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Influence of the Amino Substituents of Potentially Bis Ortho Chelating Aryl Ligands $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$ on the Synthesis and Properties of Their Organonickel(II) Complexes

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Two series of square-planar organometallic Ni(II) complexes that contain various monoanionic, potentially terdentate ligands $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$ (=R^1R^2NCN') have been synthesized. In the first series [NiX(R^1R^2NCN')], i.e., [NiBr(Me_2NCN')], [NiX(Et_2NCN')] (X = Br, I), [NiBr(*i*-Pr_2NCN')], [NiX((*i*-Pr)MeNCN′)] (X = Br, I), and [NiBr((*t*-Bu)MeNCN′)], this ligand is terdentate bonded to the Ni(II) center via C(ipso) and the two N donor atoms. In the second series [NiX(R^1R^2NCN')$(PR_3)_2$], i.e., [NiBr((*t*-Bu)MeNCN′)$(PR_3)_2$] (R = Me, Et) and [NiX((Ph)MeNCN′)$(PR_3)_2$] (X = Br, R = Me, Et, Bu; X = Cl, I, R = Et), the Ni(II) center is bonded to a halide anion, to two phosphorus ligands, and to only C(ipso) of the R^1R^2NCN' ligand. From two Ni(II) complexes [NiBr(Et_2NCN')] and [NiBr((*i*-Pr)MeNCN′)] were synthesized the corresponding ionic complexes [Ni(R^1R^2NCN')(OH_2)]Otf (Otf = CF_3SO_3), by reaction with 1 equiv of AgOtf, and the organonickel(III) species [$NiBr_2$(R^1R^2NCN')], by reaction with 0.5 equiv of Br_2. The molecular structures of three complexes have been determined by X-ray crystallographic methods. [NiBr($C_6H_3\{CH_2N$(*i*-Pr)Me$\}_2$-2,6)] (**4b**): $C_{16}H_{27}N_2NiBr$, monoclinic, space group $P2_1/n$, with unit cell dimensions a = 11.632 (6) Å, b = 14.259 (7) Å, c = 10.636 (2) Å, β = 99.12 (4)°, and Z = 4. [NiBr($C_6H_3\{CH_2N$(*t*-Bu)Me$\}_2$-2,6)] (**5**): $C_{18}H_{31}N_2NiBr$, monoclinic, space group $P2_1/n$, with unit cell dimensions a = 14.148 (6) Å, b = 13.044 (2) Å, c = 11.149 (3) Å, β = 112.04 (2)°, and Z = 4. [NiBr($C_6H_3\{CH_2N$(Ph)Me$\}_2$-2,6)$(PEt_3)_2$]·0.5Et_2O (**8b**): $C_{34}H_{53}N_2P_2NiBr\cdot 0.5C_4H_{10}O$, monoclinic, space group $P2_1/c$, with unit cell dimensions a = 20.044 (2) Å, b = 9.8127 (7) Å, c = 20.857 (1) Å, β = 110.519 (5)°, and Z = 4. The crystal structures were solved either by direct methods (**4b**, **5**) or Patterson methods (**8b**). Anisotropic least-squares refinement converged at R = 0.059 (1371 observed reflections) for **4b**, 0.069 (1318 observed reflections) for **5** and 0.055 (3164 observed reflections) for **8b**. The ligand strength of the various amino groups toward the Ni(II) center decreases in the order Me_2N > Et_2N > (*i*-Pr)MeN > (*t*-Bu)MeN > (Ph)MeN. Resonance Raman spectroscopic data indicate that in solution the complexes [NiI(Et_2NCN')] and [NiI((*i*-Pr)MeNCN′)] interact with added I_2.

Introduction

As nickel is often used in organic synthesis[1] and homogeneous catalysis,[2] one would expect organonickel chemistry to be a major and extensive research topic. The study of organonickel complexes is, however, somewhat restricted, and such complexes are generally stabilized by PR_3 or $P(OR)_3$ ligands,[1b,3] whereas in nickel coordination chemistry nitrogen donor ligands, e.g. tetraaza macrocycles with[4] or without[5] pendant side arms, are more frequently used.

Previously, we have reported the synthesis and characterization of many complexes with the potentially bis ortho chelating aryl ligand system $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$ (=Me_2NCN').[6] In the square-planar nickel(II) species [NiX(Me_2NCN')] (X = halide), the two CH_2NMe_2 substituents function as donor systems and the ligand is indeed bonded in the terdentate mode; an X-ray study of [Ni(O_2CH)(Me_2NCN')] has been reported.[7] The oxidation of these Ni(II) complexes has been studied, and several organonickel(III) compounds having either pentacoordinate square-pyramidal[8,9] or hexacoordinate octahedral geometries[9] have been prepared. These results are extremely relevant since the Ni(III) oxidation state is important in bioinorganic systems[10] (e.g. nickel hydrogenase), in coordination compounds[11] and in organometallic intermediates in certain C–C coupling reactions.[12]

The chemistry of nickel and palladium complexes with chelating C,N ligands is known to be influenced by the substituents on the N donor atom.[13,14] We have now studied this influence in more detail with organonickel complexes by using the ligands $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$ (=R^1R^2NCN') containing a range of alkyl–amino substituents. The results of the study presented here, show that steric bulk of the N donor alkyl substituents in these ligands is important in determining both the type of organonickel complex that can be synthesized and the chemical and structural properties of the resulting species.

Experimental Section

The aryl bromides $2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3Br$ were obtained from reactions of $2,6\text{-}\{BrCH_2\}_2C_6H_3Br$[15] with dialkylamines R^1R^2NH.[16] [Ni$(COD)_2$] (COD = 1,5-cyclooctadiene),[17] [$NiX_2(PR_3)_2$][18] (X = halide,

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R = alkyl or phenyl), and [NiBr(Me_2NCN')][7] were prepared according to literature methods. Commercial [Ni(Acac)$_2$] (Acac = acetylacetonate) was dried by azeotropic distillation in toluene. All reactions were performed undere a nitrogen atmosphere using Schlenk techniques. Solvents were freshly distilled and dried before use. ^1H NMR spectra were recorded on Bruker AC 100 and WM 250 spectrometers. ^{13}C–^1H correlation spectroscopy measurements were carried out on a Bruker AC 100 spectrometer and ^{31}P spectra on a Bruker WP 80 spectrometer. ESR spectra were measured on a Bruker ER200D MR X-band spectrometer. Infrared spectra were measured on a Perkin-Elmer 283 spectrometer and UV/Vis spectra on a Perkin-Elmer Lambda 5 spectrophotometer. Mass spectra (FD and FI; solutions in CH_2Cl_2) were measured on a Varian MAT 711 spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Preparation of the New Organonickel Complexes. Four general procedures, described below as methods A–D, were used for the synthesis of the complexes [NiX(R^1R^2NCN')] (**1**–**5**; X = halide). The complexes [NiX(R^1R^2NCN')(PR_3)$_2$] (**7**, **8**; X = halide) were obtained exclusively by method B. Attempts to synthesize complexes of the latter series with PPh_3 ligands by reacting [$NiBr_2(PPh_3)_2$] failed (see Discussion), and therefore no data on these reactions are given.

Method A. To a cooled suspension (−56 °C; CO_2/EtOH) of [Ni(COD)$_2$] (0.55 g, 2 mmol) in 25 mL of THF was added a solution of 2,6-{$R^1R^2NCH_2$}$_2C_6H_3Br$ (3 mmol, 1.5 equiv) in 10 mL of THF. The resultant mixture was allowed to warm to room temperature over a period of 2 h during which time the color changed from yellow to dark green/brown. The solution was filtered to remove some metallic nickel, and the filtrate was evaporated to dryness. The crude product was washed with hexane (2 × 10 mL) and dried in vacuo.

Method B. To a cooled solution (−56 °C) of 2,6-{$R^1R^2NCH_2$}$_2C_6H_3Br$ (1.5 mmol) in 20 mL of diethyl ether was added 1.07 mL of a 1.4 M solution of *n*-BuLi in hexane (1.5 mmol, 1 equiv). The resultant solution was brought to room temperature after which it was added to a solution of [$NiX_2(PR_3)_2$] (1.2 mmol, 0.8 equiv) in 20 mL of diethyl ether. Almost immediately, a solid precipitated, and after additional stirring for 20 min, this was collected by filtration. The solid was washed with 5 mL of diethyl ether and 10 mL of hexane and then dried in vacuo.

Method C. A 3.57-mL aliquot of a 1.4 M *n*-BuLi/hexane solution was added to a solution of 2,6-{$R^1R^2NCH_2$}$_2C_6H_3Br$ (5 mmol, 1 equiv) in diethyl ether (30 mL) at −56 °C. The reaction mixture was slowly warmed to room temperature over 1 h and then added to a solution of [Ni(Acac)$_2$] (1.28 g, 5 mmol) in diethyl ether (20 mL). The color changed from green to brown/red, and a precipitate of Li(Acac) was formed. After the mixture was stirred for 2 h, the precipitate was filtered off and the filtrate was stored at −20 °C for 24 h. The crystals produced were filtered off, washed with hexane (2 × 10 mL), and dried in vacuo.

Method D. A solution of [Ni(R^1R^2NCN')(OH_2)]Otf (0.5 mmol) in acetone (10 mL) was stirred for 10 min with a 5-fold excess of the appropriate sodium salt (NaX). Then, the solution was evaporated to dryness. The residue was washed with H_2O (10 mL) to remove excess NaX and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and after filtration evaporated to dryness.

[NiCl(C_6H_3{CH_2NEt_2}$_2$-2,6)] (2a). Solid orange **2a** was obtained by method B in 35% yield from [$NiCl_2(PEt_3)_2$]. By method D, **2a** was isolated in 90% yield (overall yield 22–27%). MS: $C_{16}H_{27}N_2NiCl^+$, *m/z* 342.

[NiBr(C_6H_3{CH_2NEt_2}$_2$-2,6)] (2b). Orange **2b** was obtained in yields of 55% (method A), 45% (method B, from [$NiBr_2(PEt_3)_2$]), and 20% (method C). Anal. Calcd for $C_{16}H_{27}N_2NiBr$: C, 49.78; H, 7.05; N, 7.26; Br, 20.70. Found: C, 49.50; H, 7.06; N, 7.16; Br, 20.63. MS: $C_{16}H_{27}N_2NiBr^+$, *m/z* 386.

[NiI(C_6H_3{CH_2NEt_2}$_2$-2,6)] (2c). Orange **2c** was isolated in 43% yield from [$NiI_2(PEt_3)_2$] by method B, and in 90% yield (overall yield 22–27%) by method D. Anal. Calcd for $C_{16}H_{27}N_2NiI$: C, 44.38; H, 6.29; N, 6.47; I, 29.31. Found: C, 44.28; H, 6.42; N, 6.25; I, 29.51. MS: $C_{16}H_{27}N_2NiI^+$, *m/z* 433.

[Ni(C_6H_3{CH_2NEt_2}$_2$-2,6)(OH_2)]Otf (2d). Solid AgOtf (0.26 g, 1 mmol) was added to a solution of **2b** (0.38 g, 1 mmol) in acetone (20 mL) with exclusion of light. The reaction mixture was stirred for 24 h, and then the precipitate of AgBr was filtered off and the filtrate evaporated to dryness. The residue was extracted with CH_2Cl_2 (2 × 15 mL), and the combined extracts were concentrated to 5 mL. Addition of 40 mL of hexane afforded a green/yellow precipitate, which was filtered off, washed with hexane (2 × 10 mL), and dried in vacuo. Yield: 0.26 g (55%). Anal. Calcd for $C_{17}H_{29}N_2O_4SNiF_3$: C, 43.15; H, 6.18; N, 5.92; F, 12.05. Found: C, 43.16; H, 5.89; N, 5.94; F, 12.08. MS: $C_{17}H_{26}N_2O_3SNi^+$, *m/z* 454.

