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Synthesis, Insertion Reactivity, and Transmetalation Reactions of the Lithium Complex $[\{2\text{-}(6\text{-R-Pyr})(Me_3Si)\}CHLi\cdot OEt_2]_2$ (R = H or Me)

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Treatment of 6-R-2-$(Me_3SiCH_2)C_5H_3N$ (R = H or Me) with *n*BuLi in diethyl ether affords the dimeric lithium complexes $[\{2\text{-}(6\text{-R-Pyr})(Me_3Si)\}CHLi\cdot OEt_2]_2$ (Pyr = pyridine, C_5H_3N) in high yields. In these complexes, the two anionic ligands have different bonding modes. These complexes easily undergo insertion reactions with nitriles to form six-membered cyclic dimeric complexes in good yields. Further transmetalations of the six-membered cyclic complexes with CuCl, $SnCl_4$, or $CoCl_2$ allow the formation of new metal complexes that maintain the frameworks of the six-membered metallacycles. All complexes represented above were fully characterized by methods including single-crystal X-ray crystallography.

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Introduction

Trimethylsilyl-substituted methylpyridines are interesting ligands with regard to their coordination chemistry and as ancillary ligands in main-group and transition-metal organometallic compounds.[1] These bulky ligands with multifunctional σ and π metal–ligand bonding modes stabilize their metal complexes by the three electronic displacement forms that the picolyl anions can adopt: carbanion, η^3-azaallyl, and enamide (Figure 1).[2] The silylated ligands are normally encountered in the azaallyl form commonly found in compounds like $[(2\text{-Pyr})(SiMe_3)CHLi\cdot(Et_2O)]_2$,[3a] while the ligands with the enamide disposition are observed in complexes like $[(2\text{-Pyr})(SiMe_3)CHLi\cdot(tmeda)]_2$[3a] or $[(2\text{-Pyr})(SiMe_3)CHLi\cdot(sparteine)]$.[3b] We have noted that all of the dimeric complexes of the type $[(2\text{-Pyr})(SiMe_3)CHLi\cdot(L)]_2$ have the common feature of a central symmetric structure; however, to date there have been no examples of compounds with dimeric complexes with an asymmetric pattern.

The insertion of α-hydrogen-free nitriles into a Li–C bond of these complexes has introduced a synthetic utility in preparing pyridyl-substituted azaallyls.[4] Metal 1-azaallyls and β-diketiminates have been studied and reported.[5] Recently, we have reported that insertion reactions of the reagent bis(trimethylsilyl)methyllithium, $Li[CHR_2]$ (R = $SiMe_3$), or the complex 1-azaallyllithium, $[LiN(R)C(tBu)CHR]_2$, with α-hydrogen-free nitriles, R′CN (R′ = Me_2N, 1-piperidyl or *o*-, *m*-, *p*-pyridyl), lead to a dimeric or a polymeric complex of β-diketiminatolithium.[6] However, little attention has been devoted to pyridyl-substituted azaallyl complexes that possess a nitrogen heterocycle aromatic ring as part of the ligand backbone relative to β-diketiminato ligands with the same substituent groups on the two terminal nitrogen atoms.[4] Recently, Leung et al. have reported the synthesis and the structures of the 2,6-pyridyl-linked bis(1-azaallyl) and 2,3-pyrazyl-linked bis(1-azaallyl)alkali-metal compounds.[7,8] Furthermore, a series of derived pyridyl-1-azaallyl low-valent group 14 compounds were described.[9,10] The synthesis of $[MCl_2\{N(SiMe_3)\text{-}C(Ph)C(H)(C_9H_6N\text{-}2)\}]$ (M = Hf and Zr) from the reaction of MCl_4 with the quinolyl-1-azaallyllithium complex $[Li\{N(SiMe_3)C(Ph)C(H)(C_9H_6N\text{-}2)\}]_2$ was reported previously,[11] as well as the synthesis of Pd complexes containing the 1-azaallyl ligand of $[\{[N(R)C(tBu)CH]_2C_5H_3N\text{-}2,6\}\{Li_2(tmen)\}]$ and $[\{[N(R)C(Ph)CH]_2C_5H_3N\text{-}2,6\}\{Li(tmen)_2\}]$.[12]

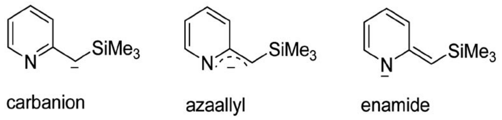

Figure 1. Tautomeric forms of the picolyl anion.

In this paper, we report the synthesis of dimeric $[\{2\text{-}(6\text{-R-Pyr})(Me_3Si)\}CHLi\cdot OEt_2]_2$ [R = H (**1a**) or Me (**1b**)], in which two lithium atoms have different bonding modes in an asymmetric pattern, and their insertion products to form the corresponding pyridyl-1-azaallyllithium complexes [{2-

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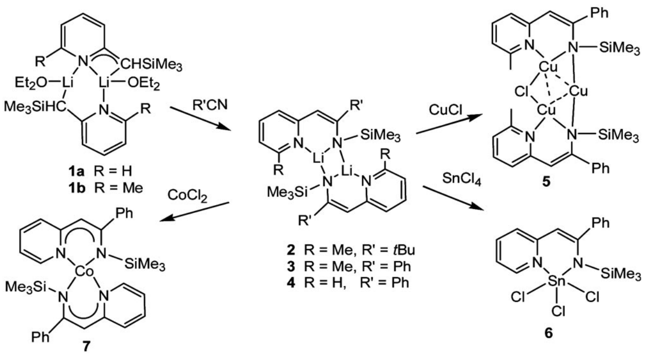
[{(6-Me-Pyr)C(H)C(R′)N($SiMe_3$)}Li]$_2$ [R′ = *t*Bu (**2**) or Ph (**3**)] or [{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}Li]$_2$ (**4**). These pyridyl-1-azaallyl-lithium salts were also used as ligand transfer reagents when reacted with a variety of metal halides, CuCl, $CoCl_2$, and $SnCl_4$, to produce the corresponding complexes [{2-(6-Me-Pyr)C(H)C(Ph)N($SiMe_3$)}Cu]$_2$(μ-CuCl) (**5**), [{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}$SnCl_3$] (**6**), and [{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}$_2$Co] (**7**). Complex **5** was obtained as an unusual trinuclear dimer in which two monomers of pyridyl-1-azaallyl-copper(I) are bridged by a neutral CuCl moiety. Complex **6** adopts an enamido bonding mode in which the pyridyl-1-azaallyl motif bonds to the metal center, whereas in complex **7** a mononuclear pyridyl-1-azaallyl–metal complex was obtained in a terminal *N*,*N*′-chelating fashion, in which the metal has a distorted tetrahedral environment. The bonding within the NCCCN ligand backbone framework for complexes **5** and **6** is highly localized, in contrast to complex **7**, in which a partial delocalization is observed.

