Transition metal complexes of a sterically demanding diimine ligand

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Abstract: The reaction of the metal halide with the sterically demanding ligand $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2$ afforded the complexes $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2MX_2$ (X = Cl, M = Fe (2), Co (3); X = Br, M = Ni (4), M = Cu (5), Zn (6)). The species of 2 reacts with Li(OEt_2)B(C_6F_5)_4 to form the yellow adduct $[(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Fe(\mu-Cl)_2Li(OEt_2)_2][B(C_6F_5)_4]$ (7) while alkylation of 2 gave $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Fe(LCH_2SiMe_3$ (8). The species $[(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Ni(\eta^3-C_3H_5)][B(3,5-CF_3C_6H_3)_4]$ (9) was obtained from reaction of 1 with $[(\eta^3-C_3H_5)NiBr]_2$ and $[Na][B(3,5-(CF_3)_2C_6H_3)_4]$ while reaction of 4 with Super-Hydride afforded $(i-Pr_2C_6H_3N)-(C(Me)(NC_6H_3-i-Pr_2))_2NiH_2BEt_2$ (10). X-ray data are reported for 2–10. The sterically demanding nature of the ligand inhibits subsequent reactivity of these species.

Key words: sterically demanding ligands, chelate complexes, X-ray structure, diimine ligands.

Résumé : La réaction d'un halogénure métallique avec le ligand stériquement encombré $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2$ conduit à la formation des complexes $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2MX_2$ (X = Cl, M = Fe (**2**), Co (**3**); X = Br, M = Ni (**4**), M = Cu (**5**), Zn (**6**)). L'espèce **2** réagit avec le Li(OEt₂)B(C₆F₅)₄ pour former l'adduit jaune [(*i*-Pr₂C₆H₃N)(C(Me)(NC₆H₃-*i*-Pr_2))₂Fe(µ-Cl)₂Li(OEt₂)₂][B(C₆F₅)₄] (**7**) alors que l'alkylation du composé **2** conduit à la formation du complexe $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-$ *i* $-Pr_2))_2Fe(µ-Cl)_2Li(OEt₂)_2][B(C₆F₅)₄] ($ **7**) alors que l'alkylation du composé**2** $conduit à la formation du complexe <math>(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-$ *i* $-Pr_2)))_2FeClCH_2SiMe_3$ (**8**). On a obtenu l'espèce $(i-Pr_2C_6H_3N)-(C(Me)(NC_6H_3-$ *i* $-Pr_2))_2FeClCH_2SiMe_3$ (**8**). On a obtenu l'espèce $(i-Pr_2C_6H_3N)-(C(Me)(NC_6H_3-$ *i* $-Pr_2))_2FeClCH_2SiMe_3$ (**8**). On a obtenu l'espèce (*i*-Pr₂C₆H₃N)-(C(Me)(NC₆H₃-*i*-Pr_2))_2Ni(\eta^3-C_3H_5)][B(3,5-CF_3C_6H_3)_4] (**9**) par réaction du composé **1** avec le [($\eta^3-C_3H_5$)NiBr]₂ et le [Na][B(3,5-(CF_3)_2C_6H_3)_4] alors que la réaction du composé **4** avec le Super-Hydrure conduit à la formation du (*i*-Pr₂C₆H₃N)(C(Me)(NC₆H₃-*i*-Pr_2))_2NiH_2BEt₂ (**10**). On rapporte les données de diffraction des rayons X par les composés **2-10**. L'encombrement stérique du ligand inhibe toute réactivité subséquente de ces espèces.

Mots clés : ligands stériquement encombrés, complexes de chélates, structure par diffraction des rayons X, diimine ligands.

[Traduit par la Rédaction]

Introduction

Recently, much attention has focused on sterically demanding chelating ligands such as the neutral, diimine-based ligand ((C(Me)NC₆H₃-*i*-Pr₂)₂) and [HC(C(Me)NC₆H₃-*i*-Pr₂)₂]⁻ (Scheme 1). Such ligands have been utilized for late transition metal olefin polymerization catalysts, as well as for the isolation of novel low-valent Al and Ga derivatives (1–4). Mindiola and co-workers (5) have used the latter ligand to isolate the first Ti–phosphinidene complex. In our labs, we have recently been probing new bulky ligands in late transition metals (6–8) and main group chemistry (9). For example, we have recently reported the use of the bulky phosphinimine–imine ligand $(i-Pr_2C_6H_3N)C(Me)CHPPh_2$ -(NC₆H₃-*i*-Pr₂) to prepare neutral and cationic Al complexes (9), while Welch et al. (10) reported related complexes based