[NiBr(C_6H_3{$CH_2N(i\text{-}Pr)_2$}$_2$-2,6)] (3). Red crystals of **3** were isolated in 18% yield by method C. Anal. Calcd for $C_{20}H_{35}N_2NiBr$: C, 54.33; H, 7.98; N, 6.34; Br, 18.07. Found: C, 54.30; H, 7.70; N, 6.55; Br, 17.86.

[NiBr(C_6H_3{$CH_2N(i\text{-}Pr)Me$}$_2$-2,6)] (4b). Orange **4b** was synthesized with a yield of 20% (method A as well as method B, from [$NiBr_2(PEt_3)_2$]). Anal. Calcd for $C_{16}H_{27}N_2NiBr$: C, 49.78; H, 7.05; N, 7.26; Br, 20.70. Found: C, 49.71; H, 7.03; N, 7.01; Br, 20.67. MS: $C_{16}H_{27}N_2NiBr^+$, *m/z* 386.

[NiI(C_6H_3{$CH_2N(i\text{-}Pr)Me$}$_2$-2,6)] (4c). Orange **4c** was isolated in 87% yield with method D (overall yield 7%). Anal. Calcd for $C_{16}H_{27}N_2NiI$: C, 44.38; H, 6.29; N, 6.47; I, 29.31. Found: C, 44.88; H, 6.41; N, 6.60; I, 29.09.

[Ni(C_6H_3{$CH_2N(i\text{-}Pr)Me$}$_2$-2,6)(OH_2)]Otf (4d). The synthesis was carried out in the same way as that of **2d** (starting from **4b**). Yield: 0.09 g (40%). Anal. Calcd for $C_{17}H_{29}N_2O_4SNiF_3$: C, 43.15; H, 6.18; N, 5.92; F, 12.05. Found: C, 42.79; H, 6.19; N, 5.91; F, 11.55.

[NiBr(C_6H_3{$CH_2N(t\text{-}Bu)Me$}$_2$-2,6)] (5). Violet **5** could be obtained by methods A and C in yields ranging from 5 to 20%. Anal. Calcd for $C_{18}H_{31}N_2NiBr$: C, 52.21; H, 7.55; N, 6.77; Br, 19.30. Found: C, 51.91; H, 7.54; N, 6.62; Br, 19.49.

[NiBr(C_6H_3{$CH_2N(t\text{-}Bu)Me$}$_2$-2,6)(PEt_3)$_2$] (7a). Yield: 50% of a yellow solid. Anal. Calcd for $C_{30}H_{61}N_2P_2NiBr$: C, 55.40; H, 9.45; N, 4.31; P, 9.52; Br, 12.29. Found: C, 54.83; H, 9.53; N, 4.32; P, 9.09; Br, 12.31. MS: $C_{18}H_{31}N_2NiBr^+$, *m/z* 414.

[NiBr(C_6H_3{$CH_2N(t\text{-}Bu)Me$}$_2$-2,6)(PMe_3)$_2$] (7b). Yield: 90% of a yellow solid. MS: $C_{24}H_{49}N_2P_2NiBr^+$, *m/z* 566; $C_{18}H_{31}N_2NiBr^+$, *m/z* 414.

[NiCl(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)(PEt_3)$_2$] (8a). Yield: 55% of yellow crystals (recrystallization from diethyl ether). MS: $C_{22}H_{23}N_2NiCl^+$, *m/z* 410.

[NiBr(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)(PEt_3)$_2$] (8b). Yield: 76% of red/brown crystals (recrystallization from diethyl ether). Anal. Calcd for $C_{34}H_{53}N_2P_2NiBr\cdot{}^1/_2C_4H_{10}O$: C, 59.44; H, 8.04; N, 3.85; P, 8.52; Br, 10.98. Found: C, 59.41; H, 8.20; N, 3.81; P, 8.27; Br, 11.07.

[NiI(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)(PEt_3)$_2$] (8c). Yield: 65% of brown crystals (recrystallization from diethyl ether). Anal. Calcd for $C_{34}H_{53}N_2P_2NiI\cdot{}^1/_2C_4H_{10}O$: C, 55.83; H, 7.55; N, 3.62. Found: C, 55.81; H, 7.58; N, 3.80.

[NiBr(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)(PMe_3)$_2$] (8d). Yield: 40% of a yellow/green solid. MS: $C_{28}H_{41}N_2P_2NiBr^+$, *m/z* 606; $C_{22}H_{23}N_2NiBr^+$, *m/z* 454.

[NiBr(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)(PBu_3)$_2$] (8e). Yield: 40% of a yellow/green solid. MS: $C_{22}H_{21}N_2NiBr^+$, *m/z* 452.

[$NiBr_2$(C_6H_3{CH_2NEt_2}$_2$-2,6)] (9). To a stirred solution of **2b** (0.10 g, 0.26 mmol) in 15 mL of CH_2Cl_2 was added 0.26 mL of a 0.5 M solution of Br_2 in CH_2Cl_2. The color of the solution immediately changed from orange to dark green/black. After 1 h, the solution was reduced in volume to 5 mL, and 10 mL of hexane was added. After 24 h at −80 °C, black (dark green) crystals were obtained, which were filtered off, washed with hexane (2 × 10 mL), and dried in vacuo. Yield: 0.05 g (41%). Anal. Calcd for $C_{16}H_{27}N_2NiBr_2$: C, 41.25; H, 5.84; N, 6.01. Found: C, 41.50; H, 6.19; N, 5.75.

[$NiBr_2$(C_6H_3{$CH_2N(i\text{-}Pr)Me$}$_2$-2,6)] (10). Synthesis was performed as described for **9**. Yield: 32% of a green/black solid. Anal. Calcd for $C_{16}H_{27}N_2NiBr_2$: C, 41.25; H, 5.84; N, 6.01. Found: C, 41.45; H, 6.21; N, 5.93.

X-ray Crystallographic Studies

Crystal data and details of the data collection and structure refinement of **4b**, **5**, and **8b** are summarized in Table I.

Data Collection and Structure Determination of [NiBr(C_6H_3{$CH_2N(i\text{-}Pr)Me$}$_2$-2,6)] (4b). A crystal with approximate dimensions 0.43 × 0.04 × 0.50 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo Kα radiation. A total of 2234 intensities were measured within the range $-12 \le h \le 12$, $0 \le k \le 15$, $0 \le l \le 11$. Of these, 863 were below the $2.5\sigma(I)$ level and were treated as unobserved.

The structure was solved by means of the heavy-atom method using the symbolic addition program system SIMPEL[19a] to find the positions of Ni and Br. The remaining non-hydrogen atoms were derived from a difference Fourier synthesis. The hydrogen atoms were introduced at

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Table I. Crystallographic Data for $[NiBr(C_6H_3\{CH_2N(i\text{-}Pr)Me\}_2\text{-}2,6)]$ (**4b**), $[NiBr(C_6H_3\{CH_2N(t\text{-}Bu)Me\}_2\text{-}2,6)]$ (**5**), and $[NiBr(C_6H_3\{CH_2N(Ph)Me\}_2\text{-}2,6)]$ (**8b**)

	4b	**5**	**8b**
formula	$C_{16}H_{27}N_2NiBr$	$C_{18}H_{31}N_2NiBr$	$C_{34}H_{53}N_2P_2NiBr\cdot 0.5C_4H_{10}O$
mol wt	386.00	414.05	727.41
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	11.632 (5)	14.148 (6)	20.044 (2)
b, Å	14.259 (7)	13.044 (2)	9.8127 (7)
c, Å	10.636 (2)	11.149 (3)	20.857 (1)
β°	99.12 (4)	112.04 (2)	110.519 (5)
V, Å^3	1742 (1)	1907 (1)	3842.0 (5)
Z	4	4	4
D(calcd), g/cm^{-3}	1.47	1.44	1.258
λ, Å	0.71073	0.71073	1.5418
μ, cm^{-1}	33.8	30.96	29.4
T, K	295	295	295
final *R*	0.059	0.069	0.055
R_w	0.094	0.109	0.065

their calculated positions. Refinement proceeded through block-diagonal least-squares calculations (anisotropic) for the non-hydrogen atoms and isotropic for the hydrogen atoms. An empirical absorption correction[20] was used, and an extinction correction was applied. The anomalous dispersion for Ni and Br was taken into account. The final *R* value was 0.059. The programs used, apart from SIMPEL, were from XRAY 76.[21] The scattering factors were taken from Cromer and Mann.[22]

Data Collection and Structure Determination for $[NiBr(C_6H_3\{CH_2N(t\text{-}Bu)Me\}_2\text{-}2,6)]$ (5). A crystal with approximate dimensions 0.15 × 0.18 × 0.38 mm was used following the same data collecting and structure determination routine as was described for **4b**. Specific data for **5**: 3330 intensities were within the range $-15 \leq h \leq 14$, $0 \leq k \leq 15$, $0 \leq l \leq 13$; 2012 were below the $2.5\sigma(I)$ level and were treated as unobserved. Final *R* value was 0.069.

Data Collection and Structure Determination for $[NiBr(C_6H_3\{CH_2N(Ph)Me\}_2\text{-}2,6)(PEt_3)_2]$ (8b). A crystal with approximate dimensions 0.50 × 0.38 × 0.13 mm was used for data collection on an Enraf-Nonius CAD-4F diffractometer employing Ni-filtered Cu Kα radiation. The cell constants and their esd's were obtained from the setting angles of 21 reflections with $10 < \theta < 25°$. A total of 5739 intensities were measured of which 5474 are unique. Of these, 2308 were below the $2.5\sigma(I)$ level and were treated as unobserved. Data were corrected for *Lp*, a linear decay of 12%, and for absorption (DIFABS[20]).

The heavy atoms (Br, Ni, and P) were located with standard Patterson techniques.[23] The remaining non-hydrogen atoms were derived from a series of subsequent difference Fourier syntheses. Refinement proceeded through blocked full-matrix least-squares techniques, minimizing $\sum w\Delta F^2$, using the SHELX76 package.[24] Hydrogen atoms were introduced on calculated positions and refined in riding mode on their corresponding carbon atoms, with separate isotropic temperature factors for hydrogen atoms in $-CH_3$, $-CH_2$, and $-CH$ groups and the diethyl ether solvate. The diethyl ether solvate molecule was found to be disordered across a center of symmetry and was refined with bond restraints. At the final stage of refinement, two reflections (100 and 435) were omitted because of bad $\Delta F/\sigma(F)$ values. The final *R* value is 0.055. Scattering factors were taken from Cromer and Mann[22] and corrected for anomalous dispersion effects.[25] No correction for extinction was done. Apart from the programs mentioned above, programs from the EUCLID package[26] were used.

Results

A. Syntheses and Properties of the New Organonickel Complexes.

We have developed several methods for the preparation of various organonickel(II) compounds containing monoanionic, potentially terdentate ligands $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$ ($=R^1R^2NCN'$). The first method (method A in the Experimental Section) is the oxidative addition of the aryl bromide $2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3Br$ to the Ni(0) substrate $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene). This reaction (eq 1) was first used successfully for the synthesis of $[NiBr(Me_2NCN')]$ (**1b**).[7]

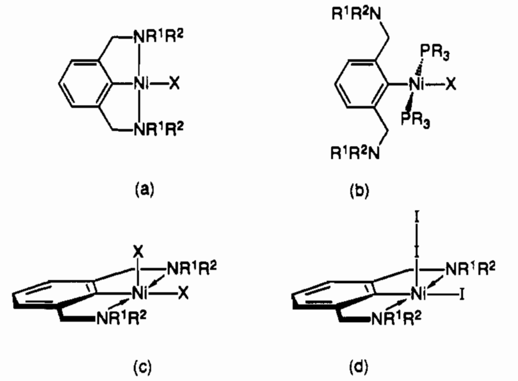
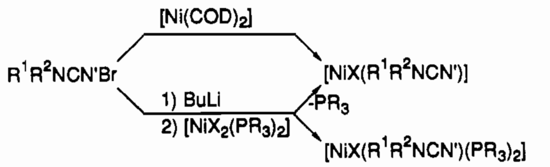


Figure 1. Schematic structures of the complexes **2–5** (a), **7** and **8** (b), and **9** and **10** (c) and of the diiodine complexes in solution ($R^1 = R^2 =$ Et, $R^1 = i$-Pr, $R^2 =$ Me) (d).