Results and Discussion

The starting material for the synthetic procedure was the trimethylsilymethyl-substituted pyridine 6-R-2-(Me_3Si-CH_2)C_5H_3N (R = H or Me)[3a,13–14] The general synthesis route for the different complexes presented in this paper are illustrated in Scheme 1.



Scheme 1. Synthetic pathway to complexes **1**–**7**.

Metalation of 6-R-2-(Me_3SiCH_2)C_5H_3N (R = H or Me) by 1 equiv. *n*BuLi in hexane and in the presence of diethyl ether yields η^3-azaallyllithium **1a** or **1b**. It is important to mention that complex **1a** has been previously reported by Papasergio.[3a]

The molecular structure of **1b** is illustrated in Figure 2, and selected bond lengths and angles are presented in Table 1. Orange crystals of complex **1b** are obtained from Et_2O as dimers, in which part of the dimer acts as an η^3-azaallyl ligand to one lithium atom and the same nitrogen atom also coordinates to the second lithium atom. This coordination mode is quite unique and is different from those reported for similar [{Li(Et_2O)[2-CH($SiMe_3$)C_5H_4N]}$_2$][3a] and [{Li(Et_2O)[C_6H_5N(C(CH_2)*t*Bu)]}$_2$][19] complexes. Complex **1b** has an eight-membered ring with respect to the *ipso* carbon and nitrogen centers, but there are additional lithium–anion contacts, viz. Li2–C11, in addition to the nitrogen bridges among the two lithium atoms.[20]

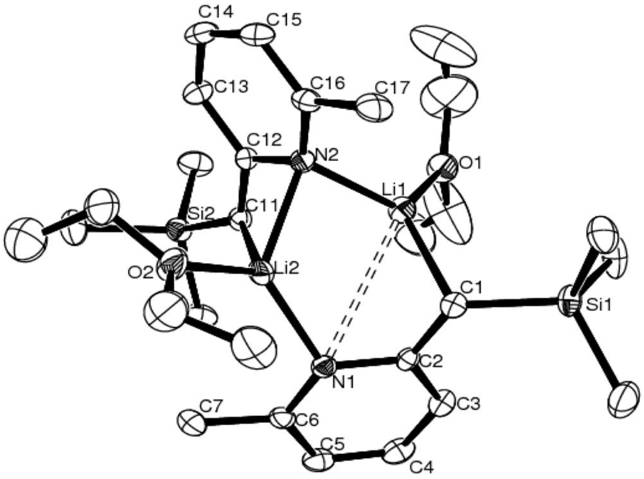


Figure 2. Molecular structure and atom numbering scheme for **1b**.

Table 1. Selected bond lengths [Å] and angles [°] for **1b** and **2**.

1b			
Li1–C1	2.207(11)	Li1–N2	2.018(10)
Li2–N1	2.023(11)	Li1–O1	1.901(10)
Li2–C11	2.544(12)	Li2–N2	2.076(11)
Li2–O2	1.962(10)	C11–C12	1.381(7)
C1–C2	1.406(7)	C2–N1	1.381(6)
C12–N2	1.396(7)		
O1–Li–N2	118.8(5)	O2–Li2–N1	127.8(6)
O1–Li1–C1	129.6(5)	N1–Li2–N2	122.6(5)
O2–Li2–N2	107.3(5)	N1–Li2–C11	96.5(4)
O2–Li2–C11	121.7(5)	N1–C2–C1	119.2(4)
N2–Li2–C11	61.4(3)	N2–C12–C11	119.0(5)
N2–Li1–C1	111.2(5)		
2			
Li–N1	2.036(4)	Li–N2	2.027(4)
N1–C6	1.346(3)	N2–C8	1.390(3)
C6–C7	1.460(3)	C7–C8	1.357(3)
N1–C6–C7	120.05(19)	C6–C7–C8	129.9(2)
C7–C8–N2	125.03(19)	Li–N2–C8	120.07(17)
Li–N1–C6	111.38(17)	N1–Li–N2	99.28(17)
N2–Li–N2	104.21(16)	Li–N2–Li′	75.79(16)

Complex **1b** consists of two different lithium environments caused by steric crowding. The bonding features of Li1 and Li2 are η^1-alkyl and η^3-azaallyl, respectively, in which the bond lengths of Li–C or Li–N are 2.01–2.54 Å. One lithium atom has three coordination sites, whereas the second lithium atom is four-coordinate. Each one of the two lithium atoms is also bound by diethyl ether, above and below the η^3-azaallyl planes. Two of the *ipso* carbon atoms are coplanar with the pyridine rings. Their mean deviations from planarity are 0.0149 and 0.0267 Å, with a dihedral angle between the two pyridyl moieties of 53.3°. The dihedral angle between the Li2N2C11 plane and the pyridine N2C12C13C14C15C16 is 52.6°. It is worth noting that the distances of Li1 and Li2 to the pyridine rings N2C12C13C14C15C16 are 1.224 and 1.562 Å, respectively.

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The bond lengths C1–C2 and N1–C2 are 1.406(7) and 1.381(6) Å, respectively, which are similar to C11–C12 [1.381(7) Å] and C12–N2 [1.396(7) Å], indicating the presence of a delocalized NCC fragment. The lithium–ligand interactions are related to the steric and electronic nature of the group at the *ipso* carbon atoms.[3a]

The pyridyl-substituted 1-azaallyl complexes **2**–**4** were prepared under mild conditions from **1** and PhCN or *t*BuCN, in a 1:1 molar ratio in diethyl ether.[4] Compounds **2**–**4** were obtained in good yields (more than 70 %), as yellow complexes that were soluble in Et_2O but had a fairly low solubility in hexane. Complex **2** was obtained as a dark-yellow crystalline material suitable for X-ray diffraction studies. Compounds **3** and **4** were also isolated as yellow solid powders and were reacted directly to continue the reaction pathway (Scheme 1) with the corresponding metal chlorides.

