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Synthesis, Structures, Characterization, Dynamic Behavior, and Reactions of Novel Late Transition Metal(II) 1-Azaallyls

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A series of homoleptic late transition metal(II) 1-azaallyl compounds ([M(L)$_2$] {L = η^3-N(SiMe$_3$)C(^{t}Bu)CH(C$_6$H$_4$Me-4), M = Fe (**5**), Co (**6**), or Ni (**7**)}, [M(L^1)$_2$] {L^1 = η^3-N(SiMe$_3$)C(Ph)CH(SiMe$_3$), M = Ni (**8**) or Pd (**9**)}, [M(L^2)$_2$] {L^2 = η^3-N(SiMe$_3$)C(^{t}Bu)CH(SiMe$_3$), M = Fe (**10**) or Co (**11**)}, or [M(L^3)$_2$] {L^3 = η^1-N(SiMe$_3$)C(^{t}Bu)CH(C$_{10}$H$_7$-1), M = Fe (**12**)} have been prepared by reactions of anhydrous late transition metal halides {MX$_2$ = FeBr$_2$, CoCl$_2$, [NiBr$_2$(dme)], or [PdCl$_2$(cod)]} with the appropriate lithium or potassium 1-azallyl KL (**1**), [LiL^1(thf)]$_2$ (**2**), [LiL^2]$_2$ (**3**), or KL^3 (**4**) in a 1:2 molar ratio. The heteroleptic 1-azallylnickel(II) complex Ni(η^3-C$_3$H$_5$)(L^3) (**13**) was prepared from [{Ni(η^3-C$_3$H$_5$)(μ-Br)}$_2$] with a stoichiometric amount of the 1-azaallylpotassium reagent KL^3 (**4**). Single-crystal X-ray analysis revealed the 1-azaallyl to be bonded to the metal center in an η^3-*NCC* mode in the mononuclear compounds **5**−**8** and **10**, whereas in **12** the 1-azallyl is *N*-bound in the κ^1-enamido fashion. The iron(II) (**5**, **10**, and **12**) and cobalt(II) (**6** and **11**) compounds are paramagnetic and have magnetic moments in the range 5.01−5.61 μ_B and 2.73−3.01 μ_B, respectively, characteristic of a high-spin d^6 and low-spin d^7 electronic configuration, respectively. The diamagnetic group 10 metal 1-azaallyl compounds (**7**−**9** and **13**) were fully characterized by multinuclear NMR spectroscopy and were found to be a mixture of isomers. Several NOE, two-dimensional, and saturation transfer NMR spectroscopic experiments were used to elucidate the nature of the three isomers. Variable-temperature and variable-temperature saturation transfer NMR spectroscopic experiments showed the isomers of each of compounds **7**−**9** to be involved in a dynamic process. Electrochemical and oxidation studies on compounds **5** and **6** are reported, as are α-olefin oligomerization reactions catalyzed by **13** with MAO or B(C$_6$F$_5$)$_3$.

Introduction

This contribution is part of our ongoing study into the diversity of ligating possibilities of the 1-azaallyl ligand system. In a series of papers we have shown that a variety of coordinated *N*-silyl-1-azaallyl anions can be formed via the interaction of an α-hydrogen-free nitrile with a trimethylsilylmethyllithium reagent Li[CH$_{3-n}$R$_n$] (R = SiMe$_3$ and n = 1, 2, or 3),[1a] Li[CH(SiMe$_3$){SiMe$_{3-n}$(OMe)$_n$}] (n = 1 or 2),[1b] or Li[CH(SiMe$_2$OMe)$_2$].[1b] The lithium 1-azaallyls[1a] were excellent ligand transfer reagents, producing various metal-1-azaallyl complexes with intriguing coordination chemistry.[2] The majority of attention paid to the chemistry of 1-aza-allylmetal complexes has been their use as reagents in carbon−carbon bond formation,[3] as in controlled aldol condensation reactions or regioselective α-functionalization of ketones.[3,4] *N*-Silyl-1-azaallyl anions (formed via insertion of a nitrile into a lithium alkyl bond) have proved to be excellent synthons for the formation of heterocycles,[5] as have 3-halo-1-azaallyllithium compounds.[6]

The 1-azaallyl anions belong to the large class of anions of the general formula [X = Y−Z or X = Y = Z]$^-$ and are part of a family of ligands which includes[7] neutral 1-azaallyls (e.g., *N*,*N*′-dialkyl-1,4-diazabuta-1,3-dienes),[8] 1-azaallyl dianions (as in [{Ru(CO)$_3$}$_2${μ-C(^{i}Pr)C-

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[1] (a) Hitchcock, P. B.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Sablong, R.; Shun, T. *J. Chem. Soc., Dalton Trans.* **2000**, 2301, and references therein. (b) Hitchcock, P. B.; Lappert, M. F.; Wei, X.-H. *J. Organomet. Chem.* **2003**, *683*, 83.

[2] Caro, C. F.; Lappert, M. F.; Merle, P. G. *Coord. Chem. Rev.* **2001**, *219*−*221*, 605.

[3] (a) Whitesell, J. K.; Whitesell, M. A. *Synthesis* **1983**, 517. (b) Evans, D. A. *J. Am. Chem. Soc.* **1970**, *92*, 7593. (c) Wittig, G.; Röderer, R.; Fischer, S. *Tetrahedron Lett.* **1973**, 3517.

[4] (a) Wittig, G.; Frommeld, H. D.; Suchanek, P. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 683. (b) Wittig, G.; Reiff, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 7. (c) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178.

[5] (a) Konakahara, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1241. (b) Konakahara, T.; Takagi, Y. *Heterocycles* **1980**, *14*, 393. (c) Konakahara, T.; Kurosaki, J. *J. Chem. Res.* **1989**, (S) 130, (M) 1068. (d) Konakahara, T.; Sugama, N.; Sato, K. *Heterocycles* **1992**, *33*, 157. (e) Konakahara, T.; Hojahmat, M.; Sujimoto, K. *Heterocycles* **1997**, *45*, 271. (f) Konakahara, T.; Watanabe, A.; Sato, K. *Heterocycles* **1985**, *23*, 383. (g) Konakahara, T.; Watanabe, A.; Maehara, K.; Nagata, M.; Hojahmat, H. *Heterocycles* **1993**, *35*, 1171. (h) Konakahara, T.; Sato, M.; Haruyama, T.; Sato, K. *Nippon Kagaku Kaishi* **1990**, 466. (i) Konakahara, T.; Hojahmat, M.; Tamura, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2803. (j) Konakahara, T.; Sugama, N.; Yamada, A.; Kakehi, A.; Sakai, N. *Heterocycles* **2001**, *55*, 313. (k) Konakahara, T.; Ogawa, R.; Tamura, S.; Kakehi, A.; Sakai, N. *Heterocycles* **2001**, *55*, 1737.

[6] (a) De Kimpe, N.; Sulmon, P.; Schamp, N. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 881. (b) Aelterman, W.; De Kimpe, N.; Tyvorskii, V.; Kulinkovich O. *J. Org. Chem.* **2001**, *66*, 53.

[7] (a) Cook, K. S.; Piers, W. E.; Hayes, P. G.; Parvez, M. *Organometallics* **2002**, *21*, 2422. (b) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *J. Chem. Soc., Dalton Trans.* **2001**, 2409.

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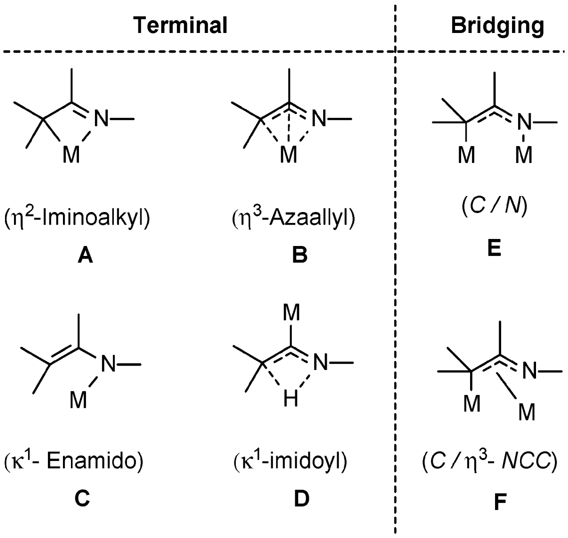
$(^i\text{Pr})\text{N}(^t\text{Bu})\text{C(O)}\}]$[9h]),[9] imidoyls (as in $[\text{Pd(Br)}\{\text{C}(\text{N}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_4\text{Br-4}\}(\text{PMe}_3)_2]$[10k]),[10] and the 2-pyridylalkyls (as in $[\text{Li}\{\mu\text{-CR}_2(\text{C}_5\text{H}_4\text{N-2})\}]_2)$.[11] The coordination chemistry of transition metal 1-azaallyl complexes is similar to that of the extensively studied class of ligands: 1-oxaallyls (or enolates),[12] η^3-1-phosphaallyls,[13] 2-azaallyls,[14] 1,3-diphosphaallyls,[15] 1-aza-3-phosphaallyls,[16] or metal-1,3-diazaallyls including benzamidinates.[17] They can bind to a metal in one of six bonding modes **A**−**F** (Scheme 1), depending on the nature of the substituent groups on the ligand and the presence or absence of neutral coligand(s). The most common bonding modes are **A**, **B**, and **C**, with bonding mode **A** predominantly found in metal 2-pyridylalkyl complexes. Bonding mode **D** is shown with a bridging hydrogen.

Scheme 1. Variation in Bonding Modes of the 1-Azaallyl Moieties



This paper deals with Fe(II), Co(II), Ni(II), and Pd(II) complexes. Published data on this theme relate to various 2-pyridylalkyls of Fe, Co, and Ni.[2] Exceptions are $[\text{M}\{\eta^3\text{-N(R)C}(^t\text{Bu})\text{C(H)R}\}\text{I(L)}]$ (M = Ni, Pd; L = PPh_3, or absent) and $[\text{Ni}\{\eta^3\text{-N}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\text{C(R)C(H)R}\}(\text{tmeda})]$ (R = SiMe_3);[18] these were prepared from $[\text{Ni(cod)}_2]$ or $[\text{Pd(dba)}_2]$ and $\text{RN}{=}\text{C}(^t\text{Bu})\text{C(H)(R)I}$ and the 1:1 adducts + PPh_3, or $[\text{Li}\{\eta^3\text{-N}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\text{C(R)C(H)R}\}(\text{tmeda})]$ with $[\text{NiBr}_2(\text{dme})]$. The compound $[\text{Ni}\{\eta^3\text{-N(R)C}(^t\text{Bu})\text{C(H)R}\}\text{I}(\text{PPh}_3)]$ was X-ray characterized, and the PPh_3-free Ni(II) or Pd(II) iodides were shown to be mixtures of isomers in solution.