(1)

The second method (B in the Experimental Section) involves lithiation of the aryl bromide with BuLi,[27] followed by addition of the aryllithium compound to $[NiX_2(PR_3)_2]$ (eq 1). This reaction yields products with and without the phosphine ligands still coordinated to the Ni(II) center, depending on the R^1 and R^2 substituents of the NCN′ ligand (vide infra).

The third method (C in the Experimental Section) also involves lithiation of the aryl bromide with BuLi. After this the aryllithium compound is added to $[Ni(Acac)_2]$ (Acac = acetylacetonate) (eq 2).

$$R^1R^2NCN'Br \xrightarrow[\text{(2) [Ni(Acac)}_2]]{\text{(1) BuLi}} [NiBr(R^1R^2NCN')] \qquad (2)$$

The fourth method (D in the Experimental Section) is the reaction of the cationic complex $[Ni(R^1R^2NCN')(OH_2)]Otf$ (Otf = CF_3SO_3) with the appropriate sodium salt NaX to yield the corresponding $[NiX(R^1R^2NCN')]$. This method can be used when other means to vary the halide substituent in the nickel complexes (vide infra) do not yield the desired complexes analytically pure. $[Ni(R^1R^2NCN')(OH_2)]Otf$ is obtained from the reaction of $[NiBr(R^1R^2NCN')]$ (derived from method A, B, or C) with AgOtf.

Both $[NiBr(Et_2NCN')]$ (**2b**) and $[NiBr((i\text{-}Pr)MeNCN')]$ (**4b**) could, like $[NiBr(Me_2NCN')]$ (**1b**), be prepared by methods A and B. For the synthesis of **2b**, route A was somewhat better (yield of 55% vs 45%); **4b** was synthesized in 20% yield by both methods. The two compounds are orange colored, are soluble in chloroform, dichloromethane, acetone, tetrahydrofuran, and benzene, and are air-stable. In **2b** and **4b** the ligands are bonded to the nickel(II) center in the same way as Me_2NCN' in **1b**, i.e. terdentate with the two nitrogen donor atoms in fixed trans positions, so that the fourth coordination site occupied by the halide is trans to metal-bonded C(ipso) (see Figure 1a).

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(26) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, England, 1982; p 528.

(27) The lithiation reactions of the aryl bromides are performed in situ (see Experimental Section); that lithiation takes place indeed has been checked by isolation and characterization of some of the Li compounds, which are dimeric in solution (see ref 16). See also: Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490.

Table II. NMR Data

^{1}H NMR Data[a] for Complexes **1–8** and ^{31}P NMR Data[b] for Complexes **7** and **8** in C_6D_6

compound	δ(^{1}H) N–R^1, N–R^2	δ(^{1}H) CH$_2$	δ(^{1}H) aryl–H[c]
[NiBr(Me$_2$NCN′)] (**1b**)[d]	2.52 (s)	2.99 (s)	7.3, 6.6
[NiCl(Et$_2$NCN′)] (**2a**)	3.24 (m), 1.74 (m)[e,f]	3.14 (s)	6.92, 6.41
[NiBr(Et$_2$NCN′)] (**2b**)	3.31 (m),[g] 1.85 (m),[g] 1.69 (t)	3.21 (s)	7.15, 6.40
[NiI(Et$_2$NCN′)] (**2c**)	3.50 (m), 1.73 (m)[e,f]	3.10 (s)	6.95, 6.34
[NiBr(*i*-Pr$_2$NCN′)] (**3**)	3.21 (m),[h] 2.15 (d),[i] 0.99 (d)[i]	3.21 (s)[h]	6.96, 6.34
[NiBr((*i*-Pr)MeNCN′)] (**4b**)[j]	3.00 (s), 2.89 (s), 3.57 (m),[h] 1.92 (d), 1.88 (d), 0.35 (d)	3.57 (m),[h] 2.52, 2.37	7.04, 6.50
[NiI((*i*-Pr)MeNCN′)] (**4c**)[j]	3.04 (s), 2.94 (s), 3.70 (m),[h] 1.87 (d), 1.83 (d), 0.33 (d)	3.70 (m),[h] 2.50, 2.34	7.03, 6.46
[Ni((*i*-Pr)MeNCN′)(OH$_2$)]Otf, (**4d**)[j]	2.85 (s), 2.67 (s), 3.15 (m),[h] 1.90 (d), 1.73 (d), 0.40 (d)	3.15 (m),[h] 2.37, 2.21	6.96, 6.35
[NiBr((*t*-Bu)MeNCN′)] (**5**)[k]	2.43 (s), 1.41 (s)	3.46, 2.83[l]	7.5–6.9,[e] 6.24

compound	δ(^{1}H) N–R^1, N–R^2	δ(^{1}H) CH$_2$	δ(^{1}H) aryl–H	δ(^{1}H) P–R	δ(^{31}P)
[NiBr((*t*-Bu)MeNCN′)(PMe$_3$)$_2$] (**7a**)	2.33 (s), 1.20 (s)	4.29 (s)	7.3 (m)	0.99[m]	−15.40
[NiBr(*t*-Bu)MeNCN′)(PEt$_3$)$_2$] (**7b**)	2.34 (s), 1.28 (s)	4.49 (s)	7.4 (m)	1.3 (m)	6.99
[NiCl((Ph)MeNCN′)(PEt$_3$)$_2$] (**8a**)	2.91 (s)	5.36 (s)	7.1 (m)	1.2 (m)	7.74
[NiBr((Ph)MeNCN′)(PEt$_3$)$_2$] (**8b**)	2.90 (s)	5.29 (s)	7.1 (m)	1.2 (m)	7.61
[NiI((Ph)MeNCN′)(PEt$_3$)$_2$] (**8c**)	2.89 (s)	5.22 (s)	7.1 (m)	1.2 (m)	8.31
[NiBr((Ph)MeNCN′)(PMe$_3$)$_2$] (**8d**)	2.76 (s)	5.00 (s)	7.1 (m)	0.94[n]	−15.93
[NiBr((Ph)MeNCN′)(PBu$_3$)$_2$] (**8e**)	2.99 (s)	5.42 (s)	7.1 (m)	1.3 (m)	2.14

(b) ^{1}H NMR Data[a] for Complexes **2d**, **3**, **4b**, and **4d** in $CDCl_3$

compound	N–R^1, N–R^2	CH$_2$	aryl–H[c]
[Ni(Et$_2$NCN′)(OH$_2$)]Otf (**2d**)[j]	3.04 (m), 2.35 (m), 1.86 (t)[o]	3.72 (s)	6.92; 6.50
[NiBr(*i*-Pr$_2$NCN′)] (**3**)	3.14 (sp), 2.18 (d), 1.29 (d)[p]	3.63 (s)	6.86; 6.40
[NiBr((*i*-Pr)MeNCN′)] (**4b**)[j]	3.20 (s), 3.15 (s), 3.39 (m), 1.96 (d), 0.90 (d)	3.92 (m), 3.12; 2.96	6.88; 6.59
[Ni(*i*-Pr)MeNCN′)(OH$_2$)]Otf (**4d**)[j]	3.20 (s), 3.10 (s), 2.89 (m), 2.06 (d), 1.95 (d), 0.99 (d), 0.97 (d)	3.95 (m), 3.04, 3.03	6.96; 6.57; 6.56

[a] δ in ppm relative to TMS. [b] δ in ppm relative to H_3PO_4; all signals are singlets. [c] The aryl protons appear as an AB$_2$ pattern with $^3J(^1H,^1H)$ = 7 Hz, unless stated otherwise. [d] Reference 7. [e] Signals not well resolved. [f] Overlapping resonances of methylene and methyl protons of ethyl groups. [g] Doublet of a quartet: $^2J(^1H,^1H)$ = 14 Hz; $^3J(^1H,^1H)$ = 7 Hz. [h] Overlapping resonances of *i*-Pr–CH and benzylic protons. [i] Doublet at δ = 2.15 ppm; $^3J(^1H,^1H)$ = 6 Hz; doublet at δ = 0.99 ppm, $^3J(^1H,^1H)$ = 6.5 Hz. [j] Two isomers; see Results. [k] Broad. [l] AB pattern, $^2J(^1H,^1H)$ = 16 Hz. [m] Apparent triplet with virtual couplings of 3 Hz. [n] Apparent triplet with virtual couplings of 3.5 Hz. [o] $^3J(^1H,^1H)$ = 7 Hz. [p] $^3J(^1H,^1H)$ = 6.5 Hz.

The preparation of [NiBr(C_6H_3{CH$_2$N(*t*-Bu)Me}$_2$-2,6)] (**5**) could be carried out by using methods A and C, but the yields were invariably very low and irreproducible. This violet complex is air-stable in the solid form, but decomposes in less than 1 h in chloroform solution and more slowly in benzene solution. The instability of **5** in solution can explain the low (and irreproducible) synthetic yields, which are indeed slightly better when the solution is worked up directly after the reaction mixture has reached room temperature (see Experimental Section).

When (*t*-Bu)MeNCN′Br was reacted with [NiBr$_2$(PEt$_3$)$_2$] by method B, not the violet complex **5** but yellow [NiBr(C_6H_3{CH$_2$N(*t*-Bu)Me}$_2$-2,6)(PEt$_3$)$_2$] (**7a**) was obtained in 40% yield. In the same way, [NiBr((*t*-Bu)MeNCN′)(PMe$_3$)$_2$] (**7b**) was synthesized in 90% yield by using [NiBr$_2$(PMe$_3$)$_2$]. Complexes **7a** and **7b** (see Figure 1) are both air-stable and stable as solutions in diethyl ether, chloroform, dichloromethane, and acetone.

Complex **7b** does not undergo reactions with trialkylphosphines such as PMe$_3$ and PEt$_3$ at room temperature or with PEt$_3$ at reflux in toluene. This result is discussed later.

Method B can be employed to prepare [NiBr((Ph)MeNCN′)(PR$_3$)$_2$] (R = Et (**8b**); R = Me (**8d**); R = Bu (**8e**)) starting from 2,6-{(Ph)MeNCH$_2$}$_2$C$_6$H$_3$Br and [NiBr$_2$(PR$_3$)$_2$]. Complexes **8** are, like the phosphine complexes **7**, soluble in diethyl ether, chloroform, dichloromethane, and acetone but they are slightly air-sensitive and can best be stored under nitrogen.

In all complexes accessible by method B, variation of the halide ligand is possible through the choice of the appropriate starting material [NiX$_2$(PR$_3$)$_2$] (X = Cl, Br, I). In this way, [NiX(Et$_2$NCN′)] (X = Cl (**2a**); X = I (**2c**)) and [NiX((Ph)MeNCN′)(PEt$_3$)$_2$] (X = Cl (**8a**); X = I (**8c**)) were synthesized. A second way of introducing various halide ligands is method D (vide supra), but then only with complexes in which the R^{1}R^{2}NCN′ ligand is bonded in the terdentate mode.