The molecular structure of **2** is illustrated in Figure 3, and selected bond lengths and angles are presented in Table 1. The molecular structure of complex **2** is that of a centrosymmetric dimer with a central LiNLiN rhombohedral geometry having $NSiMe_3$ as bridging groups. The angles at the nitrogen atom [75.79(16)°] are narrower than those at the Li atom [104.21(16)°]. Each lithium atom is coordinated with three nitrogen atoms from two corresponding ligands. These features are similar to those of several other known *N*,*N′*-chelating monoanionic ligands, including the pyridyl-substituted 1-azaallyls **I** and **II**,[6] and the β-diketiminates **III** (Figure 4).[21]

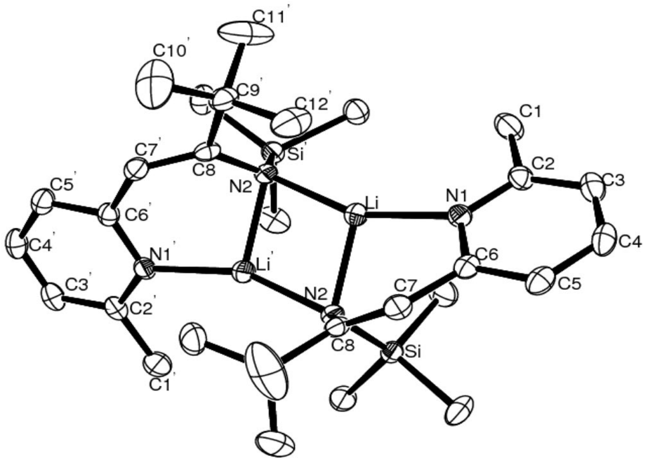

Figure 3. Molecular structure and atom numbering scheme for **2**.

A comparison of some of the relevant bond lengths for complex **2** with those of **I**,[6] **II**,[6] and **III**[21] is presented in Table 2. The bonding within the NCCCN ligand backbone in **2**, **I**,[6] and **II**[6] is highly localized: RC=C double bonds (R = Ph or *t*Bu) leave the aromaticity of the pyridine ring largely unaffected. This is, however, in contrast to $[LiN(SiMe_3)C(Ph)C(H)C(Ph)N(SiMe_3)]_2$, which displays, at least to some extent, delocalization in the ligand backbone.[7] The Li–N distances of the bridging $NSiMe_3$ groups (Li1–N2) are almost identical, and the Li–pyridyl bonds [2.036(4) (**2**), 1.968(6) (**I**) and 1.981(7) Å (**II**)] are considered to be unexceptionally dative and can be compared with the Li–pyridine distance in the three-coordinate lithium complex **1b** [2.018(10) Å] and in $[Li\{2\text{-}C(SiMe_3)_2C_5H_4N\}\{CH(SiMe_3)_2\text{-}C_5H_4N\text{-}2\}]$ [2.010(10) Å],[4] all of them falling in the normal range 1.895–2.087 Å for Li–N (amido) bonds.[3a,22–24] The metallacycle LiNCCCN is highly puckered and exhibits a dihedral angle between the N1Li1N2 and N2C7C8 planes of 65.0°.

Table 2. Comparison of selected bond lengths [Å] (as marked in complexes **I**–**III**) for **2** and **I**–**III**.

Complex	Bond a	Bond b	Bond c	Ref.
2	2.036(4)	2.027(4)	2.040(4)	this work
I	1.968(6)	2.012(9)	2.032(6)	[6]
II	1.981(7)	1.998(6)	2.026(6)	[6]
III	1.952(10)	1.965(9)	2.095(9)	[22]

Treatment of complex **3** with anhydrous CuCl in a 2:3 molar ratio in Et_2O or THF at low temperature afforded complex **5**. Cu^I complex **5** was isolated by crystallization from diethyl ether as a brown-yellow crystalline solid in good yields (ca. 60 %). To the best of our knowledge, several diketiminate Cu^I compounds such as $[Cu\{[N(Ar)C(Me)]_2CH\}(L)]$ $\{L = C_2H_4,$[15] $Ge(NR_2)_2$[16]$\}$, $[Cu\{[N(R)C(Ar)]_2SiR\}]_2(thf)$ ($R = SiMe_3$, $Ar = C_6H_3Me_2\text{-}2,6$),[17] and $[Cu\{N(Ar)C(Me)C(H)C(Me)N[C_6H_3(iPr\text{-}2)\text{-}(CH_2SMe\text{-}6)]\}]_4$[18] have been described. However, among all of them, complex **5** is the first structurally characterized dimeric trinuclear pyridyl-1-azaallyl–Cu^I complex, in which the dimeric NCCCN backbone is bridged by a neutral CuCl molecular moiety.

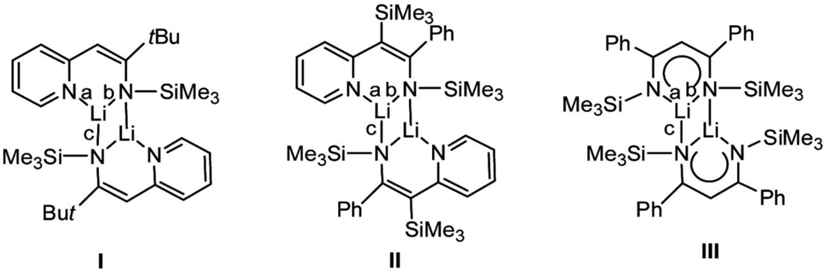

Figure 4. 1-azaallyl complexes **I**–**III**.