In a preliminary communication, we drew attention to the five compounds $[\text{M}\{\eta^3\text{-N(R)C}(^t\text{Bu})\text{C(H)R}^1\}_2]$ (M = Fe, Co; R^1 = R, $\text{C}_6\text{H}_4\text{Me-4}$; M = Ni, R^1 = $\text{C}_6\text{H}_4\text{Me-4}$) and $[\text{Fe}\{\text{N(R)C}(^t\text{Bu}){=}\text{C(H)C}_{10}\text{H}_7\text{-1}\}_2]$.[19] We now describe the synthesis, characterization, and fluxional processes of these and four other 1-azaallylmetal(II) (Fe, Co, Ni, Pd) complexes, including the X-ray structures of six of them; some of these data were alluded to in a review.[2]

Results and Discussion

Synthesis and Characterization of 1-Azaallyl Group 8−11 Transition Metal Complexes. The starting potassium or lithium 1-azaallyls KL (**1**),[20] $[\text{LiL}^1(\text{thf})]_2$ (**2**),[1a] $[\text{LiL}^2]_2$ (**3**),[1a] and KL^3 (**4**)[21] were prepared by literature procedures [L = $\{\text{N(R)C}(^t\text{Bu})\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}$, L^1 = $\{\text{N(R)C(Ph)CH(R)}\}$, L^2 = $\{\text{N(R)C}(^t\text{Bu})\text{CH(R)}\}$, L^3 = $\{\text{N(R)C}(^t\text{Bu})\text{CH}(\text{C}_{10}\text{H}_7\text{-1})\}$; R = SiMe_3].

Reaction of 2 equiv of the appropriate lithium or potassium 1-azaallyl with the anhydrous metal(II) halide (FeBr_2, CoCl_2, $[\text{NiBr}_2(\text{dme})]$, or $[\text{PdCl}_2(\text{cod})]$) in tetrahydrofuran at ambient temperatures afforded the crystalline, colored, monomeric transition metal(II) 1-azaallyls **5**−**12** in good yields (Scheme 2). Each of **5**−**12** was soluble in diethyl ether, but much less so in hydrocarbon solvents (except for **5**), and surprisingly air- and moisture-stable in the solid. The allylnickel(II)

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(8) (a) de Lange, P. P. M.; Frühauf, H.-W.; van Wijnkoop, M.; Vrieze, K.; Wang, Y.; van Heijdenrijk, D.; Stam, C. H. *Organometallics* **1990**, *9*, 1691. (b) De Lange, P. P. M.; Van Wijnkoop, M.; Frühauf, H.-W.; Vrieze, K.; Goubitz, K. *Organometallics* **1993**, *12*, 428. (c) Meca, L.; Císařová, I.; Dvořák, D. *Organometallics* **2003**, *22*, 3703.

(9) (a) Nakamura, Y.; Bachmann, K.; Heimgartner, H.; Schmid, H.; Daly, J. J. *Helv. Chim. Acta* **1978**, *61*, 589. (b) Song, J.-S.; Han, S.-H. H.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2386. (c) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 7279. (d) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 2809. (e) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800. (f) Mirkin, C. A.; Oyer, T. J.; Wrighton, M. S.; Snead, T. E.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1992**, *114*, 1256. (g) Mul, W. P.; Elsevier, C. J.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1991**, *10*, 2247. (h) Beers, O. C. P.; Delis, J. G. P.; Mul, W. P.; Vrieze, K.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1993**, *32*, 3640. (i) Elsevier, C. J.; Mul, W. P.; Vrieze, K. *Inorg. Chim. Acta* **1992**, *200*, 689. (j) Polm, L. H.; Elsevier, C. J.; Mul, W. P.; Vrieze, C. J.; Christophersen, M. J. N.; Muller, F.; Stam, C. H. *Polyhedron* **1988**, *7*, 2521. (k) Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H.; van Tunen, W. C. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1177.

(10) (a) Durfee, L. D.; Rothwell, I. A. *Chem. Rev.* **1988**, *88*, 1059, and references therein. (b) Seyferth, D.; Hoke, J. B. *Organometallics* **1988**, *7*, 524. (c) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583. (d) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 4530. (e) Henderson, W.; Kemmitt, R. D. W.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1990**, 781. (f) Henderson, W.; McKenna, P.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1989**, 345. (g) Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301. (h) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, L. *Organometallics* **1993**, *12*, 4899. (i) Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1998**, *17*, 5620. (j) Cámpora, J.; Hudson, S. A.; Carmona, E. *Organometallics* **1995**, *14*, 2151. (k) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L.; van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948. (l) Cámpora, J.; Hudson, S. A.; Massiot, P.; Maya, C. M.; Palma, P.; Carmona, E.; Martínez-Cruz, L. A.; Vegas, A. *Organometallics* **1999**, *18*, 5225.

(11) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem Commun.* **1983**, 1419.

(12) For example: Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

(13) (a) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. (b) Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955. (c) Hugel-Le Goff, C.; Mercier, F.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1989**, *363*, 325. (d) Mercier, F.; Mathey, F. *Organometallics* **1990**, *9*, 863.

(14) (a) Keable, H. R.; Kilner, M. *J. Chem. Soc., Dalton Trans.* **1972**, 153. (b) Andrews, P. C.; Armstrong, D. R.; Clegg, W.; Craig, F. J.; Dunbar, L.; Mulvey, R. E. *J. Chem. Soc., Chem. Commun.* **1997**, 319.

(15) Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416.

(16) (a) Wang, Z.-X.; Wang, D.-Q.; Dou, J.-M. *J. Organomet. Chem.* **2003**, *665*, 205. (b) Hitchcock, P. B.; Lappert, M. F.; Uiterweerd, P. G. H.; Wang, Z.-X. *J. Chem. Soc., Dalton Trans.* **1999**, 3413.

(17) See: (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403.

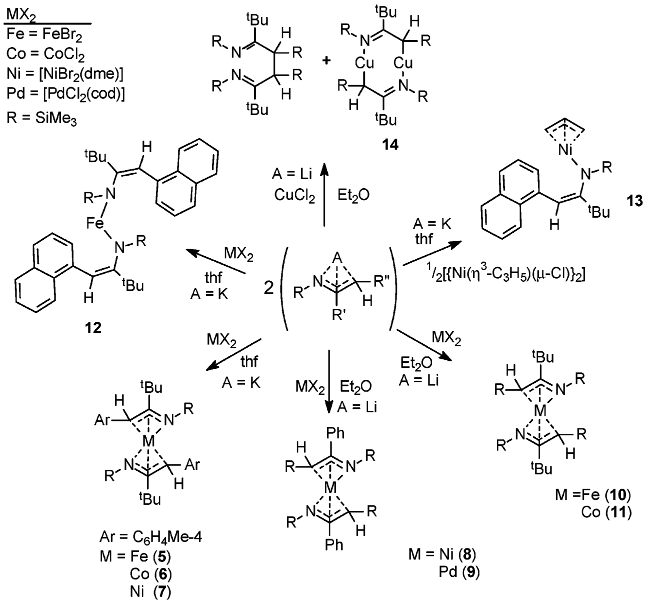
(18) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1081.

(19) Daniéle, S.; Deelman, B.-J.; Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Sablong, R.; Severn, J. R. *Education in Advanced Chemistry*; Marciniéc, B., Ed.; Wydawnictwo Poznanskie: Poznán-Wroclaw, 1999; Vol. 6, Chapter 12.

(20) Lappert, M. F.; Liu, D.-S. Neth. Pat. Appl. 9500085, 1995.

(21) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637.

Scheme 2. Routes to Compounds 5−14



complex $[Ni(L^3)(\eta^3\text{-}CH_2CHCH_2)]$ (**13**) was obtained from $[\{Ni(\eta^3\text{-}CH_2CHCH_2)(\mu\text{-}Cl)\}_2]$ and KL^3.

An attempt to synthesize a Cu(II) analogue from anhydrous $CuCl_2$ with 1 equiv of $[LiL^2]_2$ in diethyl ether led instead to the C−C ligand-coupled product[22] and the (1-azaallyl)copper(I) dimer[23] (Scheme 2).

Each of the complexes **5**−**13** was characterized by microanalyses and mass spectra, with ^1H and ^{13}C NMR spectroscopic data for the diamagnetic Ni(II) (**7**, **8**, **13**) and Pd(II) (**9**) complexes, and single-crystal X-ray structures for **5**, **6**, **7**, **8**, **10**, and **12**. The ambient-temperature NMR spectroscopic data revealed that in solution **7**, **8**, **9**, and **13** existed as a mixture of isomers.

For the paramagnetic Fe(II) (**5**, **10**, **12**) and Co(II) (**6**, **11**) complexes, further measurements were of (a) magnetic moments in benzene at 298 K, recorded using Evans' method[24] (with diamagnetic corrections[25,26]), and (b) irreversible oxidation potentials (relative to the $FeCp_2^+/FeCp_2$ couple), by cyclic voltammetry on **5** and **6** (in thf as solvent; $[N^nBu_4][BF_4]$ as supporting electrolyte, at a scan rate of 200 mV s^{-1}). These data, as well as yields and colors, are shown in Table 1, with corresponding information on some 2-pyridylalkyl analogues.[27,28]

While the magnetic moments for the homoleptic d^6 Fe(II) 1-azaallyls **5**, **6**, and **12** are significantly larger than those of the cited 2-pyridylalkyl analogues (for which μ_{eff} is in one case close to the calculated spin-only high-spin value of 4.90 μ_B), they are in line with much data in the literature. Thus, for various tetrahedral salen-type Fe(II) complexes, μ_{eff} was generally around 5.2 μ_B, attributed to orbital contributions to the magnetic moment.[29] A value of ca. 6 μ_B on such a complex has been recorded, but the possibility of a trace of an Fe(III) impurity could not be discounted.[30] In contrast to the above high-spin Fe(II) 1-azaallyls, the d^7 Co(II) complexes **6** and **11** are clearly of low spin (both at ambient temperature). Observed magnetic moments for low-spin Co(II) complexes have generally exceeded the spin-only value of 1.73 μ_B, usually being in the range 2.2−3.2 μ_B,[28] due to a large orbital contribution. Despite the precedents on the related Fe(II) and Co(II) 2-pyridylalkyls (Table 1), it is the d^7 rather than the d^6 analogue that is of low spin at ambient temperature. Measurements on a wider temperature range would be useful to determine whether spin-crossover was readily accessible.

Attempted oxidation of **5** or **6** was carried out with TCNE, $Ag[BF_4]$, $Ag[SbF_6]$, or *p*-benzoquinone. For the Fe complex **5** there was in each case rapid precipitation of metal even at −78 °C. For the Co complex **6**, the solution changed from a deep orange to dark green, which persisted at <−30 °C, whereafter the color reverted to deep orange. The resultant filtrate contained approximately half of unreacted **5** or **6** and the C−C ligand-coupled product $[N(R){=}C(^tBu)\{C(H)(C_6H_4Me\text{-}4)\}]_2$. Consistent with these observations, the CV of **5** and **6** (Table 1) showed ready irreversible oxidation.