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on the ligand (i-Pr₂C₆H₃N)C₆H₄PPh₂(NC₆H₃-i-Pr₂). In recent efforts, we have also reported the synthesis of the sterically demanding N-aryl-imidoyl amidine ligand i- $Pr_2C_6H_3N(C(Me)NC_6H_3-i-Pr_2)_2$ and its use in the synthesis of Al-based alkyl and hydride cations.² Several previous reports have described metal complexes involving the Nimidoyl amidine systems (R = H) (11–19) and the related 2,2'-dipyridylamino ligand (20-34). Cotton et al. (31) serendipitously obtained [PhNCHN(Ph)CHNPh]CoCl₂ while the related species [(4-MePh)NCHN(4-MePh)(4-MePh)-NC]Pd(C_6F_5)₂ was reported by Uson et al. (33). Finally, Wilkinson and co-workers (32) characterized the species $(C_5Me_5)Ir[N(2,6-MeC_6H_3)CHNRCNC_6H_3(Me)CH_2]$ (R = t-Bu, 2,6-i-PrC₆H₃). In this manuscript, we report the use of this bulky ligand $i-Pr_2C_6H_3N(C(Me)NC_6H_3-i-Pr_2)_2$ in the synthesis of a series of transition metal complexes. Structural studies of these complexes are presented and discussed.

Experimental

General data

All preparations were done under an atmosphere of dry, O_2 -free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs'-type solvent purification system manufactured by Innovative Technology. Deuterated

Scheme 1. Bulking chelating ligand complexes.



solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods. ¹H, ³¹P, ¹¹B, ¹⁹F, and ¹³C NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C₆D₆ at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references and chemical shifts are reported relative to SiMe₄. ³¹P, ¹¹B, and ¹⁹F NMR spectra were referenced to external 85% H₃PO₄, BF₃·Et₂O, and CFCl₃, respectively. Combustion analyses were done in-house employing a PerkinElmer CHN analyzer. [Na][B(3,5-CF₃C₆H₃)₄] was prepared as outlined (36). LiCH₂SiMe₃ and Super-Hydride were purchased from Aldrich Chemical Co. as solutions and crystallized. The ligand (*i*-Pr₂C₆H₃N)C(Me)(NC₆H₃*i*-Pr₂)C(Me)(NC₆H₃*i*-Pr₂)(1) was prepared by published methods.²

Synthesis of $(i-\Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-\Pr_2))_2MCl_2$ (M = Fe (2), Co (3))

These compounds were prepared in a similar fashion and thus one preparation is detailed. To a solution of **1** (200 mg, 0.345 mmol) in 5 mL toluene was added FeCl₂ (43 mg, 0.345 mmol). The mixture was heated to 110 °C for 3 days after which the insoluble, off-white FeCl₂ had been replaced with a yellow solid. The toluene was then removed in vacuo and the remaining solids dissolved in approximately 10 mL CH₂Cl₂. This solution was then filtered through Celite[®] and layered with 10 mL toluene. After several days, 213 mg of bright yellow – orange crystals were isolated. **2**: Yield: 79%; magnetic susceptibility 5.79 μ_B . Anal. calcd. for C₄₀H₅₇N₃FeCl₂: C 67.99, H 8.13, N 5.95; found: C 68.22, H 8.40, N 6.00. **3**: Blue crystals. Yield: 87%; magnetic susceptibility 3.35 μ_B . Anal. calcd. for C₄₀H₅₇N₃CoCl₂: C 67.69, H 8.09, N 5.92; found: C 67.55, H 7.84, N 5.87.