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The molecular structure of **5** is illustrated in Figure 5, and selected bond lengths and angles are presented in Table 3. The core of **5** exhibits a six-membered NCuNCuClCu puckered ring, with an unusual CuCl bridging mode. It may be regarded as being an adduct of CuCl and two [{2-(6-Me-Pyr)C(H)C(Ph)N($SiMe_3$)}Cu] moieties, in which Cu1 and Cu2 atoms are bridged by a Cl atom, while the Cu3 atom bridges atoms N2 and N4. The two three-coordinate Cu1 and Cu2 atoms are in a distorted trigonal-planar environment, and the dihedral angle between the Cu1N1N2Cl1 and Cu2N3N4Cl1 planes is 85.6°, while the Cu3 atom chelated to nitrogen atoms shows an approximately linear coordination mode, in which the angle of N2–Cu3–N4 is 171.0(3)°. The linear N–Cu–N coordination imposes a relatively short distance between Cu3–Cu1 [2.460(14) Å] and Cu3–Cu2 [2.579(14) Å], as compared to the chlorine atom bridging distance between Cu1–Cu2 [2.850(15) Å]. In searching for different molecular structures of β-diketiminatocuprate complexes, we encounter some dimeric structures with short Cu···Cu′ contacts that have been reported, such as in [Cu{[N(R)C(Ar)]$_2$SiR}]$_2$,[17] [Cu{N(*i*Pr)C(Me)N(*i*Pr)}]$_2$,[25] [Cu{N(*s*Bu)C(Me)N(*s*-Bu)}]$_2$,[26] [Cu{N($C_6H_3Me_2$-2,6)C(Ph)N($C_6H_3Me_2$-2,6)}]$_2$,[27] [Cu{N(R)C(Ph)N(R)}]$_2$,[28] and 1-azaallyl [Cu{N(R)C(*t*Bu)C(H)R}]$_2$;[29] however, in all these complexes the Cu···Cu′ distances are between 2.40–2.49 Å. The bond lengths Cu1–N1, Cu1–N2, Cu2–N3, and Cu2–N4 are 1.989(6)–2.093(6) Å, which are longer than the bridging bond lengths Cu3–N2 [1.916(6) Å] and Cu3–N4 [1.875(6) Å]. The geometries of the two β-diketiminate backbones are different; the N1C6C7C8N2 backbone is planar (mean deviation 0.0079 Å) and is coplanar with the pyridine ring (mean deviation 0.0176 Å), while the N3C23C24C25N4 backbone is twisted away from the plane of the pyridine and possesses a half-chair conformation. The short C7–C8 and C24–C25 and long N2–C8 and N4–C25 bond lengths correspond to double and single bonds, respectively. Thus, the bonding within the NCCCN ligand backbone is localized, and the pyridyl-1-azaallyl ligand bonds to the metal center can be related to an enamido bonding model.

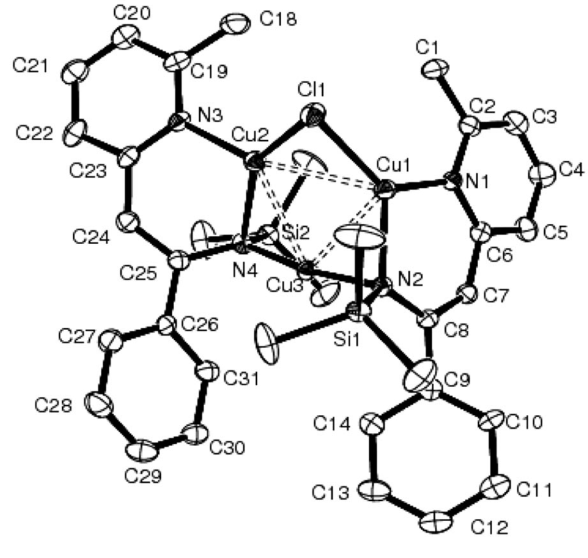

Figure 5. Molecular structure and atom numbering scheme for **5**.

Table 3. Selected bond lengths [Å] and angles [°] for **5**.

Cu1–N1	1.991(6)	Cu1–N2	2.067(6)
Cu1–Cl1	2.251(2)	Cu1–Cu2	2.8507(15)
Cu2–N3	2.061(6)	Cu2–N4	2.093(6)
Cu2–Cl1	2.216(2)	Cu2–Cu3	2.5793(14)
Cu3–N2	1.916(6)	Cu3–N4	1.875(6)
Cu3–Cu1	2.4602(14)	N1–C6	1.360(10)
C6–C7	1.438(11)	C7–C8	1.355(11)
N2–C8	1.407(9)	C23–C24	1.456(11)
C24–C25	1.366(11)	C25–N4	1.419(10)
N3–C23	1.365(11)		
N1–Cu1–N2	104.6(3)	N2–Cu1–Cl1	126.03(19)
Cu3–Cu1–Cu2	57.55(4)	N3–Cu2–N4	45.87(17)
N4–Cu2–Cl1	143.11(18)	Cu3–Cu2–Cu1	53.59(3)
N4–Cu3–N2	171.0(3)	Cu1–Cu3–Cu2	68.86(4)
C6–N1–Cu1	117.0(5)	C8–N2–Cu3	107.3(4)
C8–N2 –Cu1	112.6(5)	Cu3–N2–Cu1	76.1(2)
C23–N3–Cu2	117.6(5)	C25–N4–Cu2	104.3(4)
Cu3–N4–Cu2	80.8(2)	N1–C6–C5	119.2(7)
C8–C7–C6	136.4(7)	C7–C8–N2	126.0(7)
N3–C23–C24	120.1(7)	C25–C24–C23	130.2(7)
C24–C25–N4	122.9(7)		

The reaction of complex **4** with an equimolar amount of $SnCl_4$ in Et_2O and the subsequent recrystallization of the reaction mixture from CH_2Cl_2 gave the metal enamide complex **6** as yellow crystals in 78 % isolated yield.