Crystal Structures. The molecular structures of the isomorphous complexes **5**−**7**, with atom-numbering schemes, are exemplified in Figure 1 for the case of the iron(II) 1-azaallyl **5**; an alternative view illustrated for the Ni(II) analogue **7** is in Figure 2. Figures 3−5 show the molecular structures for complexes **8**, **10**, and **12**, respectively. Selective bond distances and the NC1C2 angle for each of the monomeric crystalline complexes **5**−**8**, **10**, and **12** are represented schematically in Scheme 3 and more extensively with comparative data on $[Ni\{\eta^3\text{-}N(R)C(^tBu)CH(R)\}I(PPh_3)]$ and Fe(II) and Co(II) 2-pyridylalkyls in Table 2. In **5**−**8** and **10** the metal is sandwiched between the two staggered η^3-1-azaallyl ligands, the metal being the centroid of a distorted octahedron. An alternative description places the metal at the center of an NC2N′C2′ or C1C2C1′C2′ square with a pendant η-alkene or η-imine (cf. ref 31), respectively. In each of these metal(II) complexes **5**−**8** and **10** the substituents on the two 1-azaallyl ligands are arranged in a mutually transoid fashion. In the centrosymmetric **5**−**7** and **10** each ligand has the *anti*-conformation, while for **8** it is *syn*. The Ni(II) complex **8** also differs from **5**−**7** and **10** in not being centrosymmetric, the N−M′−N′ bond angle of 163.1(2)^0 diverging from the linear arrangement found in the other four. This is probably a general feature of the L^1 ligand, having a Ph rather than a ^tBu substituent at C1. The other geometric parameters for each of **5**−**8** and **10** are unexceptional (Table 2) and clearly demonstrate the η^3-

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[22] Hitchcock, P. B.; Lappert, M. F.; Tian, S. *J. Organomet. Chem.* **1997**, *549*, 1.

[23] Hitchcock, P. B.; Lappert, M. F.; Layh, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1619.

[24] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[25] O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

[26] See Supporting Information for general procedure.

[27] Leung, W.-P.; Lee, H.-K.; Weng, L.-H.; Luo, B.-S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1996**, *15*, 1785.

[28] Leung, W.-P.; Lee, H.-K.; Weng, L.-H.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 779.

[29] Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83.

[30] Calvin, M.; Bailes, R. H. *J. Am. Chem. Soc.* **1946**, *68*, 949.

[31] (a) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3025. (b) Karsch, H. H.; Leithe, A. W.; Reisky, M.; Witt, E. *Organometallics* **1999**, *18*, 90. (c) Hoberg, H.; Götz, V.; Krüger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1979**, *169*, 209. (d) Gabor, B.; Krüger, C.; Marczinke, B.; Mynott, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666. (e) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1980**, *185*, 367. (f) Clemens, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1620. (g) Mukhedkar, V. A.; Mukhedkar, A. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2801.

Table 1. Yields and Selected Properties of the Fe(II) and Co(II) 1-Azaallyls and Some Comparative Data

compound^a	yield (%)	color	mp (°C)	μ_{eff} (μ_B)	E_p^{Ox} (V)
5 [$\mathrm{FeL_2}$]	79	red	163−165	5.27	0.22
10 [$\mathrm{FeL^2{}_2}$]	91	red	135−138	5.61	
12 [$\mathrm{FeL^3{}_2}$]	78	red	>60 dec	5.01	
[$\mathrm{Fe\{CR_2(C_5H_4N\text{-}2)\}_2}$][27]	80	yellow	110−112	4.24	0.85
[$\mathrm{Fe\{CPh(R)(C_5H_4N\text{-}2)\}_2}$][27]	52	red	118−120 dec	4.92	0.64
6 [$\mathrm{CoL_2}$]	89	orange	128−130 dec	3.01	0.7
11 [$\mathrm{CoL^2{}_2}$]	86	orange	120−123	2.73	
[$\mathrm{Co\{CR_2(C_5H_4N\text{-}2)\}_2}$][28]	63	red	116−118	3.11	0.86
[$\mathrm{Co\{CPh(R)(C_5H_4N\text{-}2)\}_2}$][28]	70	red	183−185 dec	2.31	

^{a} $\mathrm{L = \{N(R)C(^tBu)CH(C_6H_4Me\text{-}4)\}}$; $\mathrm{L^2 = \{N(R)C(^tBu)CH(R)\}}$, $\mathrm{L^3 = \{N(R)C(^tBu)CH(C_{10}H_7\text{-}1)\}}$; R = $\mathrm{SiMe_3}$.

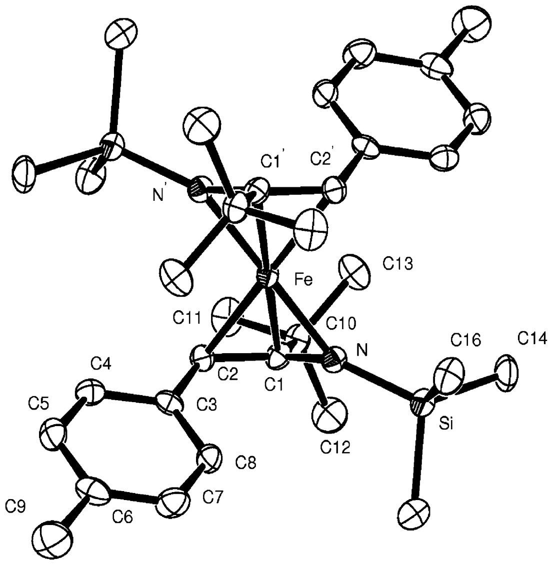


Figure 1. Molecular structures of the isomorphous compounds **5**−**7**, illustrated for the iron compound **5**.

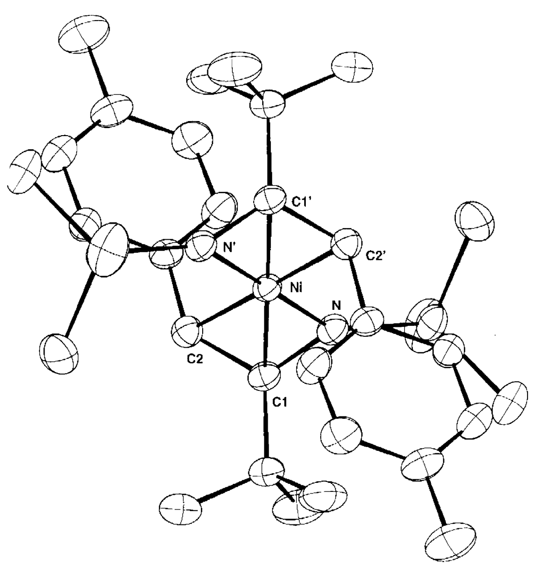
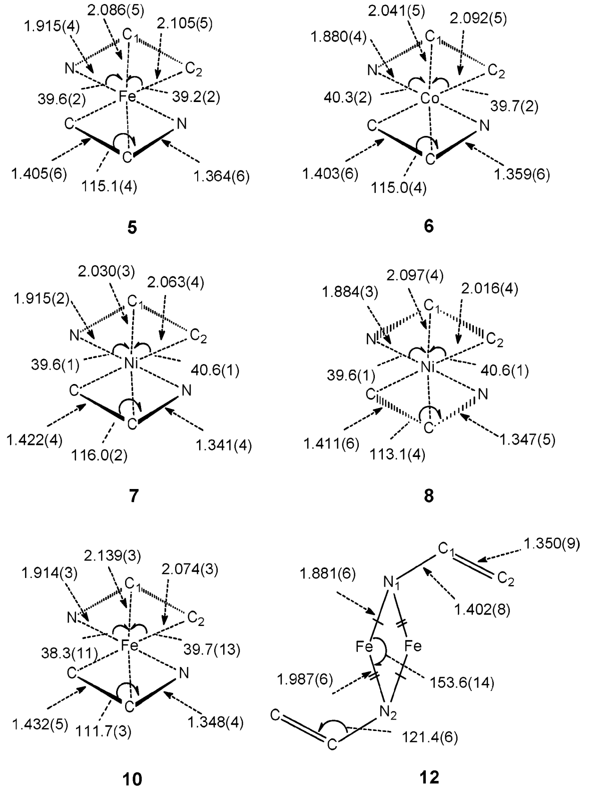


Figure 2. Alternative view of the molecular structures of compounds **5**−**7**, illustrated for the nickel compound **7**.

1-azaallyl bonding mode **B** to the metal; in each of the isoleptic complexes **5**−**7**, the central M−C bond is slightly shorter than the terminal M−C, whereas the reverse is the case for **8** and **10**.

The structure of the centrosymmetric crystalline Fe(II) complex **12** is unique within the present series of homoleptic metal(II) 1-azaallyls in that it is an enamidometal complex; that is, the bonding mode is **C**. Consistent with that view are the significantly longer N−C1 and shorter C1−C2 bonds in **12** than in the other five complexes, which may be compared with the N−C1 and C1−C2 bond lengths of 1.435(4) or 1.38(1) Å and 1.349(5) or 1.35(1) Å in the tin(II) $\mathrm{Sn[N(R)C(^tBu){=}C(H)\text{-}C_6H_3Me_2\text{-}2,5]_2}$[32] or the copper(I) $\mathrm{[Cu\{N(R)C(^tBu){=}C(H)R\}\text{-}(PPh_3)]}$[33] complex, respectively. A significant feature is the deviation in **12** of N−Fe−N′ from linearity (the iron is disordered across the inversion center), although there are ample precedents in other crystalline two-coordinate Fe(II) complexes $\mathrm{FeX_2}$ [$\mathrm{X_2 = (NSiMe_{3-\mathit{n}}Ph_\mathit{n})_2}$ (n = 1[34] or 2[35]) or $\mathrm{(C_6H_2{}^tBu_3\text{-}2,4,6)_2}$:[36,37] 172.1(1)°, 169.0-

Scheme 3. Schematic Representation of the Molecular Structures of Compounds 5−8, 10, and 12, with Selected Bond Lengths (Å) and Angles (deg) with the Atom-Labeling Scheme



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(32) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M. Severn, J. R. *J. Chem. Soc., Chem. Commun.* **1997**, 1189.

(33) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1619.

(34) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4338.

(35) Bartlett, R. A.; Power P. P. *J. Am. Chem. Soc.* **1987**, *109*, 7563.

(36) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264.