Synthesis of $(i-\Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-\Pr_2))_2NiBr_2$ (4)

To a solution of **1** (1.000 g, 1.72 mmol) in 15 mL xylenes was added NiBr₂ (377 mg, 1.72 mmol). The mixture was heated to 140 °C for 3 days. This resulted in the formation of a purple solid suspended in a bright blue solution. The xylenes were then decanted, the solids washed with 2 × 10 mL pentane, and dried in vacuo to give 1.186 g of powder **4**. X-ray quality dark purple crystals were grown from a solution in CH₂Cl₂ layered with toluene. **4**: Yield: 86%; magnetic susceptibility 4.98 $\mu_{\rm B}$. Anal. calcd. for C₄₀H₅₇N₃NiBr₂: C 60.17, H 7.19, N 5.26; found: C 60.38, H 7.23, N 5.25. The decanted xylenes and pentane washings were combined and after a few weeks, a small amount of blue crystals formed. Crystallographic analysis proved this to be [CH₃C(*i*-Pr₂C₆H₃N)₂HNiBr₃][CH₃C(*i*-Pr₂C₆H₃NH)₂] resulting from a

small amount of $CH_3C(i-Pr_2C_6H_3N)_2H$ impurity in the 1 starting material.

Synthesis of $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2MBr_2$ (M = Cu (5), Zn (6))

These compounds were prepared in a similar fashion and thus one preparation is detailed. To a solution of 1 (100 mg, 0.172 mmol) in 5 mL THF was added 38 mg (0.172 mmol) CuBr₂ and the mixture was left to stir overnight, after which a copious amount of burgundy colored solids formed. The solids were filtered from the reaction mixture to give 83 mg of material. 5: Yield: 60%; magnetic susceptibility 1.99 $\mu_{\rm B}$. X-ray quality burgundy colored crystals were grown from a hot MeCN solution slowly cooled to -35 °C. Anal. calcd. for C₄₀H₅₇N₃CuBr₂: C 59.81, H 7.15, N 5.23; found: C 59.43, H 7.30, N 5.15. 6: Yield: 90%. X-ray quality colorless crystals were grown by cooling a CHCl₃ solution to -35 °C. ¹H NMR (CD₂Cl₂): 7.24–7.57 (m, 9H, m, p-Ar), 3.42 (sept, 4H, CH, $|J_{H-H}| = 6.9$ Hz), 3.41 (sept, 2H, CH, $|J_{H-H}| = 6.9$ Hz), 1.76 (s, 6H, Me), 1.37 (d, 12H, *i*-Pr, $|J_{H-H}| = 6.9$ Hz), 1.30 (d, 12H, *i*-Pr, $|J_{H-H}| = 6.9$ Hz), 1.13 (d, 12H, *i*-Pr, $|J_{H-H}| =$ 6.9 Hz). ¹³C NMR (CD₂Cl₂): 167.8, 146.4, 141.3, 141.1, 137.2, 132.0, 127.9, 126.8, 125.5, 29.1, 28.8, 26.0, 24.8, 24.7, 24.0. Anal. calcd. for C₄₀H₅₇N₃ZnBr₂: C 59.67, H 7.14, N 5.22; found: C 59.26, H 7.12, N 5.12.

Synthesis of $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Fe(\mu-Cl)_2Li(OEt_2)_2][B(C_6F_5)_4]$ (7)

To a rapidly stirring suspension of **2** (100 mg, 0.142 mmol) in 5 mL toluene was added 107 mg (0.142 mmol) Li(OEt₂)₂B(C₆F₅)₄ in 5 mL of diethyl ether. The reaction was allowed to stir overnight after which the mixture turned from yellow-orange to a bright yellow color. Filtration of the mixture through Celite[®] and removal of the solvent gave a yellow oil, which crystallized upon addition of pentane. Yield: 41%; magnetic susceptibility 5.23 μ_B . X-ray quality crystals were grown by diffusion of pentane vapor into a diethyl ether – toluene solution of the material. Anal. calcd. for C₇₂H₇₇N₃FeCl₂LiBF₂₀O: C 56.12, H 5.03, N 2.73; found: C 56.30, H 4.73, N 2.50.

Synthesis of $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2FeClCH_2SiMe_3$ (8)

To a rapidly stirring suspension of **2** (100 mg, 0.142 mmol) in 5 mL toluene cooled to -35 °C was added LiCH₂SiMe₃ (13 mg, 0.142 mmol) in 3 mL of cold toluene. The reaction was allowed to warm to 25 °C over several hours. The mixture became deep purple in color. Filtration of the mixture and cooling the filtrate to -35 °C overnight gave fine purple needles. The crystals were filtered off and washed with 2 × 10 mL of cold pentane. Yield: 55%; magnetic susceptibility 5.61 μ_B . X-ray quality purple crystals were grown from a toluene solution layered with pentane. Anal. calcd. for C₄₄H₆₈N₃FeSiCl: C 69.68, H 9.03, N 5.54; found: C 70.18, H 8.56, N 6.20.