The molecular structure of **6** is illustrated in Figure 6, and selected bond lengths and angles are presented in Table 4. Crystalline complex **6** has a tin atom in a distorted trigonal-bipyramidal environment with the Cl2 and N1 atoms in the axial position [N1–Sn–Cl2 176.52(14)°]. The diketiminato ligand acts in an η^2 bonding mode with Sn–N bond lengths of 2.025(5) and 2.236(5) Å. The NCCCN backbone is essentially planar, with a mean deviation of 0.0679 Å, and the dihedral angle between the NCCCN and the pyridine ring is 19.9°, whereas the Sn atom is 0.9966 Å out of the NCCCN plane. In the NCCCN moiety, the bond lengths N1–C5, C5–C6, C6–C7, and C7–N2 are 1.348(8), 1.442(9), 1.346(8), and 1.414(7) Å, respectively, indicating an obvious short-long-short-long pattern of bond lengths. This pattern indicates that the β-diketiminato ligand is a characteristic example for a conjugated system. In comparing the compounds [Sn{[N(H)C(Ph)]$_2$CH}Cl(Me)$_2$], [Sn{[N($SiMe_3$)C(Ph)]$_2$CH}Cl(Me)$_2$],[30] and complex **6**, the main difference is the {SnN^{a}C–C–CN^b(*Sn-N^b*)} skeleton plane, which is almost planar for [Sn{[N(H)C(Ph)]$_2$CH}-Cl(Me)$_2$], whereas the Sn atoms in [Sn{[N($SiMe_3$)C(Ph)]$_2$-CH}Cl(Me)$_2$] and in complex **6** are approximately 1.37 and 1.00 Å out of the NCCN plane, respectively.

A similar reaction of complex **4** with $CoCl_2$ in a 2:1 molar ratio in Et_2O afforded red crystals of complex **7** in 64 % isolated yield. The molecular structure of **7** is illustrated in Figure 7, and selected bond lengths and angles are pre-

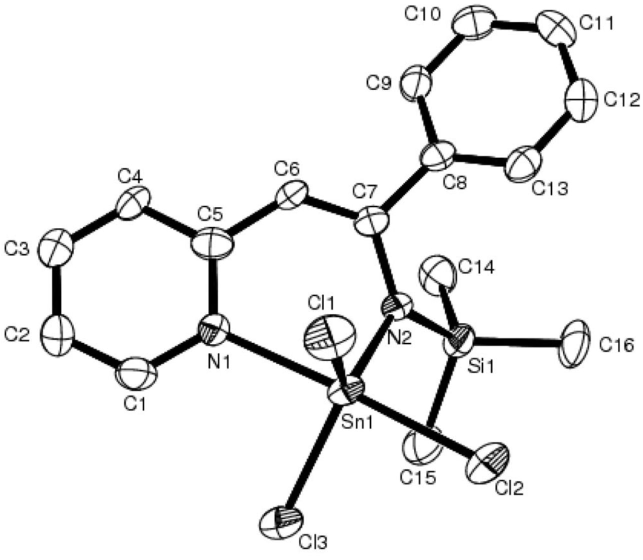

Figure 6. Molecular structure and atom numbering scheme for **6**.

Table 4. Selected bond lengths [Å] and angles [°] for **6**.

Sn1–N2	2.025(5)	Sn1–N1	2.236(5)
Sn1–Cl3	2.3277(19)	Sn1–Cl1	2.3277(17)
Sn1–Cl2	2.3954(18)	N1–C5	1.348(8)
C5–C6	1.442(9)	C6–C7	1.346(8)
N2–C7	1.414(7)	C7–C8	1.493(9)
N2–Sn1–N1	88.46(18)	N2–Sn1–Cl3	125.42(15)
N1–Sn1–Cl3	87.14(14)	N2–Sn1–Cl1	115.93(14)
N1–Sn1–Cl1	86.14(13)	Cl3–Sn1–Cl1	117.97(8)
N2–Sn1–Cl2	95.03(14)	N1–Sn1–Cl2	176.52(14)
Cl3–Sn1–Cl2	90.92(8)	Cl1–Sn1–Cl2	92.22(7)
C5–N1–Sn1	117.4(4)	C7–N2–Sn1	114.3(4)
N1–C5–C6	121.7(6)	C7–C6–C5	129.9(6)
C6–C7–N2	124.8(6)		

sented in Table 5. The central cobalt atom is located in a tetrahedral environment defined by the four nitrogen atoms from the two bidentate 2-pyridyl-1-azaallyl ligands with a fully perpendicular dihedral angle (90.0°) between N1CoN2 and N3CoN4. The Co–N bond lengths are in the range 1.964(4)–1.995(4) Å, which are shorter than corresponding values found in complex [Co{[N(SiMe$_3$)C(Ph)]$_2$CH}$_2$][5c] [Co–N 1.994(7)–2.007(6) Å]. The bond angles N1–Co–N2 and N3–Co–N4 are 99.01(16) and 99.59(17)°, respectively, which are smaller than those in [Co{[N(SiMe$_3$)C(Ph)]$_2$-CH}$_2$] [103.0(2) and 119.4(3)°]. Each bidentate 2-pyridyl-1-azaallyl ligand forms a six-membered metallacycle MNCCCN, where the MNCCCN ring is highly coplanar with the pyridine ring with a mean deviation of 0.0122 Å. The congestion at the NCCCN skeleton is revealed by the large out-of-plane rotation of the phenyl group relative to the NCCCN plane, and the dihedral angle between the phenyl and N_2C_3 moiety is 93.1°, which prevents a steric hindrance with the hydrogen atoms attached to the C6=C7 double bond. This steric congestion has also been observed in the molecular structure of complexes **5** and **6**.

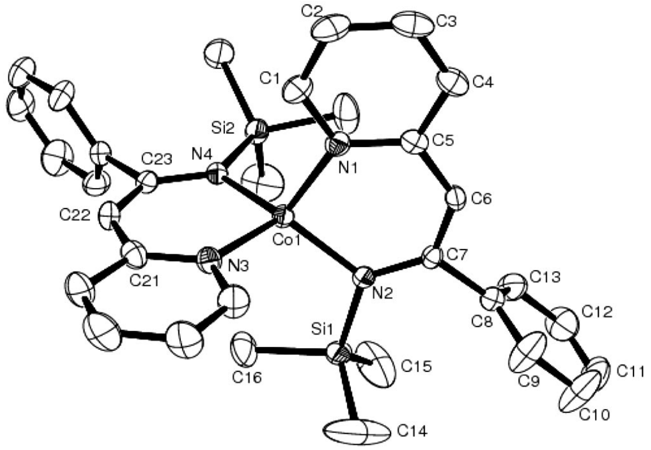

Figure 7. Molecular structure and atom numbering scheme for 7.

Table 5. Selected bond lengths [Å] and angles [°] for **7**.