(37) Müller, H.; Seidel, W.; Görls, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 325.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5, 6, 7, 8, 10, and 12 and Some Comparative Data

compound[a]	M−N	M−C$_1$	M−C$_2$	N−C$_1$	C$_1$−C$_2$	N−M−N′	N−C$_1$−C$_2$	N−M−C$_2$	N′−M−C$_2$
5 [FeL$_2$]	1.916(4)	2.086(5)	2.105(5)	1.364(6)	1.405(6)	180	115.1(4)	70.9(2)	109.1(2)
6 [CoL$_2$]	1.880(4)	2.041(4)	2.092(5)	1.359(6)	1.403(6)	180	115.0(4)	71.6(2)	108.4(2)
7 [NiL$_2$]	1.915(2)	2.030(3)	2.063(3)	1.341(4)	1.422(4)	180	116.0(3)	72.1(1)	108.0(1)
8 [NiL$^1{}_2$]	1.884(3)	2.097(4)	2.016(4)	1.347(5)	1.411(6)	163.1(2)	113.1(4)	72.2(2)	110.2(2)
10 [FeL$^2{}_2$]	1.914(3)	2.139(3)	2.074(3)	1.347(4)	1.433(5)	180	111.7(3)	70.3(1)	109.7(1)
12 [FeL$^3{}_2$]	1.881(6)	n.a.	n.a.	1.403(8)	1.349(8)	153.6(1)	121.4(5)	n.a.	n.a.
	1.987(6)								
[Fe{CR$_2$(C$_5$H$_4$N-2)}$_2$]^{27}	2.135(5)	n.a.	2.154(0)	1.347(10)	1.489(9)	180	112.7(6)	66.8(2)	
	2.139(5)		2.131(7)	1.341(6)	1.469(6)		113.6(9)	67.2(3)	
[Co{CPh(R)(C$_5$H$_4$N-2)}$_2$]^{28}	1.897(3)	/	2.071(3)	1.358(5)	1.484(5)	180.0(1)	107.6(1)	68.5(2)	
[Co{CR$_2$(C$_5$H$_4$N-2)}$_2$]^{28}	1.923(4)	/	2.092(6)	1.345(8)	1.482(7)	180	108.8(1)	69.3(2)	
[NiL^2(I)(PPh$_3$)]^{18}	1.932(5)	2.139(7)	1.982(6)	1.334(8)	1.409(9)		111.4(1)	70.7(2)	

[a] L = {N(R)C(^{t}Bu)CH(C$_6$H$_4$Me-4)}; L^1 = {N(R)C(Ph)CH(R)}, L^2 = {N(R)C(^{t}Bu)CH(R)}, L^3 = {N(R)C(^{t}Bu)CH(C$_{10}$H$_7$-1)}; R = SiMe$_3$.

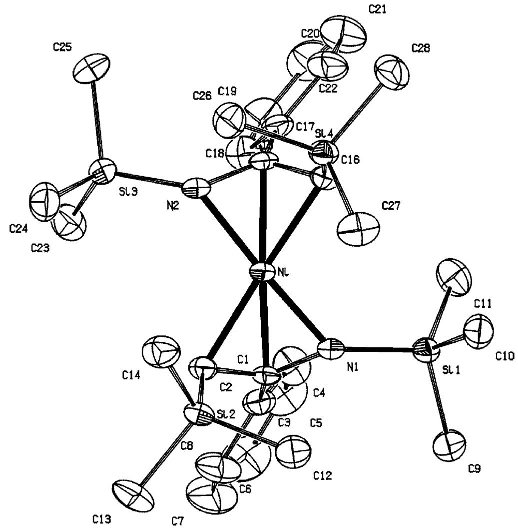

Figure 3. Molecular structure of compound **8**.

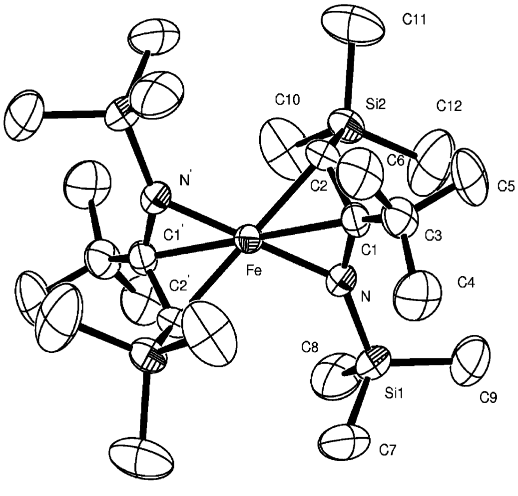

Figure 4. Molecular structure of compound **10**.

(1)°, 157.9(2)°, or 158.9(3)°, respectively]. The N−Fe−N′ bond angle in gaseous [Fe(NR$_2$)$_2$] is, however, 180°.[38]

NMR Spectroscopic Characterization of the Isomers of [Ni{η^3-N(R)C(^{t}Bu)CH(C$_6$H$_4$Me-4)}$_2$] (7). The three isomers of each of the Ni(II) complexes [NiL$_2$] (**7**) and [NiL$^1{}_2$] (**8**) are designated as **a**, **b**, and **c** in Figure 6; assignments for **7** and **8**, based on nuclear Overhauser (NOE) experiments in toluene-d_8 at ambient temperature, are summarized in Table 3. Under these conditions the three isomers of **7** were shown to be present in relative proportions 40 (**7a**):7 (**7b**):3 (**7c**). The experiments relating to **7** are described below.

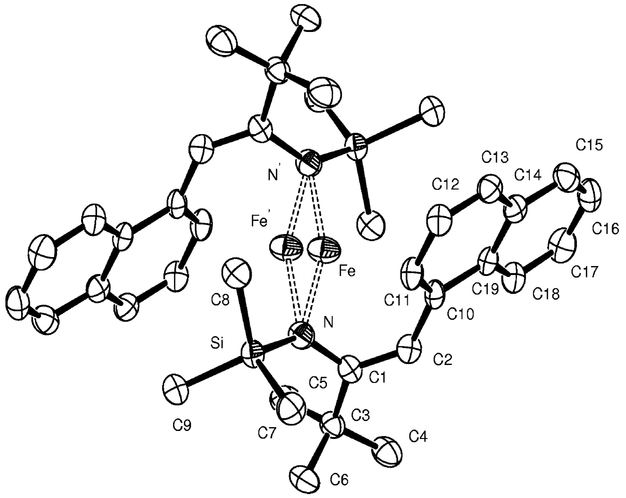

Figure 5. Molecular structure of compound **12**.

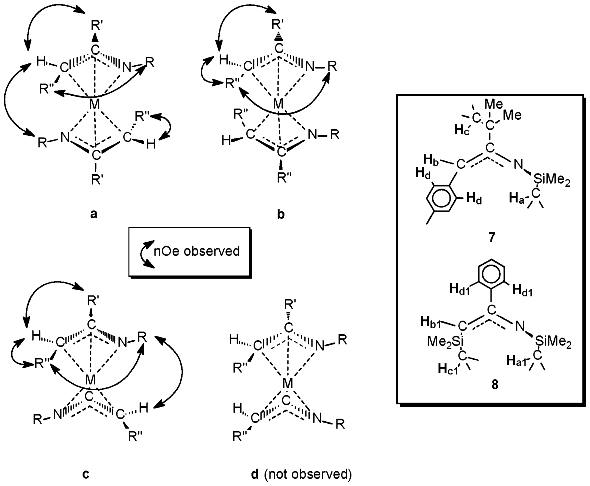

Figure 6. Isomers of complexes **7** and **8**.

Each of the isomers **7a**, **7b**, and **7c** showed NOEs between the trimethylsilyl proton (H$_a$) and the *tert*-butyl proton (H$_c$) and between the methine proton (H$_b$) and both the *tert*-butyl (H$_c$) and *ortho*-aryl protons (H$_d$). This is consistent with the 1-azaallyl ligand adopting the least sterically hindered *anti*-conformation for each isomer.

The molecular structure of crystalline **7** corresponds to that of **7a**. The observation that isomer **7b** did not show NOEs between the trimethylsilyl and methine

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[38] Andersen, R. A.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W.-P.; Rypdal, K. *Inorg. Chem.* **1988**, *27*, 1782.

Table 3. ^{1}H NMR NOE Data of the Isomers of 7 and 8 (in toluene-d_8 at 298 K, 500 MHz)[a]

isomer	irradiated peak (δ, H_x)	affected peaks (δ) and increased intensity (%) (δ)	%	(δ)	%	(δ)	%
7a	0.34 (H_a)	5.51 (H_b)	4.0	7.36 (H_d)	8.1		
	5.51 (H_b)	0.34 (H_a)	0.6	1.0 (H_c)	1.0	7.36 (H_d)	6.8
7b	0.44 (H_a)	7.30 (H_d)	5.0				
	4.53 (H_b)	0.88 (H_a)	1.1	7.30 (H_d)	8.2		
7c	0.25 (Ha)	5.22 (H_b)	4.6	7.45 (H_d)	7.1		
	5.22 (H_b)	0.25 (H_a)	0.4	1.10 (H_c)	1.2	7.45 (H_d)	6.2
8a	−0.08 (H_{c1})	3.36 (H_{b1})	10.3	7.32 (H_{d1})	5.2		
	0.44 (H_{a1})	3.36 (H_{b1})	4.0	7.32 (H_{d1})	1.3		
	3.36 (H_{b1})	−0.08 (H_{c1})	0.6	0.44 (H_{a1})	0.4	7.32 (H_{d1})	3.3
	7.32 (H_{d1})	−0.08 (H_{c1})	0.8	0.44 (H_{a1})	0.3	3.36 (H_{b1})	7.9
8b	0.08 (H_{a1})	7.68 (H_{d1})	5.2				
	0.24 (H_{c1})	2.20 (H_{b1})	8.6	7.68 (H_{d1})	3.4		
	2.20 (H_{b1})	0.24 (H_{c1})	0.8	7.68 (H_{d1})	4.5		
	7.68 (H_{d1})	0.08 (H_{c1})	0.7	0.24 (H_{c1})	0.8	2.20 (H_{b1})	9.1
8c	0.11 (H_{c1})	3.36 (H_b1)	3.3				
	0.35 (H_{a1})	3.36 (H_{b1})	5.4				

[a] For H_x abbreviations, see inset of Figure 6.

protons is consistent with **7b** having the two 1-azaallyl ligands in an *anti*-conformation but with a *trans*-configuration with eclipsed nitrogens. The final isomer, **7c**, showed NOEs attributed to the trimethylsilyl (H_a) and methine (H_b) protons. This, and the fact that isomer **7c** contains the 1-azaallyl ligand in the *anti*-conformation, points to isomer **7c** existing in the *cis*-configuration.

NMR Characterization of the Isomers of [Ni{η^3-N(R)C(Ph)CH(R)}$_2$] (8). NMR spectroscopy showed that compound **8** existed in solution as three isomers, **a**, **b**, and **c** in relative ratios 15.8:8.3:1, respectively. Indeed, the ^{1}H NMR spectrum (298 K, C_6D_6) revealed three sets of two inequivalent $SiMe_3$ signals, at δ −0.08 ($CHSiMe_3$) and 0.44 ($NSiMe_3$) (**a**), δ 0.05 ($NSiMe_3$) and 0.24 ($CHSiMe_3$) (**b**), and δ 0.08 ($CHSiMe_3$) and 0.32 ($NSiMe_3$) (**c**). Three signals were also noticed for the protons in the 2-position of the phenyl ring, at δ 7.41 (**a**), 7.75 (**b**), and 7.85 (**c**). Only two methine proton resonances were present at δ 2.28 (**b**) and 3.45 (**a** and **c**); the latter signal split at 263 K in toluene-d_8 into δ 3.36 (**c**) and 3.39 (**a**). The ^{13}C{^{1}H} NMR spectrum showed four $SiMe_3$ [at δ 2.3 and 2.6 (**a**), 1.9 and 3.3 (**b**)] and two methine carbon [at δ 55.9 (**a**) and 44.3 (**b**)] resonances. Signals corresponding to the minor isomer **c** were either hidden or not observed. Nevertheless, the three species were distinguishable by the ^{29}Si{^{1}H} NMR spectroscopic INEPT technique at 263 K, with $NSiMe_3$ at δ −4.1 (**a**), −3.7 (**b**), and −3.4 (**c**) and $SiMe_3$ signals at δ 0.8 (**b**), 1.0 (**c**), and 3.3 (**a**). The *N*-trimethylsilyl resonances were assigned unambiguously to their corresponding isomers by 2D ^{29}Si{^{1}H}/^{1}H correlation.