Synthesis of $[(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Ni(\eta^3-C_3H_5)][B(3,5-(CF_3)_2C_6H_3)_4]$ (9)

To a solution of 1 (100 mg, 0.174 mmol) in 8 mL CH₂Cl₂ was added $[(\eta^3-C_3H_5)NiBr]_2$ (32 mg, 0.174 mmol) and $[Na][B(3,5-(CF_3)_2C_6H_3)_4]$ (155 mg, 0.174 mmol). The mixture was stirred overnight. The resulting brown solution was filtered to remove NaBr and the filtrate was cooled to -35 °C overnight to give brown crystals, which were separated from the solution by decantation and washed with 3×5 mL of cold pentane. Yield: 33%. ¹H NMR (CD₂Cl₂): 7.71 (br s, 8H, o-Ar_F), 7.56 (br s, 4H, p-Ar_F), 7.00-7.58 (m, 9H, m, p-Ar), 5.74 (dt, 1H, allyl CH, $|J_{H-H}| = 13.5$ Hz, $|J_{H-H}| =$ 7.1 Hz), 3.69 (sept, 2H, CH, $|J_{H-H}| = 6.9$ Hz), 3.01 (sept, 2H, CH, $|J_{\text{H-H}}| = 6.9$ Hz), 2.87 (sept, 1H, CH, $|J_{\text{H-H}}| = 6.9$ Hz), 2.72 (sept, 1H, CH, $|J_{H-H}| = 6.9$ Hz), 2.16 and 2.11 (d, 2H, allyl-syn, $|J_{H-H}| = 13.5$ Hz), 1.79 and 1.77 (d, 2H, allyl-anti, $|J_{\text{H-H}}| = 7.1 \text{ Hz}$, 1.66 (s, 6H, Me), 1.55 (d, 6H, *i*-Pr, $|J_{\text{H-H}}| =$ 6.9 Hz), 1.44 (d, 6H, *i*-Pr, $|J_{H-H}| = 6.9$ Hz), 1.33 (d, 6H, *i*-Pr, $|J_{\text{H-H}}| = 6.9 \text{ Hz}$), 1.29 (d, 6H, *i*-Pr, $|J_{\text{H-H}}| = 6.9 \text{ Hz}$), 1.28 (d, 6H, *i*-Pr, $|J_{\text{H-H}}| = 6.9$ Hz), 1.21 (d, 6H, *i*-Pr, $|J_{\text{H-H}}| = 6.9$ Hz). ¹³C NMR (CD₂Cl₂): 163.7, 162.4 (q, $J_{CF} = 49$ Hz), 149.4, 145.0, 149.9, 137.8, 136.9, 136.5, 135.4, 132.7, 130.6, 130.1 (br m), 129.7 (br m), 129.6, 129.3 (br m), 128.9 (br m), 128.7, 128.3, 127.3, 127.2, 127.0, 125.8, 125.5, 123.4, 119.8, 118.1 (br m), 65.6, 29.9, 29.4, 29.3, 29.1, 25.0, 24.9, 24.8, 24.2, 24.0, 23.7, 23.4, 21.7. ¹¹B NMR (CD₂Cl₂): -10.9. ¹⁹F NMR (CD₂Cl₂): -63.2. Anal. calcd. for C₇₅H₇₄N₃NiBF₂₄: C 58.38, H 4.83, N 2.72; found: C 58.07, H 4.89, N 2.66.

Synthesis of $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2NiH_2BEt_2$ (10)

To a rapidly stirring slurry of **4** (200 mg, 0.251 mmol) in 10 mL toluene was added Super-Hydride (0.551 mL, 1.0 mol/L in THF). An immediate evolution of gas was observed. The purple solution was allowed to stir for 4 h after which the solvent was removed in vacuo. The solid was dissolved in approx. 5 mL toluene, filtered through Celite[®], layered with 5 mL pentane, and cooled to -35 °C overnight. The resulting brown-red crystals were separated from the solution and washed with 3 × 10 mL of cold pentane. Yield: 47%; magnetic susceptibility 1.11 µ_B. Anal. calcd. for C₄₄H₆₉N₃NiB: C 74.48, H 9.80, N 5.92; found: C 74.93, H 9.81, N 5.92.

X-ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2 -free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data

were collected in a hemisphere of data in 1448 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected $(4.5^{\circ} < 20 < 45^{\circ}-50.0^{\circ})$. A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages (37). An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package (37).