Co1–N2	1.958(4)	Co1–N4	1.964(4)
Co1–N1	1.985(4)	Co1–N3	1.995(4)
N1–C5	1.354(6)	N2–C7	1.345(6)
N3–C21	1.353(6)	N4–C23	1.339(6)
C5–C6	1.428(7)	C6–C7	1.374(7)
C21–C22	1.426(7)	C22–C23	1.381(7)
N2–Co1–N1	99.01(16)	N4–Co1–N3	99.59(17)
C5–N1–Co1	122.6(3)	C7–N2–Co1	118.5(3)
N1–C5–C6	120.3(4)	C7–C6–C5	131.3(4)
N2–C7–C6	127.4(4)		

Conclusions

We have here disclosed a simple and effective synthesis for a family of pyridyl-substituted 1-azaally ligands and their corresponding metal complexes starting from lithiated 2-methylpyridine or 2,6-dimethylpyridine followed by a 1,2-insertion of a suitable nitrile and with a concomitant 1,3-trimethylsilyl shift. Both of the nitrogen atoms of these monoanionic ligand complexes are expected to be good σ- and π-donors, and like cyclopentadienyl ligands, they can formally be considered as six-electron donors. In addition, the substituents on the ligand backbone can be easily varied, which is important for the fine tuning of the steric and electronic properties of the ligands. Compound such as complex **5** may serve as a precursor for Metal Organic Chemical Vapor Deposition (MOCVD) or as a magnetic material in microeletronics.[31] Complex **7** is a potential catalyst in olefin polymerization, and further studies are underway.[32] In addition, complementary research on the coordination chemistry of this interesting class of pyridyl-1-azaallyl ligands and other applications of their metal complexes are presently in progress.

Experimental Section

All manipulations and reactions were performed under an inert atmosphere of nitrogen by means of standard Schlenk techniques. Solvents were predried with sodium, distilled from sodium/potassium alloy (hexane), sodium/benzophenone (diethyl ether, tetrahydrofuran), and stored over molecular sieves (4 Å). Deuterated

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solvents were dried with sodium/potassium alloy (C_6D_6) and molecular sieves (4 Å) ($CDCl_3$). All solvents were degassed prior to use. Chemicals were purified by distillation before use. CuCl, $CoCl_2$, $SnCl_4$, trimethylacetonitrile, and *n*-butyllithium in hexane (2.8 mol dm^{-3}) were purchased from Alfa Aesar and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX-300 spectrometer. Elemental analyses were performed with a Vario EL-III instrument.

[(2-Pyr)(Me_3Si)CHLi·OEt_2]$_2$ (1a): *n*BuLi (9.5 mL, 27.59 mmol in hexane) was added with a syringe to a stirred solution of 2-methylpridine (2.569 g, 27.59 mmol) in Et_2O (30 mL) at 0 °C. The resulting red solution was warmed to room temperature and stirred for a further 3–4 h. At 0 °C, $ClSiMe_3$ (3.49 mL, 27.59 mmol) was added to the above solution, and the mixture was stirred at room temperature for 4 h and then filtered. The pale yellow filtrate was added to *n*BuLi (8.8 mL, 25.66 mmol in hexane) at 0 °C. The resulting solution was stirred for 4 h at room temperature to give a heavy red solution. Then PhCN (2.49 mL, 24.37 mmol) was added at 0 °C. The resulting brown mixture was warmed to room temperature and stirred for a further 3–4 h, and then filtered. The filtrate was concentrated and allowed to stand for 3 d at –30 °C to afford yellow crystals of **1a** (6.1 g, 91%). $C_{26}H_{48}Li_2N_2O_2Si_2$ (490.72): calcd. C 63.64, H 9.86, N 5.71; found C 63.88, H 9.98, N 5.66. ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ = 0.51 [s, 9 H, -Si(CH_3)$_3$], 2.90 (s, 1 H, -C*H*-SiMe$_3$), 5.9 (m, 1 H, -C*H*- of pyridyl), 6.7 (m, 2 H, -C*H*- of pyridyl), 7.8 (m, 1 H, -C*H*- of pyridyl) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 166.95, 148.20, 134.32, 117.53, 103.24 (-*C*H- of pyridyl), 65.70 (Si*C*H-), 1.43 [-Si(*C*H$_3$)$_3$] ppm.

[2-(6-Me-Pyr)(Me_3Si)CHLi·OEt_2]$_2$ (1b): *n*BuLi (7.58 mL, 2.57 M in hexane) was added with a syringe to a stirred solution of 2,6-dimethylpridine (2.162 g, 20.18 mmol) in Et_2O (30 mL) at 0 °C. The resulting orange solution was warmed to room temperature and stirred for a further 4 h. At 0 °C, $ClSiMe_3$ (2.55 mL, 20.18 mmol) was added to the above solution, and the mixture was stirred at room temperature for 5 h and then filtered. The pale yellow filtrate was added to *n*BuLi (7.58 mL, 2.57 M in hexane) at 0 °C. The resulting solution was stirred for 4 h at room temperature to give a red solution. This clear solution was concentrated to give orange crystals of **1b** (7.3 g, 70%). The X-ray diffraction *R* values of **1b** are not very good, because of coordination by solvent, causing disorder of ether. $C_{28}H_{52}Li_2N_2O_2Si_2$ (518.78): calcd. C 64.83, H 10.10, N 5.40; found C 62.82, H 9.59, N 5.38. ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ = 0.02 [s, 9 H, -Si(C*H*$_3$)$_3$], 2.40 (s, 1 H, -C*H*-SiMe$_3$), 2.51 (s, 3 H, pyridyl -C*H*$_3$), 6.63, 6.65, 7.14 (m, 3 H, -C*H*- of pyridyl) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 163.95, 160.54 (*ipso-C* of pyridyl), 138.58, 121.74, 120.94 (-*C*H- of pyridyl), 63.74 (-*C*H-Si), 32.81 (-*C*H$_3$ of pyridyl), 27.28 (-*C*H- of pyridyl), 1.98 [-Si(*C*H$_3$)$_3$] ppm.

