room temperature were added $TlBF_4$ (0.44 g, 1.5 mmol) and 2,4,6-collidine or 2,4-lutidine (2 mmol). After 30 min of stirring the precipitate formed was filtered. The solvent was partially removed under vacuum, and ether was added. Compounds **7f** and **8 f** were precipitated as lemon yellow solids. Data for **7f:** 0.40 g, 60%. Molar conductivity $\Lambda_M = 123$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 52.1; H, 6.6; N, 9.3. Calcd for $C_{20}H_{30}BF_4N_3Ni$ (M_r = 458): C, 52.45; H, 6.60; N, 9.17. Data for **8f:** 0.44 g, 67%. Molar conductivity $\Lambda_M = 135$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 48.9; H, 5.9; N, 8.8. Calcd for $C_{19}H_{28}BF_4N_3Ni$ (M_r = 444): C, 51.40; H, 6.36; N, 9.46. MS: *m/z* = 356 (M − BF$_4$).

Magnetic Measurements. Magnetic measurements were carried out at room temperature on polycrystalline samples with a pendulum type magnetometer (Manics DSM8) equipped with a Drusch EAF 16UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables.

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Electrochemical Measurements. The cyclic voltammetry studies were made on 10^{-3} M THF solutions of the neutral imine complexes, introduced in a three-electrode cell under Ar with platinum working and auxiliary electrodes. The reference electrode SCE was separated from the solution by a bridge compartment. The supporting electrolyte was 0.1 M Bu_4NBF_4. The cyclic voltammograms were taken with a scan rate of 0.1 V s^{-1}, recorded on an Electrokemat potentiostat.

X-ray Crystallographic Study of [NiCl{2-(CH═NCH$_2$-CH$_2$NMe$_2$)-3-ClC$_6$H$_3$}] (2c). Data Collection. A prismatic crystal (0.1 × 0.1 × 0.2 mm) of **2c** was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \le \theta \le 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. A total of 3716 reflections were measured in the range $2.55 \le \theta \le 30.05$; 1764 reflections were assumed as observed, applying the condition $I \ge 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz−polarization, but not absorption, corrections were made.

Structure Solution and Refinement. The structure was solved by Patterson synthesis, using the SHELXS computer program[18] for crystal structure determination, and refined by the full-matrix least-squares method, with the SHELXS computer program,[19] using 2880 reflections (very negative intensities were not assumed). The function minimized was $\sum w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0753P)^2 + 7.5828P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f', and f'' were taken from ref 20. The extinction coefficient was 0.000(14). Fourteen hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R (on F) factor was 0.029, R_w (on $|F|^2$) = 0.072, and the goodness of fit was 0.528 for all observed reflections. The number of refined parameters was 147. Maximum shift/esd = 0.12; mean shift/esd = 0.00. Maximum and minimum peaks in final difference syntheses were 0.659 and −0.286 e Å^{-3}, respectively.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, final hydrogen coordinates, and anisotropic displacement parameters for **2c** (3 pages). Ordering information is given on any current masthead page.

OM960309K

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