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy atom positions were determined using direct methods employing the SHELXTL direct-methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using fullmatrix least-squares techniques on F. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they were bonded. The Hatom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Addition details are provided in the Supplementary data.³ See Table 1 for the crystallographic data for 2-10.

Results and discussion

The reaction of the metal halide in toluene or xylenes with ligand 1 at elevated temperatures afforded the complexes (i- $Pr_2C_6H_3N(C(Me)(NC_6H_3-i-Pr_2))_2MX_2$ (X = Cl, M = Fe (2), Co (3); X = Br, M = Ni (4)) in yields of 79%, 87%, and 86%, respectively (Scheme 2). In the latter case, formation of the Ni complex required the more forcing conditions of 4 days of heating in xylenes at 140 °C to form 4. These vigorous conditions stand in stark contrast to those required for the formations of $H_2C(C(Me)NC_6H_3-i-Pr_2)_2NiBr_2$ (37) and $(C(Me)(NC_6H_3-i-Pr_2)_2)NiBr_2$ (38), which form readily at room temperature. Magnetic susceptibility measurements for **2**, **3**, and **4** gave a magnetic moment of 4.79, 3.35, and 4.98 $\mu_{\rm B}$, respectively, consistent with these formulations. In a similar fashion, the straightforward reaction of 1 with equimolar amounts of CuBr₂ or ZnBr₂ in THF at room temperature gave compounds (*i*-Pr₂C₆H₃N)(C(Me)(NC₆H₃*i*-Pr₂))₂MBr₂ (M = Cu (5), Zn (6)). The ¹H NMR spectrum of 5 gave se-

³ Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3657. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 256368–256376 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

	$2 \cdot 2 C H_2 C I_2$	3	4	5	6
Formula	C42H61Cl6FeN3	C40H57Cl2CoN3	C40H57Br2N3Ni	C40H57Br2CuN3	C40H57Br2ZnN3
Formula weight	876.48	709.72	798.41	803.25	805.08
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/n$	<i>P</i> -1	$P2_1/c$
a (Å)	10.369(5)	10.7514(14)	10.462(9)	10.536(6)	10.512(7)
<i>b</i> (Å)	19.199(9)	17.395(3)	43.18(4)	11.758(7)	43.32(3)
<i>c</i> (Å)	11.990(6)	11.4237(18)	18.187(16)	18.189(11)	18.257(11)
α (°)				81.676(11)	
β (°)	101.554(10)	111.716(4)	106.392(19)	74.302(10)	106.732(9)
γ (°)				67.424(12)	
V (Å ³)	2 338.5(19)	1 984.9(5)	7 882(12)	2 001(2)	7 962(9)
Ζ	2	2	8	2	8
d(calcd.) (g cm ⁻¹)	1.245	1.187	1.346	1.333	1.343
Abs. coeff. (μ , mm ⁻¹)	0.696	0.597	2.550	2.572	2.654
Data collected	10 074	4 578	36 954	8 599	34 217
Data $F_0^2 > 3\sigma(F_0^2)$	3 469	2 596	11 284	5 676	11 329
Variables	253	226	829	415	829
R	0.0446	0.0574	0.0536	0.0769	0.0660
Rw	0.0996	0.1477	0.1241	0.1815	0.1528
GOF	0.827	1.043	0.937	0.851	0.770

 Table 1. Crystallographic data.

Scheme 2. Synthesis of neutral and cationic complexes: (i) MX₂; (ii) Li[B(C₆F₅)₄]; (iii) LiCH₂SiMe₃; (iv) Super-Hydride.



verely broadened lines, while the spectrum of **6** was similar to the free ligand. Magnetic susceptibility measurements of **5** gave a magnetic moment of $1.99 \mu_B$.