NOE studies similar to those performed on complex **7** were carried out on solutions of crystalline **8** in C_6D_6 at 298 K. The *N*-trimethylsilyl (H_{a1}), methine (H_{b1}), *C*-trimethylsilyl (H_{c1}), and aryl (H_{d1}) proton signal (Figure 6) of each of the three isomers was irradiated in turn, and the effects on the rest of the spectrum were noted, as summarized in Table 3.

An interesting feature of complexes **7** and **8** is the fact that the signal for the methine proton for **7b** (δ 4.53) or **8b** (δ 2.28) appeared at much lower frequency than those assigned to the other isomers: **7a** (δ 5.51), **7c** (δ 5.22), **8a** (δ 3.39), and **8c** (δ 3.36). This is attributed to a *trans*-influence, as only in isomer **b** is the methine carbon *trans* to nitrogen, whereas in **a** and **c** they are arranged in a *cis* fashion.

Fluxional Processes. Variable-temperature (VT) ^{1}H NMR spectroscopic experiments were performed on **7** and **8** in toluene-d_8. When the temperature of the solution of **7** was raised to 358 K, the resonances for **7b** and **7c** broadened; at 373 K, those of **7b** and **7c** disappeared only to reappear on cooling to 298 K. Line shape analysis of **7a** showed no observable change. For **8**, however, no change in the ratio of the three isomers was observed (298−383 K). A very minor new species appeared at δ 4.5, probably from decomposition/hydrolysis of the ligand; its concentration remained very low (~2%). At 373 K, the three methine signals became broad and broadened further at 383 K. For complex **13**, a VT-NMR spectroscopic experiment (C_6D_6) showed that broadening of the signals, particularly those attributed to the methine protons (both allyl and azaallyl) and to the trimethylsilyls, began already at 313 K. At 333 K, only a single species was observed (but the signals of both methines remained broad; they became sharp at 353 K). By cooling to 298 K, the two isomers were once more observed in the same relative ratio, 2.7:1.

Variable-temperature saturation transfer (VTST) ^{1}H NMR spectroscopic experiments in toluene-d_8 were performed on complexes **7** and **8**. Irradiation of the methine singlet H_b of isomer **7b** at δ 4.53 reduced the intensity by 5% of its methine singlet H_b, at δ 5.22, but had no effect on the methine singlet H_b at δ 5.51 of **7a**; the latter had shown NOEs for the aryl (H_d) and *tert*-butyl (H_c) signals of isomer **7b**. The second VTST experiment, at 328 K, involved irradiation of H_b for **7b** at δ 4.53, which greatly reduced the intensity (60%) of H_b at δ 5.22 of **7c**, with H_b (δ 5.51) of **7a** unaffected. Irradiation of the *C*-trimethylsilyl (H_{c1}) singlet of **8a** at δ −0.08 reduced strongly the intensity of the H_{c1} of **8b** and **8c** at δ 0.11 and 0.24, respectively. Similar irradiation of the *N*-trimethylsilyl (H_{a1}) protons at δ 0.44 also significantly decreased the corresponding signals of **8b** and **8c** at δ 0.08 and 0.35, respectively, indicating a dynamic exchange between the three species.

The VT and VTST ^{1}H NMR spectroscopic experiments for compound **7** indicate that each of the isomers **7b** and **7c** was involved in a dynamic exchange process with the other, but not with **7a**. In contrast, for **8** all three isomers (**8a**−**c**) were interconverting. Several dynamic processes have been described for complexes containing 1-azaallyl or 2-pyridylalkyl moieties: (i) for conversion of 1-azaallyl anions (Li,[39] Mg,[40] Al,[40] and Zn[40]) having the kinetically controlled *E*-configuration into the thermodynamically stable *Z*-configuration; and (ii) the fluxional behavior of the tin(II) 2-pyridylalkyls [Sn{η^2-$CR_2C_5H_4N$-2}$_2$], [Sn{η^2-$CR_2C_5H_4N$-2}Cl], and [Sn{η^2-$CR_2C_5H_4N$-2}N(R)$_2$].[41] As for (ii), the significant variation of δ[^{119}Sn{^{1}H}] with temperature for the three compounds was attributed to a weak dative pyridyl-N−Sn bond. The ^{1}H NMR spectrum of [Sn{$CR_2C_5H_4N$-2}-Cl] at 193 K showed two distinct $SiMe_3$ signals, which merged at 220 K. The proposed mechanism[41] for the

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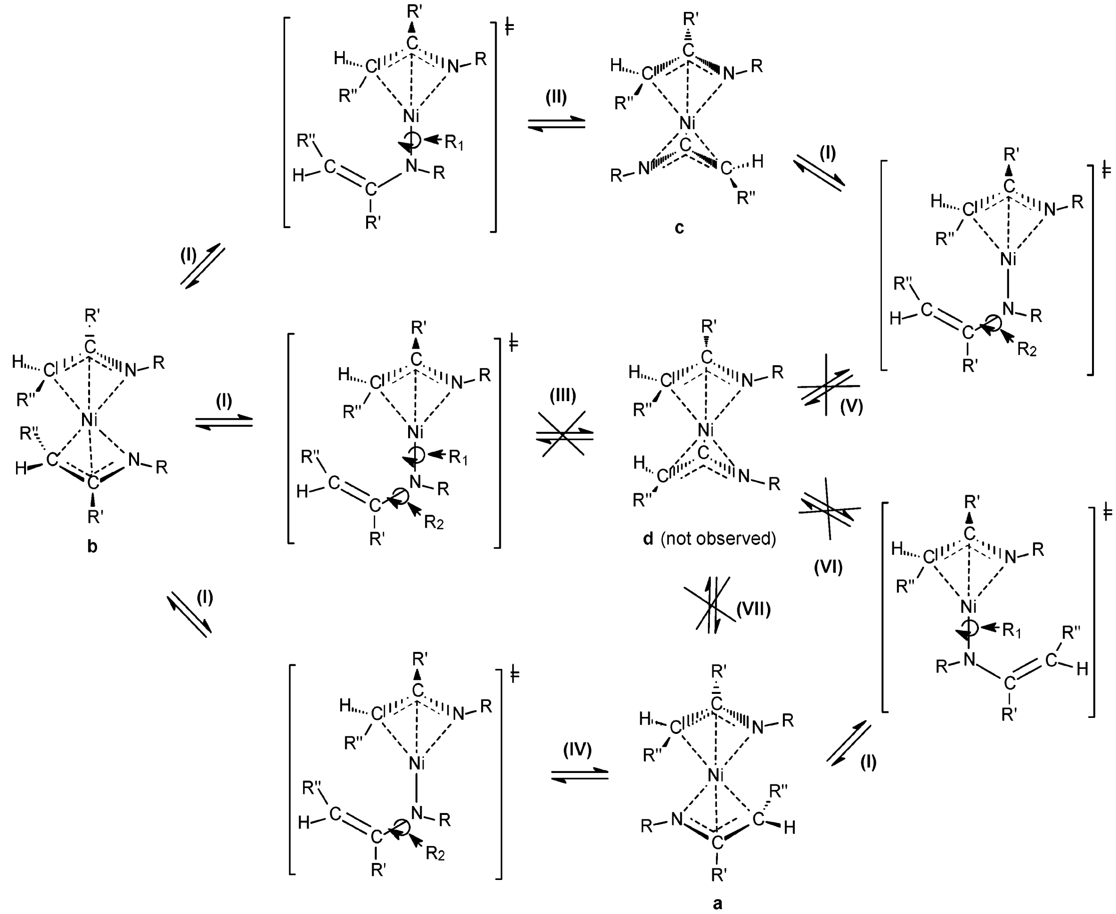
[39] (a) Knorr, R.; Löw, P. *J. Am. Chem. Soc.* **1980**, *102*, 3241. (b) Knorr, R.; Weiss, A.; Löw, P. J.; Räpple, E. *Chem. Ber.* **1980**, *113*, 2462.

[40] (a) Lalonde, J. J.; Bergbreiter, D. E.; Newcomb, M. *J. Org. Chem.* **1986**, *51*, 1369.

[41] Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336.

Scheme 4. Proposed Mechanism for Dynamic Processes in Compounds 7 and 8



interconversion involved η^2-κ^1-slippage and rotation around the terminal tin−carbon bond. A similar mechanism had been postulated to explain the fluxional behavior of a series of (η^3-1-azaallyl)di(carbonyl)nitrosyliron complexes, which at ambient temperature showed interconversion of the *syn* and *anti* methine protons of the terminal carbon;[42] the proposed mechanism was via an η^3-κ^1 slippage, followed by rotation around the terminal carbon. The single-crystal X-ray diffraction study of $[\mathrm{Sn}\{\eta^3\text{-N(R)C(Ph)CR}_2\}\{\mathrm{N(R)C(Ph){=}CR_2}\}]$ showed it to exist in the crystalline state as a mixed (iminoalkyl)(enamido) complex.[36] VT ^{1}H and ^{13}C NMR spectroscopic experiments on crystalline $[\mathrm{Sn}\{\eta^3\text{-N(R)C(Ph)CR}_2\}\{\mathrm{N(R)C(Ph){=}CR_2}\}]$ showed the two ligands to be equivalent in solution down to 183 K, indicating that there was a rapid exchange between the κ^1- and η^3-coordinated ligands.[33]

On the basis of our experiments on the isomers of **7** and **8** and the above literature precedents, the proposed mechanism of the exchange processes is summarized in Scheme 4 (the isomers shown in parentheses are intermediates or transition states); the failure to observe an isomer **7d** or **8d** is attributed to the excessively high barrier for the possible rearrangement III, V, or VI. The **7b** ↔ **7c** exchange is suggested to involve from **7b** successive (I and II in Scheme 4) C−Ni dissociation ($\eta^3 \rightarrow \kappa^1$ slippage) followed by a 180° rotation about the Ni−N bond. The lack of exchange between **7a** and **7b** or **7c** is attributed to possible restricted rotation (R$_2$ in step I or R$_1$ in step VI) about the N−C(^{t}Bu) or Ni−N bond, respectively, due to the two sets of $\mathrm{C(^tBu){=}CH(C_6H_4Me\text{-}4)}$ moieties; a possible corollary is that **7a** may not undergo $\eta^3 \rightarrow \kappa^1$ slippage (I in Scheme 4). For **8**, the exchange between each of the three isomers is accounted for in the case of **8a** ↔ **8b** (from **8a**) by the successive steps IV and I; the barrier R$_2$ for steps I is lower, involving two sets of sterically less encumbered $\mathrm{C(^tBu){=}CH(SiMe_3)}$ moieties. The variation in the relative proportions (e.g., the greater prominence of isomer **b** for **8** rather than **7**) may be due to steric effects.