Method C was used with the intention of synthesizing complexes of the type [Ni(Acac)(R^{1}R^{2}NCN′)]. Instead, starting from Et$_2$NCN′Br and (*t*-Bu)MeNCN′Br, this method afforded the bromide complexes **2b** and **5** in poor yields of 20 and 5%, respectively. Although method C is not very useful for the synthesis of **2b** and **5** (they can be obtained in higher yields by methods A and B), it is useful for the synthesis of [NiBr(C_6H_3{CH$_2$N(*i*-Pr)$_2$}$_2$-2,6)] (**3**). By this method, **3** was obtained in 18% yield as a violet solid. The complex is soluble in chloroform, dichloromethane, acetone, and benzene. Reaction of 2,6-{(*i*-Pr)$_2$NCH$_2$}$_2$C$_6$H$_3$Br with [Ni(COD)$_2$] did not afford **3**. Although **3** can be made by method B, it proved difficult to separate it from the starting complex [NiBr$_2$(PEt$_3$)$_2$].

The nickel(II) complexes [NiBr(Et$_2$NCN′)] (**2b**) and [NiBr((*i*-Pr)MeNCN′)] (**4b**) can be oxidized by dibromine (0.5 equiv) affording the novel Ni(III) species [NiBr$_2$(Et$_2$NCN′)] (**9**) and [NiBr$_2$((*i*-Pr)MeNCN′)] (**10**) (see eq 3 and Figure 1). Complex

$$[\mathrm{Ni^{II}Br(R^1R^2NCN')}] + 0.5\mathrm{Br_2} \rightarrow [\mathrm{Ni^{III}Br_2(R^1R^2NCN')}] \quad (3)$$

9 was not obtained when 1 equiv of CuBr$_2$ was added to **2b**; this result stands in contrast to the finding that the oxidation of the nickel center in [NiBr(Me$_2$NCN′)] (**1b**) is achieved more easily with CuBr$_2$ than with Br$_2$[7]. When **2b** and **4b** are treated with 1 equiv of I$_2$, no oxidation takes place, and after workup, the complexes are recovered unchanged. In solution, however, there exists an interaction between molecules of **2b** and **4b** and molecules of diiodine (see Discussion).

Reaction of the tertiary phosphine complex [NiBr((Ph)MeNCN′)(PEt$_3$)$_2$] (**8b**) with Br$_2$ afforded, instead of a Ni(III) oxidation product, the species [NiBr$_2$(PEt$_3$)$_2$] and (Ph)MeNCN′Br (identified by ^{1}H NMR).

B. Characterization of the Complexes: Interpretation of the Spectroscopic Data and Behavior of the Complexes in Solution. Characterization of the new complexes (**2–5**, **7**, **8**) has been achieved by elemental analyses and FD/FI mass spectrometry (see Experimental Section), and ^{1}H, ^{31}P, and ^{13}C NMR (Tables II and III), and UV/Vis spectroscopy (Table IV). Three of the complexes were characterized crystallographically (**4b**, **5**, and **8b**; vide infra, Results, section C). The ^{1}H NMR data in particular give valuable information on the geometrical structure of these complexes in solution.

Table III. ^{13}C NMR Data[a] of Complexes **2c** (in CD_2Cl_2), **3**, and **4b** (in $CDCl_3$)

compound	N–R^1, N–R^2	CH_2	aryl–H
[NiBr(Et_2NCN′)] (**2b**)	(H_2)C, 57.58; (H_3)C, 13.71	65.69	149.65, 147.09, 124.38, 117.26
[NiBr(*i*-Pr_2NCN′)] (**3**)	(N)C(H), 58.69; (HC)C(H_3), 24.10, 19.13	59.63	150.50, 138.85, 124.05, 115.86
[NiBr((*i*-Pr)MeNCN′)] (**4b**)[b]	(N)C(H), 57.40, 57.24; (N)C(H_3), 47.52, 46.86; (HC)C(H_3), 23.05, 22.53, 12.26, 12.01	61.60, 61.48	148.31, 148.17, 145.29, 144.67, 124.47, 124.16, 118.15, 117.91

[a] δ in ppm relative to TMS. [b] Two isomers; see Results section B.

Table IV. UV Data[a] for Complexes **1–8**

compound	λ_{max} (ϵ)
[NiBr(Me_2NCN′)] (**1b**)	306.6 (3980), 459.0 (310)
[NiCl(Et_2NCN′)] (**2a**)	302.1 (4360), 454.4 (410)
[NiBr(Et_2NCN′)] (**2b**)	299.1 (4290), 459.0 (320)
[NiI(Et_2NCN′)] (**2c**)	275.8 (15980), 470.1 (300)
[NiBr(*i*-Pr_2NCN′)] (**3**)	293.8 (4600), 498.8 (300)
[NiBr((*i*-Pr)MeNCN′)] (**4b**)	300.6 (4760), 469.5 (370)
[NiI((*i*-Pr)MeNCN′)] (**4c**)	289.3 (12600), 482.3 (350)
[Ni((*i*-Pr)MeNCN′)(OH_2)]Otf (**4d**)	286.3 (5100), 442.5 (400)
[NiBr((*t*-Bu)MeNCN′)] (**5**)	265.3 (10360), 516.1 (280)

[a] λ_{max} in nm; ϵ in L mol^{-1} cm^{-1}; measured in CH_2Cl_2.

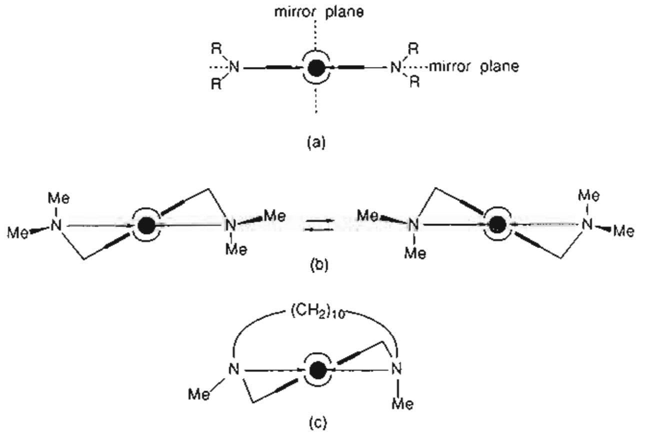

Figure 2. (a) Theoretically possible mirror-plane structure of [NiX(R^{1}R^{2}NCN′)]. (b) Interconversion of the cyclometalated rings of [PtBr(Me_2NCN′)] by wagging about Pt–C(ipso). (c) Square-planar Pt(II) complex containing a terdentate macrocyclic ligand.[16]

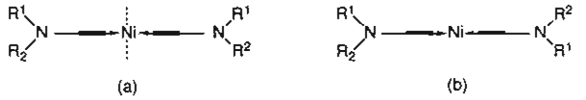

Figure 3. Time-averaged schematic structures of [NiX(R^{1}R^{2}NCN′)] (provided there is a fast ring-flip process as described in Figure 2b, vide supra): (a) *meso* compound, (b) *RR* (*SS*) diastereomer (--- = mirror plane).

General Features of the ^{1}H NMR Spectra of Complexes [NiX(R^{1}R^{2}NCN′)]. The ^{1}H NMR spectra of complexes of the type [NiX(R_2NCN′)] show one set of resonances for the aryl, the benzylic, and the R group protons (vide infra), i.e. there is magnetic equivalency of the four R groups and of the four benzylic protons. This can be interpreted in two ways: (i) The R substituents on each nitrogen possess the same chemical environment and the two cyclometalated rings are coplanar with the aryl ring. In such an unlikely strained structure, see Figure 2a, the molecule possesses a mirror plane through the aryl plane perpendicular to the coordination plane. (ii) The situation is comparable to that in related square-planar complexes [MX(Me_2NCN′)] (M = Ni, Pd, Pt; X = Cl, Br, I).[7,28a,b] In the solid-state structure of [PtBr(Me_2NCN′)][29] there is also puckering in the two cyclometalated rings of the "2-fold axis" type; this results in two different positions for the Me substituents with one benzylic carbon held below and the second benzylic carbon held above the coordination plane (see Figure 2b). However, in solution at 190 K, the ^{1}H NMR spectrum of this complex merely exhibits singlet patterns for both the Me and the CH_2 protons, and it can therefore be concluded that there is a fast intramolecular process involving conformational interconversion of the cyclometalated rings (Figure 2b). For the platinum complex shown in Figure 2c, the ligand system is more rigid and the different positions of the Me substituents and the benzylic protons are reflected in its ^{1}H NMR spectra at temperatures below 203 K (in CD_2Cl_2); there are then two singlets for the Me groups and four doublets for the benzylic protons.[30]

In complexes [NiX(R^{1}R^{2}NCN′)] with different R substituents on each N atom, two additional features are encountered. First, in these complexes with stable Ni–N interactions the N atoms are chiral centers and in principle four stereoisomers are possible: the enantiomeric pair *RS*/*SR* and the enantomeric pair *RR*/*SS*. Since both N atoms have the same substituents, the *RS* and the *SR* enantiomers are the same; when ring inversion is fast on the NMR time scale, this is the *meso* compound with an apparent internal mirror plane (Figure 3a). The *RR*/*SS* diastereomers can not be distinguished from each other by NMR; one of these diastereomers is shown, as a time-averaged schematic solution structure, in Figure 3b. The second feature is that the two protons of each benzylic group are inequivalent, independent of both the symmetry of the compound and of possible fluxional processes involving the five-membered cyclometalated rings described above.

^{1}H NMR Spectra of the Complexes 2–8 and ^{31}P NMR Spectra of 7 and 8. In the 250-MHz ^{1}H NMR spectrum of [NiBr(C_6H_3{CH_2NEt_2}$_2$-2,6)] (**2b**) in C_6D_6 the two methylene protons of each ethyl group are nonequivalent;[31] the resonances of the NCH_2Me protons occur at δ = 3.31 and 1.85 ppm with a geminal coupling of 14 Hz and vicinal couplings (with the NCH_2CH_3 protons) of 7 Hz. This nonequivalence is direct evidence for nickel–nitrogen interactions that are stable on the NMR time scale; i.e., inversion of the nitrogen atom is prevented. The interpretation of the ^{1}H NMR spectrum was confirmed by a 2D ^{1}H–^{13}C correlated spectrum, which showed that the proton resonances at δ = 3.31 and 1.85 ppm are both associated with the single methylene carbon ^{13}C resonance at δ = 57.58 ppm. The spectra of **2a**, **2c**, and **2d** are more readily interpreted if recorded in $CDCl_3$ rather in C_6D_6 solution since the NCH_2CH_3 signals do not then overlap with the signals of four of the NCH_2H_3 protons (see Table II).

The ^{1}H NMR spectrum of [NiBr(C_6H_3{CH_2N(*i*-Pr)$_2$}$_2$-2,6)] (**3**) in $CDCl_3$ shows the *i*-Pr NC*H* protons as a septet at δ = 3.14 ppm and two methyl group doublets at δ = 2.18 and 1.29 ppm with $^3J(^1H,^1H)$ = 6.5 Hz. The Me groupings are diastereotopic as a result of the stable Ni–N interactions. The benzylic protons are seen as a singlet at δ = 3.63 ppm.

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(28) Examples of square-planar (a, b, refs 6 and 26), octahedral (c), and square-pyramidal complexes with the Me_2NCN′ ligand: (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Vrieze, K.; Niemann, L. C.; Stam, C. H. *J. Chem. Soc., Dalton Trans.* **1986**, 717. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285. (c) Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882. (d) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010. (e) Terheijden, J.; van Koten, G.; Mul, W. P.; Stufkens, D. J.; Muller, F.; Stam, C. H. *Organometallics* **1986**, *5*, 519.

(29) Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, C. H. *J. Organomet. Chem.* **1986**, *315*, 401.