[{2-(6-Me-Pyr)C(H)C(*t*Bu)N($SiMe_3$)}Li]$_2$ (2): *t*BuCN (0.40 mL, 3.57 mmol) was added with a syringe to a stirred solution of **1b** (1.85 g, 3.57 mmol) in Et_2O (20 mL) at 0 °C. The resulting orange solution was warmed to room temperature and stirred for a further 10 h. The clear orange solution was concentrated and left to stand for one week at –30 °C, affording dark yellow crystals of **2** (0.66 g, 69%). $C_{30}H_{50}Li_2N_4Si_2$ (536.80): calcd. C 67.12, H 9.39, N 10.44; found C 66.78, H 9.37, N 10.28. ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ = 0.38 (s, 9 H, -SiMe$_3$), 1.36 [s, 9 H, (C*H*$_3$)$_3$C=N-], 2.50 (s, 3 H, -C*H*$_3$ of pyridyl), 6.09 (s, 1 H, CH of -C*H*-C=N-), 6.38, 6.57, 7.05 (d, d, t, *J* = 7.2, 7.4, 7.9 Hz, 3 H, -C*H*- of pyridyl) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 178.03 (*C*N, of *t*Bu-*C*=N-), 163.46, 157.64 (*ipso-C* of pyridyl), 120.55, 123.43, 140.10 (-*C*H- of pyridyl), 108.29 (-*C*H-C=N), 42.70 [(CH$_3$)$_3$*C*=N-], 32.85 [(*C*H$_3$)$_3$C=N-], 27.46 (-*C*H$_3$ of pyridyl), 6.65 (-*C*H$_3$ of -SiMe$_3$) ppm.

[{2-(6-Me-Pyr)C(H)C(Ph)N($SiMe_3$)}Li]$_2$ (3): PhCN (1.08mL, 10.57 mmol) was added with a syringe to a stirred solution of **1b** (5.48 g, 10.57 mmol) in Et_2O (20 mL) at 0 °C. The resulting brown solution was warmed to room temperature and stirred for a further 10 h. The solvents were removed in vacuo to give a yellow solid (4.34 g, 70% yield). $C_{34}H_{42}Li_2N_4Si_2$ (558.80): calcd. C 70.80, H 7.34, N 9.71; found C 69.88, H 7.62, N 9.82. ^{1}H NMR (C_6D_6): δ = 0.085 [s, Si(C*H*$_3$)$_3$, 9 H], 2.200 (s, 3 H,C*H*$_3$), 6.286 (m, 1 H, -C*H*- of pyridyl), 6.651 (m, 1 H, -C*H*- of pyridyl), 6.983 (m, 1 H, -C*H*- of pyridyl), 7.155 (m, 3 H, -C*H*- of benzene), 7.890 (m, 2 H, -C*H*- of benzene) ppm. ^{13}C NMR (C_6D_6): δ = 2.087 [s, Si(*C*H$_3$)$_3$], 24.086 (s, -*C*H$_3$ of pyridyl), 105.650, 116.654, 118.722, 120.251, 136.868, 147.555, 154.807, 159.684 (-*C*H- of pyridyl and -*C*H- of ph), 99.820 (-*C*H-C=N), 163.600 (-*C*N of PhCN) ppm.

[{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}Li]$_2$ (4): *n*BuLi (9.5 mL, 27.59 mmol in hexane) was added with a syringe to a stirred solution of 2-methylpridine (2.569 g, 27.59 mmol) in Et_2O (30 mL) at 0 °C. The resulting red solution was warmed to room temperature and stirred for a further 3–4 h. At 0 °C, $ClSiMe_3$ (3.49 mL, 27.59 mmol) was added to the above solution, and the mixture was stirred at room temperature for 4 h and then filtered. The pale yellow filtrate was added to *n*BuLi (8.8 mL, 25.66 mmol in hexane) at 0 °C. The resulting solution was stirred for 4 h at room temperature to give a heavy red solution. Then PhCN (2.49 mL, 24.37 mmol) was added at 0 °C. The resulting brown mixture was warmed to room temperature and was stirred for a further 3–4 h, and then filtered. The filtrate was concentrated and allowed to stand for 3 d at –30 °C to give yellow crystals (6.08 g, 91% yield). $C_{32}H_{38}Li_2N_4Si_2$ (548.72): calcd. C 70.04, H 6.98, N 10.21; found C 69.88, H 7.62, N 9.82. ^{1}H NMR (C_6D_6): δ = 0.077 [s, Si(C*H*$_3$)$_3$, 9 H], 6.48 (m, 1 H, -C*H*- of pyridyl), 6.81 (m, 1 H, -C*H*- of pyridyl), 7.066 (m, 2 H, -C*H*- of pyridyl), 7.598 (m, 3 H, -C*H*- of benzene), 7.968 (m, 2 H, -C*H*- of benzene) ppm. ^{13}C NMR (C_6D_6): δ = 1.974 [s, Si(*C*H$_3$)$_3$], 116.794, 123.362, 136.561, 146.542, 147.990, 159.83 (-*C*H- of pyridyl and -*C*H- of ph), 106.089 (-*C*H-C=N), 164.996 (-*C*N of PhCN) ppm.

[{2-(6-Me-Pyr)C(H)C(Ph)N($SiMe_3$)}Cu]$_2$(μ-CuCl) (5): CuCl (0.56 g, 5.66 mmol) was added to a solution of **3** (4.476 mmol) in Et_2O at –78 °C. The mixture was warmed to room temperature slowly, stirred for 24 h, and filtered. The brown filtrate was concentrated and allowed to stand for one week at –30 °C to give yellow crystals of **5** (1.82 g, 60%). $C_{34}H_{42}ClCu_3N_4Si_2$ (788.97): calcd. C 51.76, H 5.37, N 7.01; found C 52.45, H 5.63, N 6.95. ^{1}H NMR (25 °C, 300 MHz, $CDCl_3$): δ = 0.05 (s, 9 H, SiMe$_3$), 2.51 (s, 3 H, -C*H*$_3$ of pyridyl), 5.25 (s, 1 H, -C*H*-C=N-), 6.76–6.79 (m, 2 H, -C*H*- of pyridyl), 7.30–7.45 (m, 6 H, -C*H*- of pyridyl and benzene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 157.4 (*C* of pyridyl), 136.1, 128.8, 128.2, 127.9, 119.0, 116.85 (-*C*H- of pyridyl and -*C*H- of ph), 46.6 (-*C*H-C=N), 45.0 (-*C*N, of PhCN), 24.3 (-*C*H$_3$ of pyridyl), 1.3 (-*C*H$_3$ of SiMe$_3$) ppm.