An alternative to the $\eta^3 \rightarrow \kappa^1 \rightarrow (\eta^3)'$ mechanism is the $\eta^3 \rightarrow (\eta^3)'$, involving rotation about one of the Ni−centroid axes. For example, isomer **7a** does not undergo such a rotation (VII in Scheme 4) to generate **7d**, because the latter would have the sterically unfavorable *cis*-configuration with eclipsed nitrogen atoms. In various η^3-allyl-metal systems, the $\eta^3 \rightarrow (\eta^3)'$ process has been confirmed spectroscopically, as in selected complexes of Mo, W, Ru, Rh, and Pt,[43a] such as $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_3(\mathrm{diphos})]^+$,[43b] and has also been proposed to account for the observed equivalence of the allyl groups in $[\mathrm{Ru}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{CO})_2]$.[44] For $[\mathrm{M}(\eta^3\text{-}\mathrm{C_3H_5})_2]$ (M = Ni, Pt), however, a qualitative MO treatment indicated that simple rotation about the allyl−metal axis was symmetry-forbidden and hence a high-energy process.[45] Both mechanisms have been put forward for [Ni(η^3-1-

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(42) Nakanishi, S.; Masuzaki, K.; Takata, T. *Inorg. Chem. Commun.* **2000**, *3*, 469.

(43) (a) Faller, J. W. *Adv. Organomet. Chem.* **1978**, *16*, 211. (b) Faller, J. W.; Haitko, D. A. *J. Organomet. Chem.* **1978**, *149*, C19.

(44) Cooke, M.; Goodfellow, R. J.; Green, M.; Parker, G. *J. Chem. Soc (A)* **1971**, 16.

(45) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656.

$MeC_3H_4)_2$], in which a total of 12 isomers, due to *syn*- or *anti*-methyl groups, is possible; spectroscopic studies, however, showed the complex to exist as a mixture of four isomers, detected in both the ^{13}C and ^1H NMR spectra at −20 °C and shown, by analysis of the proton−proton coupling constants, to contain exclusively *syn*-substituted η^3-allyl groups.[46] These four isomers underwent fluxional processes with one another, but with retention of the *syn*-configuration, suggesting that any $\eta^3 \rightarrow \kappa^1$ ligand slippage occurred at the CH_2 carbon.

Polymerization Experiments. Compounds **8** and **13** were used as catalyst precursors for ethylene polymerization. The reactions were carried in toluene at ca. 298 K under 1.4 bar of ethylene, in the presence of MAO (500 equiv/Ni) or $B(C_6F_5)_3$ (1.5 equiv/Ni). Limited amounts of oligomer were obtained (but not analyzed) with **8**/$B(C_6F_5)_3$. No poly-(oligo-)merization was observed for the other experiments.

Conclusions

Nine crystalline 1-azaallylmetal(II) complexes have been prepared in good yield from the appropriate potassium or lithium 1-azaallyl and the metal(II) halide MX_2 or [{Ni{η^3-C_3H_5}(μ-Cl)}$_2$]: [FeL_2] (**5**), [CoL_2] (**6**), [NiL_2] (**7**), [NiL^1_2] (**8**), [PdL^1_2] (**9**), [FeL^2_2] (**10**), [CoL^2_2] (**11**), [FeL^3_2] (**12**), and [Ni{η^3-C_3H_5}(L^3)] (**13**) (L = {N(R)C(^{t}Bu)CH(C_6H_4Me-4)}, L^1 = {N(R)C(Ph)CH(R)}, L^2 = {N(R)C(^{t}Bu)CH(R)}, L^3 = {N(R)C(^{t}Bu)CH($C_{10}H_7$-1)}; R = $SiMe_3$; MX_2 = $FeBr_2$, $CoCl_2$, [$NiBr_2$(dme)], [$PdCl_2$(cod)]). X-ray structures show that (i) the complexes **5**, **6**, and **7** are isomorphous, and (ii) in each of **5**−**8** and **10** the staggered pair of 1-azaallyl ligands binds to the pseudooctahedral metal ion in an η^3-fashion, whereas the two-coordinate Fe(II) complex **12** has the ligands bound in the κ^1-enamido mode. Remarkably, although the Fe(II) 1-azaallyls **5**, **10**, and **12** are high-spin d^6 complexes with magnetic moments (in solution at ambient temperature) in the range 5.01−5.61 μ_B, the cobalt(II) analogues **6** and **11** are low-spin d^7 complexes, with μ_{eff} = 2.73−3.01 μ_B. The diamagnetic Ni(II) (**7**, **8**, **13**) and Pd(II) (**9**) 1-azaallyls exist as a mixture of three (**7**, **8**, **9**) or two (**13**) isomers in C_6D_6 or toluene-d_8 at 298 K; their structures have been elucidated from NOE, 2D, and saturation transfer NMR spectroscopic data. Dynamic processes in toluene-d_8 have been revealed by further variable-temperature NMR spectral data and mechanisms suggested in terms of $\eta^3 \rightarrow \kappa^1 \rightarrow (\eta^3)'$ Ni−C dissociative/associative processes.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of pure argon using Schlenk apparatus and a vacuum line, unless otherwise stated. The solvents used were of reagent grade or better and were freshly distilled under dry dinitrogen and freeze/thaw degassed prior to use. The drying agents employed were (i) sodium benzophenone (benzene, diethyl ether, thf, toluene, and dme), (ii) sodium−potassium alloy (light petroleum, bp 30−40 and 60−80 °C), and (iii) phosphorus(V) oxide (dichloromethane). Reaction solvents and deuterated solvents for NMR spectroscopy were stored over a potassium mirror (thf-d_8, C_6D_6, and toluene-d_8) or A4 molecular sieve ($CDCl_3$).

Elemental analyses were performed on a CEC 240 XA analyzer by Medac Ltd, Brunel University (the %C reported for **5** and **13** were lower than calculated, a feature we have noted previously on Si-containing compounds examined by Medac). EI-MS data were recorded using VG Autospec or Kratos MS 80 RF instruments at 70 eV. The carrier gas was helium, at a flow rate 2 cm^3 min^{-1}. Melting points were determined under argon in sealed capillaries on an electrothermal apparatus and were uncorrected.

NMR spectra were recorded using a Bruker AC-P250 (^1H, 250.1; ^{13}C, 62.9 MHz), DPX-300 (^1H, 300.1; ^{13}C, 75.5 MHz), AMX-400 (^1H, 400.1; ^{13}C 100.6 MHz), or AMX-500 (^1H, 500.1; ^{13}C, 125.7; ^{29}Si, 99.3 MHz) spectrometer and referenced internally (^1H, ^{13}C) to residual solvent. The ^{29}Si spectra were referenced externally to $SiMe_4$. Unless otherwise stated, all NMR spectra other than ^1H were proton-decoupled and recorded at ambient probe temperature. IR spectra were recorded either as Nujol mulls between KBr plates or as KBr pellets using a Perkin-Elmer 1720 FT spectrometer.

Compounds KL (**1**),[20] [LiL^1(thf)]$_2$ (**2**),[1a] LiL^2 (**3**),[1a] KL^3 (**4**),[21] [$NiBr_2$(dme)],[47] [{Ni(η^3-C_3H_5)(μ-Br}$_2$],[48] and [$PdCl_2$(cod)][49] were synthesized according to published procedures, while $FeBr_2$ (Aldrich) was purchased and used without further purification. $CoCl_2$ (BDH) was dried using refluxing trimethylsilyl chloride and then heated at 140 °C in vacuo.

[Fe{η^3-N(SiMe$_3$)C(^{t}Bu)CH(C$_6$H$_4$Me-4)}$_2$] (5). A solution of KL (**1**) (1.20 g, 4 equiv) in thf (ca. 40 cm^3) was slowly added to a stirred suspension of $FeBr_2$ (0.43 g, 2 mmol) in thf (ca. 10 cm^3) at −78 °C. The suspension was allowed to warm to room temperature and stirred for a further 16 h. The resultant dark red solution, with a fluffy white precipitate (KBr), was filtered. The solvent was removed from the filtrate in vacuo to afford a dark red microcrystalline solid, which was washed with light petroleum (bp 30−40 °C, ca. 20 cm^{-3}). The residue was dissolved in CH_2Cl_2 (ca. 30 cm^3) and filtered to remove further KBr. The filtrate was concentrated to ca. 10 cm^3 and cooled at −30 °C, yielding complex **5** (0.91 g, 79%), as bright red single crystals, mp 163−5 °C. MS: *m*/*e* (%, assignments), 576 (37), $[M]^+$; 420 (27, $[M - N(SiMe_3)C(^tBu)]^+$); 316 (68, $[M - L]^+$); 261 (54, $[L + 1]^+$); 246 (13, $[L - Me]^+$); 204 (30, $[L - {}^tBu]^+$). Anal. Calcd for $C_{32}H_{52}FeN_2Si_2$: C, 66.6; H, 9.11; N, 4.85. Found: C, 65. 8; H, 9.09; N, 4.91.

[Co{η^3-N(SiMe$_3$)C(^{t}Bu)CH(C$_6$H$_4$Me-4)}$_2$] (6). A solution of KL (**1**) (1.61 g, 5 equiv) in thf (ca. 40 cm^3) was slowly added to a stirred suspension of $CoCl_2$ (0.34 g, 3 mmol) in thf (ca. 10 cm^3) at −78 °C. After warming to room temperature and stirring for a further 12 h, a dark red solution was obtained. Tetrahydrofuran was removed in vacuo; the residual red solid was heated at ca. 70 °C for 3 h. The residue was washed with light petroleum (bp 60−80 °C, ca. 10 cm^3) and extracted with CH_2Cl_2 (ca. 30 cm^3). The dark orange extract was filtered and the solvent was removed from the filtrate in vacuo to afford an orange crystalline solid, which was redissolved in Et_2O (ca. 40 cm^3), concentrated to ca. 15 cm^3, and cooled at −30 °C to yield bright orange single crystals of complex **6** (1.36 g, 89%), mp >130 °C dec. MS: *m*/*e* (%, assignments), 580 (17, $[M]^+$); 522 (10, $[M - {}^tBu]^+$); 423 (18); 320 (31, $[M - L]^+$); 261 (51, $[L + 1]^+$), 246 (15, $[L - Me]^+$); 204 (32, $[L - {}^tBu]^+$). Anal. Calcd for $C_{32}H_{52}CoN$: C, 66.3; H, 9.10; N, 4.83. Found: C, 66.3; H, 9.16; N, 4.73.

[Ni{η^3-N(SiMe$_3$)C(^{t}Bu)CH(C$_6$H$_4$Me-4)}$_2$] (7). A solution of KL (**1**) (0.98 g, 3 equiv) in thf (ca. 40 cm^3) was slowly added to a stirred suspension of [$NiBr_2$(dme)] (0.5 g, 1.6 mmol) in thf (ca. 10 cm^3) at −78 °C. The suspension was allowed to warm to room temperature and was stirred for a further 12 h,

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[46] Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425.

[47] Ward, L. G. D. *Inorg. Synth.* **1972**, *13*, 162.

[48] Fischer, E. O.; Bürger, G. *Z. Naturforsch.* **1961**, *16b*, 77.