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The situation with the ^{1}H NMR spectra of the complexes [NiX((*i*-Pr)MeNCN′)] (X = Cl (**4a**); X = Br (**4b**); X = I (**4c**); X = (OH_2)Otf) (**4d**) is more complicated. As in **3**, the Me groups of the *i*-Pr substituents are diastereotopic (as described above). One therefore expects the following resonances for the two NMR distinguishable diastereomers (i.e. the *RS*/*SR* and *RR*/*SS* pairs): two AB_2 patterns for the aryl protons, two AB/AX patterns for the benzylic protons, two singlets for the N–Me protons, four doublets for the *i*-Pr methyl group protons (doublet structure is due to coupling with the NC*H*Me_2 proton), and two septets (or quartets of quartets) for the *i*-Pr NC*H*Me_2 protons. The spectrum of **4d** in $CDCl_3$ at room temperature is consistent with this expectation. The aromatic protons appear as a triplet at $\delta = 6.96$ ppm with two doublets at $\delta = 6.57$ and 6.56 ppm (the AB_2 patterns overlap). There are two singlets for the N–Me protons of the two isomers ($\delta = 3.20$ and 3.10 ppm). Four doublets are seen for the *i*-Pr Me protons at $\delta = 2.06$, 1.95, 0.99, and 0.97 ppm, while the signal for the *i*-Pr CH protons is found at 2.89 ppm as a multiplet. The benzylic protons do not appear as two AB/AX patterns but as a multiplet at $\delta = 3.95$ ppm and two singlets at $\delta = 3.04$ and 3.03 ppm. Only in the spectrum of **4d** in toluene-d_8 at room temperature are the benzylic protons observed in the form of two AB patterns. In the spectra of other complexes of type **4** in $CDCl_3$ or C_6D_6 more signals coincide: diastereotopicity of the *i*-Pr methyl groups is not always seen, and the aryl protons show only one AB_2 pattern (see Table II). In all solutions, the diastereomers (*RR*/*SS* and the meso compound *RS*/*SR*) are present in a 1:1 molar ratio.

The ^{13}C NMR spectrum of **4b** in $CDCl_3$ (see Table III) shows, as expected for the two diastereomers, two sets of peaks. In the 2D COSY ^{1}H–^{13}C correlated spectrum of **4b** in $CDCl_3$, the ^{13}C Me group resonances at $\delta = 23.05$ and 22.53 ppm correlate with one ^{1}H NMR doublet at $\delta = 1.96$ ppm, and those at $\delta = 12.26$ and 12.01 ppm correlate with the other ^{1}H NMR doublet at $\delta = 0.90$ ppm. Thus, although the diastereotopicity of the *i*-Pr Me groups within one diastereomer is not evident in the 1D ^{1}H NMR spectrum, it is evident in the ^{13}C NMR spectrum.

Furthermore, the 2D^{1}H–^{13}C spectrum confirms the interpretation of the ^{1}H (1D) spectrum and shows that the signals at $\delta = 3.92$, 3.12, and 2.96 ppm correlate with the resonances of the benzylic carbons at $\delta = 61.60$ and 61.48 ppm and that the proton signals at $\delta = 3.39$ ppm correlate with the *i*-Pr C(H) resonances at $\delta = 57.40$ and 57.24 ppm. This situation, where two AB patterns are expected for the benzylic protons but are not observed (vide supra), is comparable to that found in the spectrum of **4d**.

The ^{1}H NMR spectrum of **4b** is temperature independent in the range 183 (CD_2Cl_2) to 333 K ($CDCl_3$), and fluxionality involving the chelate rings is thus fast on the NMR time scale.

The spectrum of [NiBr(C_6H_3{CH_2N(*t*-Bu)Me}$_2$-2,6)] (**5**) in C_6D_6 shows singlets at $\delta = 1.41$ and 2.43 ppm for the *t*-Bu and the Me protons and a single benzylic AB pattern at $\delta = 2.83$ and 3.46 ppm with $^2J(^1H,^1H) = 16$ Hz. It seems, in contrast to the situation with complexes **4b–d**, that **5** is present in solution as only one diastereomer. Furthermore, the signals in the spectrum of **5** are broadened, most probably as a result of tetrahedral distortion of the square-planar geometry (see Discussion) and instability of **5** in solution (see Results A).

The ^{1}H NMR spectra of complexes **7** and **8** containing tertiary phosphine ligands are straightforward. They show singlets for the benzylic and the *N*-methyl protons at chemical shifts that are downfield with respect to the resonances of the corresponding aryl bromides 2,6-{$R^1R^2NCH_2$}$_2C_6H_3Br$. The spectra of complexes **7b** and **8d** show apparent triplets for the P–Me protons with virtual couplings of 3 and 4 Hz, respectively.[32] In the series **8d–8b–8e** the chemical shifts of the *N*-methyl and the benzylic protons are shifted downfield with increasing size of the phosphorus substituents. The ^{31}P spectra of all these complexes display singlets confirming the trans-P arrangement which is always found in complexes [NiR_2L_2] and [$NiRXL_2$] with R = organo, X = halide, and L = phosphorus ligands.[1b]

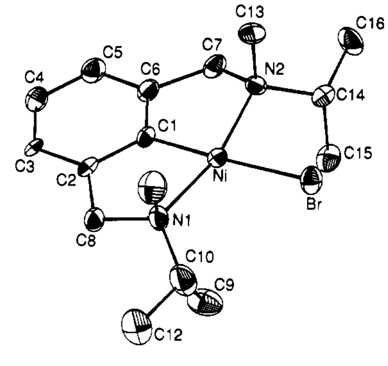

Figure 4. ORTEP drawing and adopted numbering scheme of [NiBr(C_6H_3{CH_2N(*i*-Pr)Me}$_2$-2,6)] (**4b**).

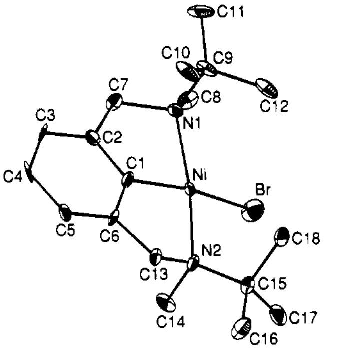

Figure 5. ORTEP drawing and adopted numbering scheme of [NiBr(C_6H_3{CH_2N(*t*-Bu)Me}$_2$-2,6)] (**5**).

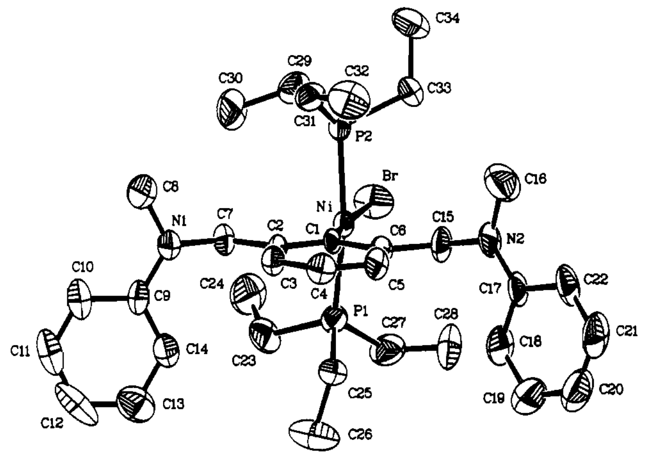

Figure 6. ORTEP drawing and adopted numbering scheme of [NiBr(C_6H_3{CH_2N(Ph)Me}$_2$-2,6)(PEt_3)$_2$] (**8b**).

Mass Spectrometry, ESR, and UV Spectroscopic Data. The FI-MS spectra of **7a**, **7b**, **8a**, **8d**, and **8e** indicate cleavage of the PR_3 ligands under the conditions used and show the presence of [NiX((Ph)MeNCN′)]$^+$ (**6**) in the gas phase. However, we were not able to synthesize the corresponding neutral phosphine-free complexes [NiX((Ph)MeNCN′)].

The paramagnetic complexes [$NiBr_2$(Et_2NCN′)] (**9**) and [$NiBr_2$((*i*-Pr)MeNCN′)] (**10**) afford ESR data that are similar to those obtained for the complexes [NiX_2(Me_2NCN′)] (X = Cl, Br, I).[8] At room temperature in toluene or diglyme solution, the spectra show broad isotropic signals, but in a diglyme glass at 193 K, three *g* values are found: $g_x = 2.38$, $g_y = 2.15$, and $g_z = 2.01$ for **9** and $g_x = 2.38$, $g_y = 2.17$ and $g_z = 2.02$ for **10**. The g_z signals show hyperfine coupling by a single Br atom of 126 and 125 G for **9** and **10**, respectively (hyperfine splitting due to the two isotopes of Br was not resolved). As in the case of [NiX_2(Me_2NCN′)] (X = Cl, Br), these data imply that the single electron is mainly located in the d_{z^2} orbital.[8]

The UV/vis spectra of complexes **1–5** show an intense absorption in the region $\lambda = 275$–300 nm originating from the aryl

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[32] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979.

Table V. Bond Lengths (Å) and Angles (deg) for **4b**[a]

Ni-Br	2.437 (2)	C6-C7	1.51 (2)
Ni-C1	1.83 (1)	C7-N2	1.52 (2)
Ni-N1	1.99 (1)	C8-N1	1.49 (2)
Ni-N2	2.01 (1)	C9-C10	1.54 (3)
C1-C2	1.40 (2)	C10-C12	1.56 (3)
C1-C6	1.38 (2)	C10-N1	1.43 (2)
C2-C3	1.36 (2)	C11-N1	1.64 (2)
C2-C8	1.49 (2)	C13-N2	1.48 (2)
C3-C4	1.36 (2)	C14-C15	1.51 (2)
C4-C5	1.39 (2)	C14-C16	1.53 (2)
C5-C6	1.37 (2)	C14-N2	1.50 (2)
Br-Ni-C1	176.6 (4)	C2-C8-N1	109.9 (12)
Br-Ni-N1	95.9 (3)	C9-C10-C12	114.9 (17)
Br-Ni-N2	96.0 (3)	C9-C10-N1	101.7 (14)
C1-Ni-N1	84.2 (5)	C12-C10-N1	115.8 (16)
C1-Ni-N2	83.5 (5)	C15-C14-C16	112.2 (12)
N1-Ni-N2	165.8 (5)	C15-C14-N2	110.5 (12)
Ni-C1-C2	119.4 (9)	C16-C14-N2	113.8 (11)
Ni-C1-C6	120.4 (10)	Ni-N1-C8	111.9 (8)
C2-C1-C6	120.1 (12)	Ni-N1-C10	116.9 (11)
C1-C2-C3	119.6 (12)	Ni-N1-C11	104.1 (9)
C1-C2-C8	113.2 (12)	C8-N1-C10	111.9 (13)
C3-C2-C8	127.2 (13)	C8-N1-C11	109.5 (12)
C2-C3-C4	119.7 (14)	C10-N1-C11	101.6 (12)
C3-C4-C5	121.5 (14)	Ni-N2-C7	111.3 (8)
C4-C5-C6	119.0 (13)	Ni-N2-C13	101.4 (7)
C1-C6-C5	120.1 (13)	Ni-N2-C14	114.9 (8)
C1-C6-C7	113.9 (12)	C7-N2-C13	106.8 (10)
C5-C6-C7	126.0 (12)	C7-N2-C14	110.0 (9)
C6-C7-N2	107.0 (10)	C13-N2-C14	111.9 (11)

[a] Standard deviations in parentheses.