The overall geometries of the complexes 2–6 as determined by X-ray crystallographic studies are similar and thus only two representative ORTEP drawings are provided (Figs. 1 and 2). In all cases, the aryl rings are approximately orthogonal to the chelate plane and the metals adopt a pseudo-tetrahedral geometry. In the case of compounds 2 and 3, the molecules crystallize such that they sit on a crystallographically imposed mirror plane bisecting the ligand and passing through the plane containing the metal atom – dichloride fragment. The key metric parameters are summarized in Table 2. The M—Cl distances in 2 and 3 and the M—Br distance in 4 increases for the Fe, Co, Ni series consistent with increasing atomic radius. The M—Br distances for 5 and 6 are longer, as expected, averaging 2.367 and 2.357 Å, respectively. The X-M-X angles found in 2-4 are slightly larger than the typical tetrahedral angle ranging from 116.79(8)° to 120.14(8)°. For 5 and 6, the Br-M-Br angles were found to be 106.82(7)° and 117.80(5)°. The M-N distances fall in a narrow range between 1.959(6) and 2.096(3) Å. Similarly, the N-C distances of the imine fragments vary from 1.287(6) to 1.317(10) Å. These latter bond lengths are slightly longer than those found in the free ligand (1.272(3) and 1.269(3) Å). The ligand bite angles ranged from $84.61(15)^{\circ}$ for the Fe species to $90.1(3)^{\circ}$ for the Cu species. The N-M-X angles, in general, fall in the range from 101.54(12)° to 123.67(13)°; however, the largest range of thse angles was observed for 5 where the N-Cu-Br angles were found to be $132.9(2)^{\circ}$ and $105.8(2)^{\circ}$. These large N-Cu-Br angles, the large bite angle, short M—N distances, and the small X-M-X angle in 5 are illustrative of the greater distortion from a tetrahedral geometry at Cu relative

Masuda and Stephan

Table 1 (concluded).

7	8.0.5C ₆ H ₆	9 •0.5C ₆ H ₆ •0.25CH ₂ Cl ₂	10 C ₄₄ H ₆₉ BN ₃ Ni	
C ₇₂ H ₇₂ BCl ₂ F ₂₀ FeLiN ₃ O ₂	C45H69Cl3FeN3Si	C _{78.25} H ₇₅ BCl _{0.50} F ₂₄ N ₃ Ni		
1535.83	842.32	1600.66	709.54	
Triclinic	Orthorhombic	Triclinic	Triclinic	
P-1	Pnma	<i>P</i> -1	<i>P</i> -1	
15.545(3)	21.1151(12)	15.178(7)	11.861(4)	
16.276(3)	19.1255(12)	16.512(7)	12.840(4)	
16.461(3)	12.6066(8)	17.583(7)	16.590(5)	
101.263(4)		107.375(8)	89.734(6)	
92.812(4)		99.173(8)	75.663(7)	
104.311(5)		97.665(9)	63.836(5)	
3 937.0(13)	5 091.0(5)	4 074(3)	2 181.1(11)	
2	4	2	2	
1.296	1.099	1.305	1.080	
0.350	0.507	0.351	0.475	
19 393	24 184	17 656	6 910	
11 181	3 782	11 702	4 018	
883	257	929	466	
0.0537	0.0473	0.1145	0.0425	
0.1267	0.1195	0.3241	0.1020	
0.837	1.190	1.211	0.966	

Fig. 1. ORTEP of 2 or 3 (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. These compounds are isomorphous.



Fig. 2. ORTEP of **5** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity.



to the other compounds (Fig. 2). In this case, it appears that steric crowding results in the displacement of the Cu atom out of the ligand plane, and a twisting of the $CuBr_2$ plane to minimize interactions with the bulky Ar groups.

The species **2** reacts with Li(OEt₂)₂B(C₆F₅)₄ to form the yellow adduct $[(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2Fe(\mu-Cl)_2Li(OEt_2)_2][B(C_6F_5)_4]$ (7) in 41% isolated yield (Scheme 2). Crystallographic characterization of **7** revealed a pseudo-tetrahedral geometry about Fe in which two chlorine atoms bridge the Fe and Li atoms (Fig. 3). The pseudo-tetrahedral coordination sphere of Li is completed by the coordination of two molecules of ether. The Fe—N distances average 2.034(4) Å, which is shorter than that observed for **2**. This is

consistent with a more electron-deficient metal center as a result of the bridging of the Cl ligands to Li. This view is also consistent with the longer avg. Fe—Cl bond length of 2.2774(17) Å. A consequence of the bridging Cl atoms is also a small increase in the diimine ligand bite angle to $86.18(14)^\circ$. The Li—Cl bond lengths in 7 were found to be 2.474(10) and 2.352(11) Å, which gives rise to an Fe—Li separation of 3.163(9) Å.