[49] Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.

yielding a dark red solution. Tetrahydrofuran was removed in vacuo. The residue was washed with light petroleum (bp 60−80 °C, ca. 15 cm^3) and was extracted with Et$_2$O (ca. 20 cm^3). The extract was filtered. The solvent was removed from the filtrate in vacuo to afford a red crystalline solid, which was redissolved in warm benzene (ca. 30 cm^3) and concentrated to ca. 10 cm^3 to afford bright red single crystals of complex **7** (0.55 g, 57%), mp 174−8 °C. In toluene-*d*$_8$ at 298 K, three isomers of relative intensities 80% (**7a**), 14% (**7b**), and 6% (**7c**) were identified by ^{1}H NMR (500 MHz): δ 7.46 (d, Ar *o-H*, **7c**), 7.36 (d, Ar *o-H*, **7a**), 7.30 (d, Ar *o-H*, **7b**), 6.78 (d, Ar *m-H*, **7a**), 6.72 (d, Ar *m-H*, **7c**), 5.51 (s, 4-MeC$_6$H$_4$C*H*C(^{t}Bu), **7a**), 5.22 (s, 4-MeC$_6$H$_4$C*H*C(^{t}Bu), **7c**), 4.53 (s, 4-MeC$_6$H$_4$C*H*C(^{t}Bu), **7b**), 2.00 (s, 4-C*H*$_3$C$_6$H$_4$, **7c**), 1.98, (s, 4-C*H*$_3$C$_6$H$_4$, **7b**), 1.95 (s, 4-C*H*$_3$C$_6$H$_4$, **7a**), 1.15 (s, C(C*H*$_3$)$_3$, **7c**), 1.10 (s, C(C*H*$_3$)$_3$, **7b**), 1.00 (s, C(C*H*$_3$)$_3$, **7a**), 0.45 (s, NSi(C*H*$_3$)$_3$, **7b**), 0.34 (s, NSi(C*H*$_3$)$_3$, **7a**), 0.25 (s, NSi(C*H*$_3$)$_3$, **7c**). ^{13}C{^{1}H} NMR (75.46 MHz): δ 151.90 (s, *C*(^{t}Bu)NSi), 137.65 (*C*$_{\mathrm{ipso}}$), 133.83 (*C*$_{\mathrm{ipso}}$), 128.88 (*C*H), 126.93 (*C*H), 64.47 (s, *C*HC(^{t}Bu)), 39.44 (s, *C*(CH$_3$)$_3$), 29.39 (s, 4-*C*H$_3$C$_6$H$_4$), 4.34 (s, NSi(*C*H$_3$)$_3$). MS: *m*/*e* (%, assignments), 580 (17, [M]$^+$); 522 (10, [M − ^{t}Bu]$^+$); 423 (18, [M − N(SiMe$_3$)C(^{t}Bu)]$^+$); 320 (31, [M − L]$^+$); 261 (48, [L + 1]$^+$); 246 (17, [L − Me]$^+$); 204 (28, [L − ^{t}Bu]$^+$). Anal. Calcd for C$_{32}$H$_{52}$NiN$_2$Si$_2$: C, 66.3; H, 9.10; N, 4.83. Found: C, 66.6; H, 9.08; N, 4.89.

[Ni{*η*^{3}-N(R)C(Ph)CH(R)}$_2$] (8). [LiL^1(thf)]$_2$ (1.52 g, 2.23 mmol) in thf (15 cm^3) was added dropwise to a solution of [NiBr$_2$(dme)] (0.69 g, 2.23 mmol) in thf (20 cm^3) at ca. 0 °C. The resulting deep purple mixture was set aside for ca. 15 min at 0 °C and then 2 h at ca. 20 °C. The solvent was removed in vacuo, and the residue was "stripped" with light petroleum (bp 30−40 °C, 3 × 10 cm^3; this procedure refers to adding the solvent and then removing it in vacuo) and then extracted into light petroleum (bp 30−40 °C, 20 cm^3). The extract was filtered. The filtrate was concentrated to ca. 3−4 cm^3 and cooled to −30 °C, yielding deep purple crystals of **8** (0.78 g, 59%), mp 95−8 °C. As for **7**, three isomers in C$_6$D$_6$ at 298 K of relative intensities 63 (**8a**), 33 (**8b**), and 4% (**8c**) were identified by ^{1}H NMR (300.1): δ −0.08 (s, Si(C*H*$_3$)$_3$, **8a**), 0.05 (s, NSi(C*H*$_3$)$_3$, **8b**), 0.08 (s, Si(C*H*$_3$)$_3$, **8c**), 0.24 (s, Si(C*H*$_3$)$_3$, **8c**), 0.32 (s, NSi(C*H*$_3$)$_3$, **8c**), 0.44 (s, NSi(C*H*$_3$)$_3$, **8a**), 2.28 (s, 1 H, C*H*, **8b**), 3.45 (s, C*H*, **8a** and **8b**), 7.05 (m, Ph *m-H*), 7.41 (d, $^3J_{\mathrm{HH}}$ = 7 Hz, Ph *o-H*), 7.75 (m, Ph *p-H*, **8a** and **8c**), 7.85 (m, Ph *p*-C*H*, **8b**). ^{13}C{^{1}H} NMR (75.5 MHz): δ 1.9, 2.3, 2.6, and 3.3 (s, Si(*C*H$_3$)$_3$ and NSi(*C*H$_3$)$_3$), 44.3 (s, *C*H, **8b**), 55.9 (s, *C*H, **8a**), 128.0, 128.2, 129.0, 129.8, and 130.5 (s, Ph *o*-, *m*-, and *p*-*C*H), 142.8 and 143.6 (s, Ph *C*$_{\mathrm{ipso}}$), 160.3 and 163.2 (s, *C*N). ^{29}Si NMR (99.3 MHz): δ −4.1 (s, N*Si*(CH$_3$)$_3$, **8b**), −3.7 (s, N*Si*(CH$_3$)$_3$, **8a**), −3.4 (s, N*Si*(CH$_3$)$_3$, **8c**), 0.8 (s, *Si*(CH$_3$)$_3$, **8b**), 1.0 (s, *Si*(CH$_3$)$_3$, **8c**) and 3.3 (s, N*Si*(CH$_3$)$_3$, **8a**). MS: *m*/*e* (%, assignments), 582 (13, [M − H]$^+$); 483 (71, [M − CHNSiMe$_3$]$^+$); 263 (56, [L^1 − H]$^+$); 248 (17, [L^1 − H − Me]$^+$); 185 (25, [L^1 − Ph]$^+$); 176 (72, [L^1 − NSiMe$_3$]$^+$); 147 (100) and 73 (85, [SiMe$_3$]$^+$). Anal. Calcd for C$_{28}$H$_{48}$N$_2$NiSi$_4$: C, 57.6; H, 8.36; N, 4.80. Found: C, 57.7; H, 8.36; N, 4.69.

[Pd{*η*^{3}-N(R)C(Ph)CH(R)}$_2$] (9). [LiL^1(thf)]$_2$ (2.24 g, 3.28 mmol) in thf (20 cm^3) was added dropwise to a suspension of [PdCl$_2$(cod)] (0.94 g, 3.29 mmol) in thf (20 cm^3) at ca. 20 °C. The resulting deep brown mixture was stirred for 20 min, the solvent was removed in vacuo, and the residue was "stripped" with light petroleum (bp 60−80 °C, 3 × 20 cm^3) and then extracted into light petroleum (bp 30−40 °C, 20 cm^3). The extract was filtered. Volatiles were removed form the filtrate in vacuo, affording a deep red-brown oil. The latter was covered with light petroleum (bp 30−40 °C, 15 cm^3). Cooling to −20 °C gave yellow-orange crystals of **9** (1.00 g, 52%), mp 73−5 °C. As for **7**, three isomers of **9** in C$_6$D$_6$ at 298 K of relative intensities 51 (**9a**), 30 (**9b**), and 19% (**9c**) were identified by ^{1}H NMR (300.1 MHz): δ 0.07 (s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$, **9a**), 0.19 (s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$, **9b**), 0.22 (s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$, **9c**), 0.32 (s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$, **9b**), 0.39 (s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$, **9c**), 0.49 (**9a**, s, Si(C*H*$_3$)$_3$ or NSi(C*H*$_3$)$_3$), 2.69 (s, C*H*, **9b**), 3.49 (s, C*H*, **9c**), 3.67 (s, C*H*, **9a**), 7.00−7.11 (m, Ph), 7.34−7.39 (m, Ph), 7.55−7.61 (m, Ph), 7.68 (m, Ph). ^{13}C{^{1}H} NMR (75.5 MHz): δ 2.4, 2.5, 2.8, and 3.3 (s, Si(*C*H$_3$)$_3$ and NSi(*C*H$_3$)$_3$), 42.0 (s, *C*H, **9b**), 48.5 (s, *C*H, **9c**), 58.1 (s, *C*H, **9a**), 128.0, 128.1, 128.3, 128.5, 128.7, 129.5, 130.1, and 130.4 (s, Ph *o*-, *m*-, and *p*-*C*H), 141.3 (**9c**), 142.5 (**9a**), and 142.6 (**9b**, s, Ph *C*$_{\mathrm{ipso}}$), 167.5 (**9a**) and 175.0 (**9b**, s, *C*N). MS: *m*/*e* (%, assignments), 630 (60, [M − H]$^+$); 616 (10, [M − Me]$^+$); 557 (13, [M − H − SiMe$_3$]); 544 (10, [M − CHSiMe$_3$]); 354 (47, [M − L^1 − Me]$^+$); 262 (89, [L^1]$^+$); 247 (75, [L^1 − Me]$^+$); 185 (29, [L^1 − Ph]$^+$); 176 (56, [L^1 − NSiMe$_3$]$^+$); 73 (100, [SiMe$_3$]$^+$). Anal. Calcd for C$_{28}$H$_{48}$N$_2$PdSi$_4$: C, 53.3; H, 7.66; N, 4.44. Found: C, 53.8; H, 7.62; N, 4.44.

[Fe{*η*^{3}-N(R)C(^{t}Bu)CH(R)}$_2$] (10). A solution of [LiL^2]$_2$ (**3**) (0.8 g, 3 mmol) in Et$_2$O (ca. 10 cm^3) was slowly added to a stirred suspension of FeBr$_2$ (0.35 g, 1.6 mol) in Et$_2$O (ca. 50 cm^3) at −78 °C. The suspension was allowed to warm to room temperature and was stirred for 4 h. The mixture was filtered and solvent removed from the dark red filtrate in vacuo. The residual orange solid was heated at ca. 80 °C in vacuo for 4 h, then extracted with light petroleum (bp 60−80 °C, ca. 40 cm^3). Crystallization was affected by concentrating to ca. 20 cm^3 and cooling to −30 °C, affording deep red single crystals of complex **10** (1.47 g, 91%), mp 135−8 °C. MS: *m*/*e* (%, assignment), 540 (47, [M]$^+$); 483 (38, [M − ^{t}Bu]$^+$); 298 (9, [M − L^2]$^+$); 186 (16, [L^2 − ^{t}Bu]$^+$); 170 (13, [L − N(^{t}Bu)]$^+$). Anal. Calcd for C$_{24}$H$_{56}$FeN$_2$Si$_4$: C, 53.3; H, 10.5; N, 5.18. Found: C, 53.1; H, 10.6; N, 5.12.