Table VI. Bond Distances (Å) and Angles (deg) for **5**[a]

Ni1-Br1	2.4459 (30)	C7-N1	1.543 (25)
Ni1-C1	1.825 (17)	C8-N1	1.490 (24)
Ni1-N1	2.060 (12)	C9-C10	1.501 (29)
Ni1-N2	2.105 (13)	C9-C11	1.518 (25)
C1-C2	1.378 (26)	C9-C12	1.562 (32)
C1-C6	1.384 (21)	C9-N1	1.559 (21)
C2-C3	1.411 (23)	C13-N2	1.524 (22)
C2-C7	1.487 (22)	C14-N2	1.485 (22)
C3-C4	1.389 (25)	C15-C16	1.542 (27)
C4-C5	1.393 (30)	C15-C17	1.565 (24)
C5-C6	1.402 (21)	C15-C18	1.549 (23)
C6-C13	1.442 (28)	C15-N2	1.530 (26)
Br1-Ni1-C1	162.2 (6)	C11-C9-C12	111.7 (15)
Br1-Ni1-N1	95.7 (4)	C11-C9-N1	111.8 (17)
Br1-Ni1-N2	98.7 (4)	C12-C9-N1	105.9 (13)
C1-Ni1-N1	83.4 (7)	C6-C13-N2	109.2 (15)
C1-Ni1-N2	83.5 (7)	C16-C15-C17	105.9 (15)
N1-Ni1-N2	165.3 (6)	C16-C15-C18	109.6 (17)
Ni1-C1-C2	120.6 (13)	C16-C15-N2	113.6 (14)
Ni1-C1-C6	118.6 (14)	C17-C15-C18	108.7 (14)
C2-C1-C6	120.5 (15)	C17-C15-N2	111.4 (16)
C1-C2-C3	120.4 (15)	C18-C15-N2	107.5 (14)
C1-C2-C7	112.2 (15)	Ni1-N1-C7	105.2 (8)
C3-C2-C7	127.4 (17)	Ni1-N1-C8	114.0 (10)
C2-C3-C4	119.2 (17)	Ni1-N1-O9	111.5 (11)
C3-C4-C5	119.9 (15)	C7-N1-C8	106.2 (15)
C4-C5-C6	120.3 (16)	C7-N1-C9	110.1 (12)
C1-C6-C5	119.4 (16)	C8-N1-C9	109.6 (12)
C1-C6-C13	116.0 (14)	Ni1-N2-C13	105.9 (10)
C5-C6-C13	124.1 (15)	Ni1-N2-C14	105.3 (12)
C2-C7-N1	110.6 (15)	Ni1-N2-C15	120.4 (9)
C10-C9-C11	110.2 (16)	C13-N2-C14	105.0 (13)
C10-C9-C12	106.5 (19)	C13-N2-C15	109.5 (14)
C10-C9-N1	110.6 (12)	C14-N2-C15	109.6 (13)

[a] Standard deviations in parentheses.

Table VII. Bond Distances (Å) and Angles (deg) for **8b**[a]

Br-Ni	2.3738 (12)	C4-C5	1.389 (9)
Ni-P1	2.234 (2)	C5-C6	1.400 (9)
Ni-P2	2.226 (2)	C6-C15	1.520 (10)
Ni-C1	1.908 (6)	C9-C10	1.394 (10)
P1-C23	1.866 (8)	C9-C14	1.390 (11)
P1-C25	1.816 (8)	C10-C11	1.371 (11)
P1-C27	1.815 (7)	C11-C12	1.348 (13)
P2-C29	1.834 (9)	C12-C13	1.391 (13)
P2-C31	1.847 (6)	C13-C14	1.397 (12)
P2-C33	1.830 (6)	C17-C18	1.370 (12)
N1-C7	1.444 (9)	C17-C22	1.407 (12)
N1-C8	1.437 (10)	C18-C19	1.398 (14)
N1-C9	1.384 (8)	C19-C20	1.365 (15)
N2-C15	1.464 (10)	C20-C21	1.348 (14)
N2-C16	1.446 (11)	C21-C22	1.367 (14)
N2-C17	1.370 (11)	C23-C24	1.466 (13)
C1-C2	1.403 (8)	C25-C26	1.528 (12)
C1-C6	1.397 (9)	C27-C28	1.511 (12)
C2-C3	1.371 (9)	C29-C30	1.516 (11)
C2-C7	1.505 (10)	C31-C32	1.479 (12)
C3-C4	1.375 (11)	C33-C34	1.546 (11)
Br-Ni-P(1)	91.03 (6)	C2-C3-C4	121.0 (6)
Br-Ni-P2	88.47 (6)	C3-C4-C5	119.9 (6)
Br-Ni-C1	171.04 (19)	C4-C5-C6	119.3 (7)
P1-Ni-P2	171.26 (9)	C1-C6-C5	121.1 (6)
P1-Ni-C1	90.50 (18)	C1-C6-C15	120.0 (6)
P2-Ni-C1	91.34 (18)	C5-C6-C15	118.9 (6)
Ni-P1-C23	112.6 (3)	N1-C7-C2	116.4 (6)
Ni-P1-C25	117.9 (2)	N1-C9-C10	121.8 (7)
Ni-P1-C27	116.9 (3)	N1-C9-C14	120.4 (6)
C23-P1-C25	102.0 (3)	C10-C9-C14	117.8 (6)
C23-P1-C27	101.6 (4)	C9-C10-C11	120.0 (7)
C25-P1-C27	103.6 (4)	C10-C11-C12	122.7 (8)
Ni-P2-C29	112.7 (2)	C11-C12-C13	118.9 (8)
Ni-P2-C31	122.4 (3)	C12-C13-C14	119.4 (8)
Ni-P2-C33	111.9 (3)	C9-C14-C13	121.1 (7)
C29-P2-C31	100.2 (4)	N2-C15-C6	116.0 (6)
C29-P2-C33	103.8 (4)	N2-C17-C18	123.4 (8)
C31-P2-C33	103.8 (3)	N2-C17-C22	121.7 (7)
C7-N1-C8	117.5 (6)	C18-C17-C22	114.9 (8)
C7-N1-C9	121.9 (5)	C17-C18-C19	123.5 (9)
C8-N1-C9	119.7 (6)	C18-C19-C20	119.4 (9)
C15-N2-C16	117.5 (7)	C19-C20-C21	118.3 (10)
C15-N2-C17	121.0 (6)	C20-C21-C22	122.9 (9)
C16-N2-C17	121.2 (7)	C17-C22-C21	121.0 (8)
Ni-C1-C2	124.3 (5)	P1-C23-C24	116.3 (6)
Ni-C1-C6	118.0 (4)	P1-C25-C26	116.3 (6)
C2-C1-C6	117.7 (5)	P1-C27-C28	114.2 (5)
C1-C2-C3	121.0 (6)	P2-C29-C30	114.2 (6)
C1-C2-C7	119.1 (5)	P2-C31-C32	116.7 (6)
C3-C2-C7	119.8 (6)	P2-C33-C34	116.1 (6)

[a] Standard deviations in parentheses.

Table VIII. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of **4b**

	x	*y*	*z*	*U*(eq), Å^2
Ni	0.02646 (13)	0.27930 (11)	0.58020 (14)	0.0429 (9)
Br	−0.14417 (12)	0.18338 (12)	0.59529 (13)	0.0667 (10)
C1	0.1488 (10)	0.3566 (9)	0.5643 (11)	0.045 (7)
C2	0.2022 (12)	0.3503 (9)	0.4551 (12)	0.054 (8)
C3	0.2858 (12)	0.4135 (8)	0.4369 (13)	0.053 (8)
C4	0.3172 (13)	0.4820 (11)	0.5253 (15)	0.070 (10)
C5	0.2675 (13)	0.4879 (11)	0.6356 (14)	0.068 (10)
C6	0.1838 (13)	0.4242 (9)	0.6545 (12)	0.058 (9)
C7	0.1245 (13)	0.4178 (10)	0.7707 (13)	0.061 (9)
C8	0.1599 (13)	0.2697 (10)	0.3720 (14)	0.067 (9)
C9	0.1336 (17)	0.0959 (15)	0.5104 (17)	0.099 (14)
C10	0.0468 (18)	0.1300 (15)	0.3954 (18)	0.112 (15)
C11	−0.0621 (19)	0.2641 (15)	0.3130 (15)	0.108 (15)
C12	0.0700 (20)	0.0927 (15)	0.2635 (19)	0.129 (17)
C13	−0.0797 (13)	0.4243 (10)	0.6823 (14)	0.068 (10)
C14	−0.0119 (12)	0.3060 (9)	0.8476 (13)	0.058 (9)
C15	0.0707 (12)	0.2248 (11)	0.8782 (13)	0.067 (10)
C16	−0.0176 (15)	0.3680 (14)	0.9637 (13)	0.086 (12)
N1	0.0528 (10)	0.2295 (8)	0.4119 (11)	0.068 (8)
N2	0.0153 (9)	0.3588 (8)	0.7336 (8)	0.050 (6)

part of the R^{1}R^{2}NCN′ ligand system. Furthermore, complexes **2** show absorptions in the region λ = 450–470 nm (MLCT bands) and **7** and **8** show absorptions in the region 380–400 nm originating from d–d transitions.

C. Description of the Structures of [NiBr(C$_6$H$_3${CH$_2$N(*i*-Pr)Me}$_2$-2,6)] (4b), [NiBr(C$_6$H$_3${CH$_2$(*t*-Bu)Me}$_2$-2,6)] (5) and

Table IX. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of **5**

	x	*y*	*z*	*U*(eq), Å^2
Ni1	0.19621 (14)	0.09501 (15)	0.44415 (19)	0.0275 (9)
Br1	0.22571 (22)	0.28014 (17)	0.46180 (24)	0.0763 (15)
C1	0.1369 (13)	−0.0306 (12)	0.4345 (16)	0.036 (10)
C2	0.1249 (12)	−0.0727 (13)	0.5413 (15)	0.036 (9)
C3	0.0729 (13)	−0.1666 (11)	0.5311 (17)	0.037 (10)
C4	0.0302 (11)	−0.2138 (12)	0.4110 (20)	0.044 (11)
C5	0.0455 (12)	−0.1724 (11)	0.3045 (18)	0.037 (10)
C6	0.0959 (12)	−0.0783 (10)	0.3151 (15)	0.028 (8)
C7	0.1719 (14)	−0.0084 (12)	0.6590 (15)	0.039 (10)
C8	0.2464 (17)	0.1606 (14)	0.7185 (17)	0.052 (13)
C9	0.3576 (12)	0.0214 (13)	0.6919 (16)	0.041 (10)
C10	0.3574 (14)	−0.0815 (17)	0.6316 (23)	0.075 (13)
C11	0.4010 (19)	0.0124 (18)	0.8384 (18)	0.073 (14)
C12	0.4235 (14)	0.0936 (20)	0.6428 (22)	0.074 (14)
C13	0.1202 (14)	−0.0325 (14)	0.2125 (17)	0.045 (11)
C14	0.0418 (13)	0.1320 (16)	0.1923 (20)	0.053 (12)
C15	0.2072 (13)	0.1204 (11)	0.1671 (15)	0.032 (9)
C16	0.1780 (19)	0.0725 (17)	0.0315 (20)	0.070 (14)
C17	0.1953 (14)	0.2390 (15)	0.1452 (22)	0.060 (12)
C18	0.3203 (14)	0.0962 (18)	0.2495 (20)	0.062 (13)
N1	0.2483 (10)	0.0684 (11)	0.6405 (11)	0.040 (8)
N2	0.1430 (10)	0.0810 (10)	0.2414 (12)	0.037 (8)

[NiBr($C_6H_3\{CH_2N(Ph)Me\}_2$-2,6)(PEt_3)$_2$] (8b). The molecular structures of **4b**, **5**, and **8b** together with the adopted numbering schemes are shown in Figures 4–6, respectively. The bond lengths and angles are given in Table V for **4b**, in Table VI for **5**, and in Table VII for **8b**. The positional parameters are listed in Tables VIII–X for **4b**, **5**, and **8b**, respectively.