Alkylation of **2** with 1 equiv. of LiCH₂SiMe₃ proceeds to give $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2FeClCH_2SiMe_3$ (**8**) in 55% isolated yield (Scheme 2). The magnetic susceptibility of **8** was determined to be 5.61 μ_B , consistent with a high-spin Fe(II) species. X-ray structural study of **8** con-

Cmpd	M—X (Å)	M—N (Å)	N _M —C (Å)	N-M-N (°)	X-M-X (°)	N-M-X (°)
2	2.235(2)	2.096(3)	1.297(4)	84.61(15)	120.14(8)	110.87(9), 112.43(9)
	2.252(2)					
3	2.219(2)	1.999(3)	1.299(4)	89.78(16)	116.79(8)	108.30(10), 115.18(9)
	2.2158(17)					
4	2.328(2)	1.996(5)	1.287(6)	89.84(19)	117.93(4)	123.67(13), 114.28(12)
	2.394(2)	1.997(4)	1.290(6)			101.54(12), 104.96(12)
5	2.3455(19)	1.959(6)	1.317(10)	90.1(3)	106.82(7)	132.9(2), 105.8(2)
	2.389(2)	1.987(8)	1.296(10)			102.31(19), 119.9(2)
6	2.3416(17)	2.050(6)	1.282(8)	88.1(2)	117.80(5)	117.08(16), 112.90(17)
	2.3729(19)	2.082(6)	1.305(8)			106.96(15), 110.04(15)

Table 2. Metric parameters (bond distances and angles) for the complexes 2-6.

Fig. 3. ORTEP of the cation of 7 (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Bond lengths (Å): Fe(1)—N(3) 2.030(4), Fe(1)—N(1) 2.034(3), Fe(1)—Cl(2) 2.2706(17), Fe(1)—Cl(1) 2.2842(17), Fe(1)—Li(1) 3.163(9), Cl(1)—Li(1) 2.474(10), Cl(2)—Li(1) 2.352(11), N(1)—C(37) 1.291(5), N(1)—C(1) 1.451(5), N(2)—C(13) 1.466(5), Li(1)—O(2) 1.943(11), Li(1)—O(1) 1.968(10). Bond angles (°): N(3)-Fe(1)-N(1) 86.18(14), N(3)-Fe(1)-Cl(2) 123.86(11), N(1)-Fe(1)-Cl(2) 114.69(11), N(3)-Fe(1)-Cl(1) 113.49(10), N(1)-Fe(1)-Cl(2) 114.69(11), N(3)-Fe(1)-Cl(1) 113.49(10), N(1)-Fe(1)-Cl(1) 121.78(11), Cl(2)-Fe(1)-Cl(1) 98.82(7), O(2)-Li(1)-O(1) 114.8(5), O(2)-Li(1)-Cl(2) 113.6(5), O(1)-Li(1)-Cl(2) 106.8(5), O(2)-Li(1)-Cl(1) 111.3(5), O(1)-Li(1)-Cl(1) 116.5(5).



firmed the formulation, with the molecule residing on a crystallographically imposed mirror plane that bisects the ligand and passes through the pseudo-tetrahedral Fe center and the plane containing Cl and the (CH₂SiMe₃) fragment (Fig. 4). The incorporation of an electron-donating alkyl group results in the expected lengthening of the Fe—N bond length to 2.114(3) Å. Similarly the Fe—Cl distance of 2.2762(15) Å in **8** is longer than that found in **2**. The longer Fe—N distance also results in a slightly smaller ligand bite angle of $82.99(13)^{\circ}$. Attempts to further alkylate Fe were unsuccessful, presumably a reflection of the steric crowding about the Fe center of **8**. In addition, attempts to alkylate with MeLi or *t*-BuLi were also unsuccessful leading to apparent compound degradation.

Fig. 4. ORTEP of **8** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Bond lengths (Å): Fe(1)—C(26) 2.038(6), Fe(1)—N(1) 2.114(3), Fe(1)—Cl(1) 2.2762(15), N(1)—C(1) 1.281(4), N(1)—C(3) 1.454(4). Bond angles (°): C(26)-Fe(1)-N(1) 117.67(13), N(1)-Fe(1)-N(1) 82.99(13), C(26)-Fe(1)-Cl(1) 124.89(18), N(1)-Fe(1)-Cl(1) 102.50(7), C(1)-N(1)-Fe(1) 127.9(2).