Co{N(R)C(^{t}Bu)CH(R)}$_2$ (11). A solution of [LiL^2]$_2$ (**3**) (1.0 g, 4 mmol) was slowly added to a stirred suspension of CoCl$_2$ (0.26 g, 2 mmol) in Et$_2$O (ca. 30 cm^3) at −78 °C. The dark orange suspension was allowed to warm to room temperature and was stirred for 4 h. Diethyl ether was removed in vacuo and the residual orange solid heated at ca. 80 °C in vacuo for 4 h, then extracted with light petroleum (bp 30−40 °C, ca. 40 cm^3), and crystallized by concentrating to ca. 10 cm^3 and cooling at −30 °C to yield bright orange single crystals of complex **11** (0.95 g, 86%), mp 120−3 °C. MS: *m*/*e* (%, assignment), 543 (100, [M]$^+$); 486 (27, [M − ^{t}Bu]$^+$); 429 (12, [M − N(SiMe$_3$)C(^{t}Bu)]$^+$). Anal. Calcd for C$_{24}$H$_{56}$CoN$_2$Si$_4$: C, 53.0; H, 10.3; N, 5.16. Found: C, 53.1; H, 10.2; N, 5.07.

[Fe{N(R)C(^{t}Bu)═CH(C$_{10}$H$_7$-1)}$_2$] (12). A solution of KL^3 (**4**) (2.0 g, 6 mmol) in thf (ca. 50 cm^3) was added to FeBr$_2$ (0.64 g, 3 mmol) suspended in thf (ca. 10 cm^3) at −78 °C. The suspension was allowed to warm to room temperature and stirred for a further 12 h, a dark red solution being obtained. Tetrahydrofuran was removed in vacuo, and the residual red solid was washed with light petroleum (bp 60−80 °C, ca. 20 cm^3) and diethyl ether (ca. 25 cm^3), then extracted with toluene (ca. 50 cm^3). The extract was filtered, and the filtrate was concentrated to ca. 10 cm^3 and cooled at −30 °C to give bright red single crystals of complex **12** (1.5 g, 78%), mp >60 °C dec. MS: *m*/*e* (%, assignment), 647 (28, [M]$^+$); 591 (41, [M − ^{t}Bu]$^+$); 492 (18, [M − N(SiMe$_3$)C(^{t}Bu)]$^+$); 352 (10, [M − L^3]$^+$). Anal. Calcd for C$_{38}$H$_{52}$FeN$_2$Si$_2$: C, 70.3; H, 8.09; N, 4.31. Found: C, 70.2; H, 8.11; N, 4.29.

[Ni{*η*^{3}-C$_3$H$_5$}{N(R)C(^{t}Bu)═CH(C$_{10}$H$_7$-1)}$_2$] (13). KL^3 (**4**) (0.93 g, 2.77 mmol) in thf (ca. 25 cm^3) was added dropwise to a cooled (0 °C) solution of [{Ni(*η*^{3}-C$_3$H$_5$)(*μ*-Br}$_2$] (0.56 g, 1.56 mmol) in thf (30 cm^3). The resulting mixture was warmed to ca. 25 °C and stirred for 3 h. The solvent was removed in vacuo and "stripped" with pentane (30 cm^3). The dark red residue was extracted with pentane (45 cm^3). The extract was filtered; the filtrate was concentrated to 3−4 cm^3 and cooled at −20 °C, affording deep red and sticky crystals, which upon recrystallization yielded **13** (0.55 g, 50%), mp 92−4 °C. Two isomers of **13** in C$_6$D$_6$ at 298 K of relative intensities 73 (**13a**) and 27% (**13b**) were identified by ^{1}H NMR (300.1 MHz): δ 0.41 (s, NSi(C*H*$_3$)$_3$, **13a**), 0.42 (s, NSi(C*H*$_3$)$_3$, **13b**), 1.05 (s, C(C*H*$_3$)$_3$, **13b**), 1.31 (s, C(C*H*$_3$)$_3$, **13a**), 1.19 (d, $^3J_{\mathrm{HH}}$ = 13 Hz, C*H*$_2$CHC*H*$_2$, **13b**), 1.53 (d, $^3J_{\mathrm{HH}}$ = 13 Hz, C*H*$_2$CHC*H*$_2$, **13a**), 1.70 (d, $^3J_{\mathrm{HH}}$ = 13

Table 4. Experimental Data for the Structure Determination of the Crystalline Complexes 5−8, 10, and 12

	5	**6**	**7**	**8**	**10**	**12**
empirical formula	$C_{32}H_{52}FeN_2Si_2$	$C_{32}H_{52}CoN_2Si_2$	$C_{32}H_{52}N_2NiSi_2$	$C_{28}H_{48}N_2NiSi_4$	$C_{24}H_{56}FeN_2Si_4$	$C_{38}H_{52}FeN_2Si_2$
M	576.8	579.9	579.7	583.7	540.9	648.9
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic
space group	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	17.949(7)	20.706(4)	20.690(3)	11.919(7)	15.865(1)	9.152(5)
b (Å)	8.668(2)	18.326(3)	18.295(2)	16.414(13)	11.671(2)	9.982(8)
c (Å)	20.850(4)	8.849(4)	8.856(1)	17.285(9)	17.936(2)	10.990(10)
α (deg)	90	90	90	90	90	75.39(8)
β (deg)	90	90	90	91.55(5)	91.02(1)	73.74(7)
γ (deg)	90	90	90	90	90	66.10(5)
V (Å^3)	3244(2)	3358(2)	3352.2(7)	3380(4)	3320.5(7)	870.1(12)
Z	4	4	4	4	4	1
$\mu_{\mathrm{abs\ coeff}}$(Mo K$\alpha$) (mm^{-1})	0.56	0.60	0.672	0.73	0.61	0.53
$\theta_{\max}$ for data colln (deg)	25	25	30			
temperature (K)	173(2)	293(2)	293(2)	173(2)	293(2)	173(2)
no. of indep reflns	2840	2955	4882	5933	2919	3051
R_{int}				0.09	0.03	
no. of reflns with $I > 2\sigma(I)$	1526	1609	2674	4426	2173	2010
no. of data/restraints/ params	2840/0/169	2955/0/169	4881/0/169	5933/0/324	2919/0/146	3051/0/199
R1 ($I > 2\sigma(I)$)	0.062	0.063	0.058	0.061	0.047	0.107
wR2 (all data)	0.145	0.149	0.153	0.174	0.138	0.313

Hz, $\mathrm{C}H_2\mathrm{CHC}H_2$, **13a**), 1.87 (d, $^3J_{\mathrm{HH}} = 13$ Hz, $\mathrm{C}H_2\mathrm{CHC}H_2$, **13b**), 3.12 (m, $\mathrm{C}H_2\mathrm{CHC}H_2$, **13a**), 3.27 (d, $^3J_{\mathrm{HH}} = 7$ Hz, $\mathrm{C}H_2\mathrm{CHC}H_2$, **13b**), 4.29 (m, $^3J_{\mathrm{HH}} = 6$ Hz, $\mathrm{CH_2C}H\mathrm{CH_2}$, **13a**), 4.52 (m, $^3J_{\mathrm{HH}} =$ 7 Hz, $\mathrm{CH_2C}H\mathrm{CH_2}$, **13b**), 5.88 (s, ArC*H*C^{t}Bu, **13b**) and 6.19 (s, ArC*H*C^{t}Bu, **13a**), 7.13−8.37 (Ar). ^{13}C{^{1}H} NMR (75.5 MHz): δ 3.9 (s, NSi(CH$_3$)$_3$, **13a** and **13b**), 29.3 (s, C(CH$_3$)$_3$, **13b**), 29.6 (s, C(CH$_3$)$_3$, **13a**), 39.4 (s, C(CH$_3$)$_3$, **13a** and **13b**), 49.2 (s, $C\mathrm{H_2CH}C\mathrm{H_2}$, **13a**), 51.4 (s, $C\mathrm{H_2CH}C\mathrm{H_2}$, **13a** and **13b**), 53.0 (s, $C\mathrm{H_2CH}C\mathrm{H_2}$, **13b**), 61.7 ($\mathrm{CH_2}C\mathrm{HCH_2}$, **13b**), 62.4 (s, $\mathrm{CH_2}C\mathrm{HCH_2}$, **10a**), 108.4 (s, Ar*C*HC^{t}Bu, **13a**), 109.4 (s, Ar*C*HC^{t}Bu, **13b**), 123.5−135.0 (s, $C_{10}H_7$-), 149.8 (s, ArCH*C*^{t}Bu, **13a**) and 150.7 (s, ArCH^{t}Bu, **13 b**). MS: *m*/*e* (%, assignments), 395 (32, [M − H]$^+$); 338 (20, [M − H − ^{t}Bu]$^+$); 297 (89, [L^{3}H]$^+$); 282 (40, [L^{3}H − Me]$^+$); 240 (67, [L^{3}H − ^{t}Bu]); 141 (64, [Ni(C_3H_5)$_2$]$^+$); 127 (21, [Ni(C_3H_5)$_2$−CH$_2$]$^+$); 100 (35, [M − L^3]$^+$), 74 (87, [SiMe$_3$]$^+$). Anal. Calcd for $C_{22}H_{31}NNiSi$: C, 66.7; H, 7.88; N, 3.53; Found: C, 65.6; H, 7.90; N, 3.45.

X-ray Crystallographic Structure Determinations of Compounds 5−8, 10, and 12. Single crystals of each of **5**, **8**, and **12** were removed from the Schlenk tube under a stream of argon and rapidly covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. Single crystals of each of **6**, **7**, and **10** were sealed under argon in Lindemann capillaries; data for these were collected at 293(2) K and for **5**, **8**, and **12** at 173(2) K on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα (λ = 0.70173 Å) radiation. The crystal structures were solved by direct methods (SHELXS-86)[50] and refined by full-matrix least-squares procedures (SHELXL-93),[51] with absorption correction by ψ-scans. All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with U_{iso}(H) = $1.2U_{\mathrm{eq}}$(C) or $1.5U_{\mathrm{eq}}$(C) for Me groups. Details of the data collection and refinement are given in Table 4. The C9 methyl group of **5** was included as disordered over two orientations related by a 60° rotation about C6−C9. The *p*-CH$_3$ group of **6** was assumed to be disordered over two likely orientations. The iron atom of **12** was disordered across the inversion center; the high *R* factor for **12** is due to weak diffraction from the crystal; there was no indication of solvent electron density in the difference map.

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Supporting Information Available: Full listings of X-ray crystallographic data, atomic coordinates, thermal parameters, bond distances and bond angles, and hydrogen parameters for **5**, **6**, **7**, **8**, **10**, and **12**; magnetic moment calculations for **5**, **6**, **10**, **11**, and **12**; and cyclic voltammograms for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[50] Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175−189.

[51] Sheldrick, G. M. *SHELXL-93*, A Program for Structure Refinement; University of Göttingen: Germany, 1993.