In **4** and **5**, the Ni(II) center is four-coordinate, being bonded to the C(ipso) and the two trans-positioned N atoms of the terdentate ligand system and to a bromide ligand that occupies the fourth coordination site, trans to C(ipso). Both structures are approximately square-planar with a primary distortion from the ideal geometry reflected in the N1–Ni–N2 angles of 165.8 (5)° and 165.3 (6)° for **4b** and **5**, respectively. These angles, which are considerably smaller than the ideal value of 180°, are the result of the small N–Ni–C1 bite angles imposed by the terdentate ligand system. This reduced N–M–N angle is a feature always found in molecular structures containing the ligand (2,6-$\{Me_2NCH_2\}_2C_6H_3)^-$.[28] In **4b**, there are no further significant deviations from a square-planar structure; the C1–Ni–Br angle is 176.6 (4)° and the distances of Ni, C1, N1, N2, and Br from the least-squares plane defined by these atoms are small and are less than 0.08 Å.

In contrast, **5** shows tetrahedral distortion from the ideal square-planar situation. The C1–Ni–Br angle is 162.2 (6)°, and only deviations (0.27 Å maximum) from the least-squares-plane defined by the Ni, C1, N1, N2, and Br atoms are observed.

In **8b**, the Ni(II) center is also four-coordinate with bonds to C(ipso) of the (Ph)MeNCN′ ligand, two trans-positioned P atoms of the PEt$_3$ ligands, and a bromide trans to C(ipso). Here, the geometry is, unexpectedly, also distorted square planar. The distortion can be readily seen from the angles C1–Ni–Br (171.04 (19)°) and P1–Ni–P2 (171.26 (9)°). The deviations of Ni, C1, P1, P2, and Br from the least-squares plane through these atoms are small (0.18 Å, maximum).

The most interesting structural feature in **8b** is the lack of Ni–N interactions, the Ni–N distances being greater than 4 Å. Instead, two PEt$_3$ ligands are attached to the Ni(II) center with bond lengths of 2.234 (2) and 2.226 (2) Å. These values are comparable to those found in the series of complexes *trans*-[NiR_2L_2] (R = aryl, L = PMe$_3$ or PMe$_2$Ph; Ni–P = 2.168 (2)–2.224 (1) Å)[33] and in *trans*-[NiBr(C_6F_5)(PPh_2Me)$_2$] (Ni–P = 2.2164 (13) and 2.2148 (13) Å).[34] The noncoordinated N atoms in **8b** have a planar conformation, the sum of the bond angles around them being 359.1 (6) and 359.7 (7)°.

Table X. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of **8b**

atom[a]	*x*	*y*	*z*	*U*(eq),[b] Å
Br	0.19621 (5)	0.27071 (7)	0.16238 (4)	0.0803 (4)
Ni	0.22324 (5)	0.09001 (9)	0.09983 (5)	0.0402 (3)
P1	0.23280 (10)	0.2361 (2)	0.02136 (9)	0.0518 (7)
P2	0.19608 (9)	−0.0562 (2)	0.16851 (8)	0.0445 (6)
N1	0.0998 (3)	−0.1901 (5)	−0.0844 (3)	0.058 (2)
N2	0.4516 (3)	−0.0530 (7)	0.1827 (3)	0.074 (3)
C1	0.2597 (3)	−0.0535 (5)	0.0598 (3)	0.0339 (19)
C2	0.2182 (3)	−0.1325 (5)	0.0040 (3)	0.036 (2)
C3	0.2485 (4)	−0.2317 (6)	−0.0232 (3)	0.048 (3)
C4	0.3203 (4)	−0.2584 (6)	0.0042 (3)	0.054 (3)
C5	0.3634 (4)	−0.1822 (6)	0.0593 (3)	0.053 (3)
C6	0.3327 (3)	−0.0804 (6)	0.0870 (3)	0.045 (2)
C7	0.1397 (4)	−0.1035 (7)	−0.0280 (3)	0.051 (3)
C8	0.0642 (5)	−0.3061 (8)	−0.0692 (4)	0.088 (4)
C9	0.0858 (4)	−0.1525 (7)	−0.1518 (3)	0.053 (3)
C10	0.0309 (4)	−0.2120 (8)	−0.2055 (4)	0.076 (3)
C11	0.0179 (4)	−0.1703 (9)	−0.2715 (4)	0.094 (4)
C12	0.0566 (5)	−0.0727 (9)	−0.2877 (4)	0.105 (5)
C13	0.1120 (5)	−0.0113 (9)	−0.2355 (5)	0.090 (4)
C14	0.1262 (4)	−0.0519 (7)	−0.1678 (4)	0.062 (3)
C15	0.3803 (4)	0.0023 (8)	0.1473 (4)	0.063 (3)
C16	0.4587 (5)	−0.1578 (11)	0.2334 (4)	0.112 (5)
C17	0.5079 (4)	−0.0171 (8)	0.1634 (4)	0.063 (3)
C18	0.5009 (4)	0.0599 (9)	0.1066 (5)	0.086 (4)
C19	0.5583 (5)	0.0976 (9)	0.0871 (5)	0.102 (4)
C20	0.6252 (5)	0.0541 (10)	0.1250 (5)	0.106 (5)
C21	0.6335 (5)	−0.0226 (10)	0.1809 (5)	0.096 (4)
C22	0.5779 (4)	−0.0590 (8)	0.2009 (4)	0.082 (3)
C23	0.1445 (4)	0.2863 (8)	−0.0420 (4)	0.078 (3)
C24	0.0886 (5)	0.3183 (10)	−0.0141 (5)	0.111 (5)
C25	0.2802 (4)	0.1799 (7)	−0.0338 (3)	0.060 (3)
C26	0.2729 (7)	0.2699 (9)	−0.0957 (5)	0.123 (5)
C27	0.2721 (4)	0.4010 (7)	0.0520 (4)	0.082 (3)
C28	0.3478 (4)	0.3942 (8)	0.1019 (4)	0.094 (4)
C29	0.1071 (4)	−0.0267 (7)	0.1721 (4)	0.069 (3)
C30	0.0473 (4)	−0.0361 (9)	0.1033 (4)	0.095 (4)
C31	0.1921 (4)	−0.2421 (6)	0.1538 (4)	0.062 (3)
C32	0.2610 (4)	−0.3147 (8)	0.1729 (4)	0.096 (4)
C33	0.2554 (4)	−0.0383 (7)	0.2576 (3)	0.062 (3)
C34	0.2340 (5)	−0.1182 (9)	0.3113 (4)	0.103 (4)
O1′	0.495 (2)	0.523 (3)	0.0091 (11)	0.205 (18)
C40′	0.539 (2)	0.616 (4)	0.1256 (13)	0.27 (3)
C41′	0.547 (2)	0.511 (3)	0.0777 (11)	0.18 (2)
C42′	0.489 (3)	0.417 (3)	−0.0404 (12)	0.22 (3)
C43′	0.4489 (18)	0.456 (3)	−0.1120 (11)	0.164 (19)

[a] A prime indicates an atom in the disordered diethyl ether solvate molecule. [b] *U*(eq) = one-third of the trace of the orthogonalized U.

The Ni–C1 distance in **4b** and in **5** is small (1.83 (1) and 1.825 (17) Å, respectively) and comparable to that of 1.814 (2) Å in [Ni(O_2CH)(Me_2NCN')] (**1f**).[7] This short bond appears to be the result of the terdentate bonding mode of the NCN′ ligands since in monodentate σ-C-bonded Ni(II) aryl complexes with a trans bromide ligand the Ni–C(aryl) bond distances are larger, e.g. 1.908 (6) Å in **8b** and 1.880 (4) Å in [NiBr(C_6F_5)(PPh_2Me)$_2$].[34] The Ni–C distance in alkyl- and arylnickel(II) complexes usually lies in the range 1.90–2.00 Å.[1b] As an apparent consequence of these relatively short Ni–C bond lengths in **4b** and **5** the Ni–Br distances (2.437 (2) and 2.4459 (30) Å, respectively) are larger than those found in the related complexes **8b** (2.3738 (12) Å) and [NiBr(C_6F_5)(PPh_2Me)$_2$] (2.3245 (8) Å).

In the series **1f**–**4b**–**5** the pairs of Ni–N distances become larger: 1.976 (1) and 1.973 (1) Å, 1.99 (1) and 2.01 (1) Å, and finally 2.060 (12) and 2.105 (13) Å.

The two five-membered chelate rings in all organometallic complexes with the ligand Me$_2$NCN′ bonded in the terdentate mode show a distinct puckering that in the solid state is dependent on the coordination geometry of the metal center. It is of a "2-fold axis symmetry" type in square-planar and octahedral complexes (see Figure 2b) and of a "mirror-plane symmetry" type in square-pyramidal complexes.[28] In **4b** and **5** the *i*-Pr and *t*-Bu groups, respectively, are on the same side of the coordination plane

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and the two Me groups are on the other side. The molecular structure of **4b** is the first example of a square-planar organometallic complex with a R^1R^2NCN' ligand in which an approximate "mirror-plane" type of symmetry is found. The mirror-plane symmetry can be seen from the angles which the C11–N1, C13–N2, C10–N1 and C14–N2 bonds make with the least-squares plane defined by Ni, C1, N1, N2, and Br (65, 77, 35, and 34°, respectively). The angles that the C(isopropyl)–N bonds make with this plane are the same though those that the C(methyl)–N bonds make with it differ by 12°. The benzylic carbon atoms are on the same side of the plane, their distances to it being −0.24 Å for C7 and −0.03 Å for C8.

The situation in **5** is different. The angles that the bonds C8–N1, C9–N1, C14–N2, and C15–N2 make with the least-squares plane (defined by Ni, C1, N1, N2, and Br) are 24, 69, 68, and 42°, respectively. Thus, the C(*t*-Bu)–N1 and the C(Me)–N2 bonds make the same angle as would be the case when a "2-fold axis" type of symmetry would be present (vide supra). The benzylic carbon atom positions on opposite sides of this plane also fit into the picture of a "2-fold axis" type of symmetry (although their distances to the plane are different: −0.69 Å for C7 and 0.34 Å for C13). However, this symmetry description for **5** is inappropriate for the whole molecule because the two *t*-Bu groups are on the same side of the coordination plane.

Excluding the ethyl substituents on the phosphorus atoms, **8b** has an approximate "mirror-plane type" of symmetry; the two phenyl (and methyl) substituents on nitrogen are both located on the same side of the aryl ring plane.

Discussion

Synthesis and Reactivities of the Organonickel(II) Complexes. By using methods A–D (vide supra), we have been able to synthesize a series of new organonickel(II) complexes containing the ligands $(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)^-$. In complexes **1–5**, these ligands are bonded in the terdentate mode, but in the complexes **7** and **8** (obtained by method B), they are monodentate bonded, and instead of the N atoms of R^1R^2NCN', PR_3 ligands are bonded to the metal. That intramolecular coordination, having the beneficial effect of chelation, is absent because of the presence of other ligands, has been found earlier with $[PtBr(Me_2NCN')]$[35] and $[PdCl(C_6H_3\{CH_2S(tBu)\}_2\text{-}2,6)]$:[36] addition of PPh_3 to these systems cleaves the Pt–N and the Pd–S bonds, respectively, and $M\text{–}PPh_3$ bonds are formed.