Reactions of **1** with $[(\eta^3-C_3H_5)NiBr]_2$ and $[Na][B(3,5-(CF_3)_2C_6H_3)_4]$ afforded the salt $[(i-Pr_2C_6H_3N)(C(Me)-(NC_6H_3-i-Pr_2))_2Ni(\eta^3-C_3H_5)][B(3,5-(CF_3)_2C_6H_3)_4]$ (**9**) in 33% isolated yield. The ¹H NMR spectrum of **9** is consistent with this formulation and indicative of a η^3 -bonding mode of the allyl fragment. Variable-temperature studies (-90 to 35 °C) show no change in the allyl signals, reflecting the absence of dynamic behavior. Attempts to react **9** with CO, ethylene, or PhPH₂ failed to show any reaction, even under forcing conditions (refluxing toluene), again reflecting the maintenance of the η^3 -bonding mode of the allyl fragment. X-ray data also confirmed this binding mode (Fig. 5). The Ni—N distances in **9** were found to be 1.915(6) and 1.916(6) Å. These distances, which are shorter than those found in **4**, are con-

Fig. 5. ORTEP for the cation of 9 (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Bond lengths (Å): Ni(1)—N(1) 1.915(6), Ni(1)—N(2) 1.916(6), Ni(1)—C(42) 1.96(2), Ni(1)—C(41) 2.019(14), Ni(1)—C(43) 2.049(11), N(1)—C(3) 1.306(8), N(2)—C(1) 1.290(8). Bond angles (°): N(1)-Ni(1)-N(2) 92.1(2), N(1)-Ni(1)-C(42) 134.4(7), N(2)-Ni(1)-C(42) 131.9(7), N(1)-Ni(1)-C(41) 168.9(4), N(2)-Ni(1)-C(41) 98.1(4), C(42)-Ni(1)-C(41) 37.1(7), N(1)-Ni(1)-C(43) 97.6(4), N(2)-Ni(1)-C(43) 170.2(4), C(42)-Ni(1)-C(43) 38.5(7), C(41)-Ni(1)-C(43) 135(2).



sistent with the presence of the formal positive charge. The Ni–allyl interaction results in Ni–C bond lengths of 1.96(2), 2.019(14), and 2.049(11) Å, typical of the η^3 -bond-ing mode (39, 40).

Finally, reactions of **4** with Super-Hydride afforded brown-red crystals of the species formulated as $(i-Pr_2C_6H_3N)$ -(C(Me)(NC₆H₃-*i*-Pr₂))₂NiH₂BEt₂ (**10**) in 45% yield (Scheme 2). The magnetic susceptibility of **10** was determined to be 2.87 μ_B . X-ray data confirmed the above formulation of **10** as a formally Ni(I) species and revealed the pseudotetrahedral geometry about Ni in which two hydride atoms bridge the Ni and B centers (Fig. 6). The Ni—N distances average 1.947(2) Å, while the Ni—B separation is 2.165(4) Å. Location and refinement of the hydride atoms revealed an avg. Ni—H distance of 1.70(1) Å and B—H distances of 1.20(1) Å. Attempts to remove borane from **10** via reaction with BuLi were unsuccessful. Similarly, **10** proved to be unreactive with primary phosphine or phenol.

Summary

This manuscript describes the synthesis and structure of a series of transition metal complexes of the bulky *N*-arylimidoyl amidine ligand $(i-Pr_2C_6H_3N)(C(Me)(NC_6H_3-i-Pr_2))_2$. While a variety of complexes are readily accessible, the resulting complexes are generally robust and unreactive, principally a result of the sterically demanding nature of the ligand. As a result, we are continuing efforts to utilize this ligand to stabilize and isolate reactive transition metal fragments. **Fig. 6.** ORTEP of **10** (30% thermal ellipsoids are shown). All hydrogen atoms except the bridging hydrogen atoms are omitted for clarity. Bond lengths (Å): Ni(1)—N(1) 1.946(2), Ni(1)—N(3) 1.949(2), Ni(1)—B(1) 2.165(4), B(1)—C(41) 1.600(6), B(1)—C(43) 1.616(6), N(1)—C(5) 1.456(4), N(3)—C(3) 1.305(4), N(3)—C(29) 1.447(4). Bond angles (°): N(1)-Ni(1)-N(3) 89.48(10), N(1)-Ni(1)-B(1) 138.37(13), N(3)-Ni(1)-B(1) 132.15(13), C(41)-B(1)-C(43) 114.6(3), C(41)-B(1)-Ni(1) 119.8(3), C(43)-B(1)-Ni(1)



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