The nature of the R substituent in the PR_3 ligands can have an effect on the synthesis of the complexes,[37] on the conformation of ligands around the Ni(II) center,[33] and on the reactivity of such complexes.[37,38] Variation of R can best be achieved by the correct choice of the $[NiX_2(PR_3)_2]$ starting complexes for route B. The compounds $[NiBr_2(PR_3)_2]$ with R = Me, Et, and *n*-Bu were successfully used in syntheses with the ligand (Ph)MeNCN'Br, but with R = Ph, no well-defined products could be isolated although a reaction did take place. The bonding of an organic moiety to Ni(II) is stabilized by π-bonding ligands,[1b] and in that case complexes with PPh_3 ligands should be more stable than complexes with $P(alkyl)_3$ ligands.[39] Nevertheless, $[NiBr((Ph)MeNCN')(PPh_3)_2]$ could not be isolated, the reason probably being that steric hindrance between the ligands prevents its formation.[40]

Complexes $[NiR_2L_2]$ and $[NiRXL_2]$ (with R = organo, X = halide, and L = phosphine ligand) can react with phosphines to give five- or six-coordinate complexes,[41] decomposition,[42] or exchange processes.[43] Using ^{31}P NMR spectroscopy, we did not find a reaction of the complex $[NiBr((t\text{-Bu})MeNCN')(PMe_3)_2]$ (**7b**) with 1 equiv of PMe_3 or 2 equiv of PEt_3 at room temperature. Complex **7b** was not affected after 6 h at reflux in benzene containing 2 equiv of PEt_3.

In reaction method C, the precipitate that is formed directly after mixing the solution of the in situ generated lithium reagent and the $[Ni(Acac)_2]$ solution is Li(Acac) (identified by IR), so probably the initially formed complex is indeed $[Ni(Acac)(R^1R^2NCN')]$. The only bromine-containing species in solution is *n*-BuBr (formed in the lithiation reaction), so we conclude that it is reaction of $[Ni(Acac)(R^1R^2NCN')]$ with *n*-BuBr that produces $[NiBr(R^1R^2NCN')]$. The attempted synthesis of Ni–Acac compounds by reacting complexes $[Ni(OH_2)(R^1R^2NCN')]Otf$ ($R^1 = R^2$ = Et (**2d**); R^1 = *i*-Pr, R^2 = Me (**4d**)) with Li(Acac) in THF (in imitation of the synthesis of $[RhMe(Acac)(Me_2NCN')]$[44]) was unsuccessful.

In contrast to the oxidative additions of dibromine to $[NiBr(Me_2NCN')]$[8] (**1b**), $[NiBr(Et_2NCN')]$ (**2b**), and $[NiBr((i\text{-Pr})MeNCN')]$ (**4b**), the complexes $[NiI(Et_2NCN')]$ (**2c**) and $[NiI((i\text{-Pr})MeNCN')]$ (**4c**) do not react with 0.5 equiv of diiodine to yield Ni(III) complexes $[NiI_2(Et_2NCN')]$ and $[NiI_2((i\text{-Pr})MeNCN')]$, respectively. When mixtures of **2c** and **4c** with diiodine in CH_2Cl_2 are worked up, **2c** and **4c** are recovered unchanged.

However, addition of a violet solution of diiodine (in CH_2Cl_2) to an orange solution of **2c** or **4c** (in CH_2Cl_2) does result in an intense dark solution. This is an indication for the formation of "diiodine complexes":[45] complexes in which an diiodine molecule is η^1-bonded to the metal center, in this case to Ni(II) (see eq 4).

$$[NiI(R^1R^2NCN')] + I_2 \leftrightarrows [NiI(R^1R^2NCN')(\eta^1\text{-}I_2)] \quad (4)$$

Resonance Raman spectra afford evidence that in solution the complexes **2c** and **4c** do indeed interact with added I_2. The spectrum of the **2c**/I_2 mixture in CH_2Cl_2 shows resonances at 108, 166, and 211 cm^{-1}, and that of the **4c**/I_2 mixture shows resonances at 108, 164, and 211 cm^{-1}. The signals at 211 cm^{-1} are attributable to free I_2 in solution, the resonances at 166 and 164 cm^{-1} to a complex with η^1 coordination of a diiodine molecule to the Ni(II) center (affording the dark color of the solution), and the signal at 108 cm^{-1} to coordination of an I_2 molecule to the iodide anion, thus giving rise to a I_3^- anion. This interpretation comes from comparison with the data obtained from solutions of platinum(II) diiodine complexes.[16,28d,45]

^{1}H NMR Spectra of $[NiBr((i\text{-Pr})MeNCN')]$ (4b) and $[NiBr((t\text{-Bu})MeNCN')]$ (5). The fact that in the solid state only one isomer of **4b** is found (vide supra, Results Section C) whereas in solution two isomers are present means that in solution there must be an isomer interconversion. This can only occur when one of the Ni–N bonds is cleaved; there then follows inversion of the N atom, rotation around the $C(H_2)$–N axis, and coordination to the Ni center. On the NMR time scale, however, the Ni–N interactions are stable. Even when crystals of **4b** are dissolved at −56 °C and a ^{1}H NMR spectrum is recorded at −60 °C, one still finds the two isomers present in a 1:1 molar ratio.

The ^{1}H NMR resonances in the spectrum of **5** are broad. This can arise from (a) traces of paramagnetic material, (b) tetrahedral distortion, (c) fluxionality (e.g. the ring flip process described in Results Section B), and (d) instability of the complex in solution.

The Relative Ligand Strengths of the Various NR^{1}R^2 Donor Atoms. Reacting the ligands $R^1R^2NCN'Br$ via route B (vide

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supra, Results Section A) brings on competition between the amino donor atoms of the NCN′ system and the PR_3 ligands for binding to the Ni(II) center. Only with ((*t*-Bu)MeNCN′)$^-$ can two types of complexes, i.e. [NiBr((*t*-Bu)MeNCN′)] (**5**) and [NiBr((*t*-Bu)MeNCN′)(PR_3)$_2$] (**7**) be synthesized; the former is accessible via routes A and C (see Experimental Section). We have not been able to synthesize [NiBr((Ph)MeNCN′)], in which the ((Ph)-MeNCN′)$^-$ ligand would be bonded in the terdentate mode. Looking at the yields of the syntheses, it seems that in the complexes [NiBr(R^1R^2NCN′)] the nitrogen donor atoms become poorer ligands in the order R^1 = Me, *i*-Pr, *t*-Bu (R^2 = Me). This trend is confirmed by the values of the Ni–N distances which become larger in the order [Ni(O_2CH)(Me_2NCN′)],[7] [NiBr((*i*-Pr)MeNCN′)], [NiBr((*t*-Bu)MeNCN′)] (vide supra, Results Section C). From these data the following decreasing ligand strength order toward Ni(II) can be given for the R^1R^2N donor atoms:

$$Me_2N > Et_2N > (i\text{-}Pr)MeN > (t\text{-}Bu)MeN > (Ph)MeN$$

The place of *i*-Pr_2N is difficult to give. [NiBr(*i*-Pr_2NCN′)] (**3**) could only be isolated via route C in poor yields (vide supra), but that is not a good criterion for the ligand strength of the *i*-Pr_2NCH_2– unit. The reactions of (*i*-Pr_2NCN′Li)$_n$ (made in situ) with [$NiBr_2(PEt_3)_2$] and *i*-Pr_2NCN′Br with [Ni(COD)$_2$] are probably hampered by the steric hindrance of the reaction sites by the four large *i*-Pr groups. This ligand strength order of the R^1R^2N groups toward Ni(II) is not the same as that for the ligand strength of various R^1R^2N groups toward Pt(II), which was found to be decreasing in the order Me_2N ~ (*t*-Bu)MeN > Et_2N > (Ph)MeN > Ph_2N.[16]

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Supplementary Material Available: For the structure determinations of **4b**, **5**, and **8b**, tables of crystal data, anisotropic thermal parameters, hydrogen atom parameters, and bond distances and angles, indicating torsion angles for **8b** (13 pages); tables listing observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular
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Incorporation of Barium for the Synthesis of Heterometallic Alkoxides: Synthesis and Structures of $[BaZr_2(O^iPr)_{10}]_2$ and $Ba\{Zr_2(O^iPr)_9\}_2$

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Barium granules and barium hexamethyldisilazide tetrahydrofuranate are used as reagents for the introduction of barium in the syntheses of heterometallic zirconium isopropoxides. Reaction with 1 or 2 equiv of $Zr_2(O^iPr)_8(HO^iPr)_2$ yields $[BaZr_2(O^iPr)_{10}]_2$ and $Ba\{Zr_2(O^iPr)_9\}_2$, respectively. The structure of the former has been determined in the solid state by X-ray diffraction studies. Crystal data (−78 °C): a = 18.066 (3) Å, b = 12.549 (2) Å, c = 19.409 (3) Å, β = 94.42° with Z = 2 in the space group $P2_1/c$. The structure reveals a dimer in which all metal centers are six-coordinate. The compound is also characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. X-ray diffraction data for $Ba\{Zr_2(O^iPr)_9\}_2$ are not acceptably refined but indicate gross skeletal features in which barium is eight-coordinate, surrounded by two $Zr_2(O^iPr)_9^-$ fragments.

Introduction

Metal alkoxides are of interest in ceramics processing technology and are used in the production of oxide monometallic materials by methods such as the sol–gel process.[1] While mixtures of alkoxides have been extensively used, heterometallic alkoxides are attractive precursors to *multi*metallic oxide materials due to a potentially fixed and homogeneous control over the desired metal stoichiometry on the molecular level.[2] It is also possible that desired structural features can be carried on from the precursor to the oxide lattice.

In order to demonstrate the utility of heterometallic alkoxides as precursors to solid-state oxide materials, synthetic strategy for control of a desired metal stoichiometry must be developed. We have recently demonstrated that the proton of an alcohol adduct of a metal alkoxide provides a manipulable functional group by which to incorporate additional metal ions.[3-5]

In this paper, redox and acid–base chemistry are employed in order to incorporate barium into a zirconium isopropoxide "matrix" via the alcoholate dimer $Zr_2(O^iPr)_8(HO^iPr)_2$. The particular interest in barium arises from its occurrence in a number of high-T_c superconducting oxides, such as $YBa_2Cu_3O_7$, and the present work with zirconium serves as a testing ground for our synthetic procedure for rational linking of distinct metallic elements.

Experimental Section

All manipulations were carried out under helium or argon in a drybox and with Schlenk techniques. All solvents were dried and distilled prior to use and stored under argon. Barium granules were purchased from Alfa Products, and $Zr_2(O^iPr)_8(HO^iPr)_2$ was obtained from Aldrich Chemical Co. The compound $Ba\{N(SiMe_3)_2\}_2(THF)_2$ was made by the previously reported procedure.[6] Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer as Nujol mulls between KBr plates. NMR spectra were obtained on a Bruker AM500 instrument, with chemical shifts referenced to solvent resonances. Elemental analyses were provided by Oneida Research Services, Whitesboro, NY.

Syntheses. Method 1. For either $[BaZr_2(O^iPr)_{10}]_2$ (**1**) or $Ba\{Zr_2(O^iPr)_9\}_2$ (**2**), the appropriate amounts of $Zr_2(O^iPr)_8(HO^iPr)_2$ (0.496 and 0.576 g, respectively) and Ba granules (0.088 and 0.051 g) were loaded into a Schlenk tube. After the addition of 5 mL of THF, the zirconium isopropoxide dissolved and the solution was heated to reflux in order to activate the barium metal surface. Evolution of H_2 began after a few minutes, and the solution was then allowed to stir for 24 h at 25 °C. After this time, all of the Ba metal had disappeared, although there was an insoluble precipitate in the solution. The solution was stripped to dryness in vacuo, and the product was redissolved in pentane. The mixture was filtered, and the product was recrystallized from cold pentane. Both products are colorless, crystalline solids.

Method 2. For either $[BaZr_2(O^iPr)_{10}]_2$ (**1**) or $Ba\{Zr_2(O^iPr)_9\}_2$ (**2**), the appropriate amount of $Ba\{N(SiMe_3)_2\}_2(THF)_2$ (0.155 and 0.078 g, re-

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