[{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}$SnCl_3$] (6): $SnCl_4$ (0.53 mL, 4.5 mmol) was added with a syringe to a solution of **4** (1.234 g, 4.5 mmol) in Et_2O (10 mL) at –78 °C. The resulting yellow mixture was warmed to room temperature slowly and stirred for 12 h. Then, the solvents were removed in vacuo, and CH_2Cl_2 was added. LiCl precipitated, and the filtrate was concentrated and allowed to stand for 3 d at room temperature to give yellow crystals of **6** (1.7 g, 78%). $C_{16}H_{19}Cl_3N_2SiSn$ (492.46): calcd. C 39.02, H 3.89, N 5.69; found C 39.23, H 3.91, N 5.59. ^{1}H NMR (300 Hz, $CDCl_3$): δ = 0.14 (s, 9 H, SiMe$_3$), 5.97 (s, 1 H, C*H*), 7.20–7.86 (m, 8 H, -C*H*- of pyridyl and -C*H*- of benzene), 8.96 (d, *J* = 6.0 Hz, 1 H, Pyr) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.48–161.29 (-*C*H- of pyridyl, -*C*H- of ph, and *C*=N), 106.63 (-*C*H-C=N), 3.14 (-*C*H$_3$ of SiMe$_3$) ppm.

Table 6. Crystallographic data for **1b**, **2**, **5**, **6**, and **7**.

	1b	**2**	**5**	**6**	**7**
Formula	$C_{28}H_{52}Li_2N_2O_2Si_2$	$C_{15}H_{25}LiN_2Si$	$C_{34}H_{42}ClCu_3N_4Si_2$	$C_{16}H_{19}Cl_3N_2SiSn$	$C_{32}H_{38}CoN_4Si_2$
Fw	518.78	268.40	788.97	492.46	593.77
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$	Pc	$Pbca$
a [Å]	9.452(2)	9.726(3)	9.528(2)	7.1641(13)	13.299(2)
b [Å]	19.319(5)	18.299(5)	11.540(3)	8.9159(16)	15.057(2)
c [Å]	18.524(4)	18.385(5)	17.630(4)	15.297(3)	32.152(5)
α [°]	90.00	90.00	78.899(4)	90.00	90.00
β [°]	95.611(4)	94.539(4)	87.297(4)	92.574(2)	90.00
γ [°]	90.00	90.00	66.846(3)	90.00	90.00
V [Å^3]	3366.4(13)	3261.7(16)	1748.1(7)	976.1(3)	6438.1(16)
Z	4	8	2	2	8
D_c [g cm^{-3}]	1.024	1.093	1.499	1.676	1.225
μ [mm^{-1}]	0.129	0.132	1.983	1.780	0.634
F(000)	1136	1168	812	488	2504
Reflections collected	5901	6657	7194	3305	5654
Independent reflections, R_{int}	4384, 0.0536	2870, 0.0307	6001, 0.0233	1978, 0.0196	4897, 0.0660
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.1354, 0.2744	0.0525, 0.1295	0.0750, 0.1489	0.0282, 0.0656	0.0904, 0.1706
$R1$, $wR2$ (all data)	0.1700, 0.2919	0.0632, 0.1363	0.0846, 0.1524	0.0287, 0.0659	0.1052, 0.1771
Goodness of fit, F^2	1.274	1.066	1.182	1.037	1.299
Largest diff. peak and hole [e Å^{-3}]	0.491 to –0.391	0.289 to –0.166	0.616 to –0.643	0.762 to –0.321	0.528 to –0.531

[{(2-Pyr)C(H)C(Ph)N(SiMe$_3$)}$_2$Co] (7): $CoCl_2$ (0.387 g, 2.98 mmol) was added to a solution of **4** (0.012 g, 2.98 mmol) in Et_2O (10 mL) at –78 °C. The resulting heavy blue mixture was warmed to room temperature slowly and stirred for 24 h, and then filtered. The filtrate was concentrated and allowed to stand for 3 d at room temperature to give pink crystals (0.57 g, 64%). $C_{32}H_{38}CoN_4Si_2$ (593.78): calcd. C 64.73, H 6.45, N 9.44; found C 64.63, H 6.41, N 9.49. Complex **7** is NMR-silent because of the paramagnetic nature of the compound.

X-ray Crystallography: Data collection for **1b**, **2**, and **5**–**7** was performed with Mo-K_α radiation (λ = 0.71073 Å) by using a Bruker Smart Apex CCD diffractometer at 298(2) or 213(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. A total of N reflections were collected in the ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption by using multiscans (*SADABS*).[33] The structure was solved by direct methods (*SHELXS-97*).[34] Then, the remaining non-hydrogen atoms were obtained from the successive difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were constrained to parent sites, by using a riding mode (*SHELXTL*).[35] Crystal data and details of data collection and refinements for **1b**, **2**, and **5**–**7** are summarized in Table 6. Selected bond lengths and bond angles are listed in Tables 1, 3, 4, and 5. CCDC-723219, -723220, -723221, -723222, -723223 (**1b**, **2**, **5**, **6**, **7**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

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[1] a) W. P. Leung, H. K. Lee, L. H. Weng, Z. Y. Zhou, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1997**, 779–783; b) G. Ossig, A. Meller, C. Bronneke, O. Muller, M. Schafer, R. Herbst-Irmer, *Organometallics* **1997**, *16*, 2116–2120; c) S. Benet, C. J. Cardin, D. J. Cardin, S. P. Constantine, P. Heath, H. Rashid, S. Teixeira, J. H. Thorpe, A. K. Todd, *Organometallics* **1999**, *18*, 389–398; d) P. C. Andrews, J. E. McGrady, P. J. Nichols, *Organometallics* **2004**, *23*, 446–453; e) T. R. v. d. Ancker, L. M. Engelhardt, M. J. Henderson, G. E. Jacobsen, C. L. Raston, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2004**, *689*, 1991–1999.

[2] P. C. Andrews, D. R. Armstrong, C. L. Raston, B. A. Roberts, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **2001**, 996–1006.

[3] a) R. I. Papasergio, B. W. Skelton, P. Twiss, A. H. White, *J. Chem. Soc., Dalton Trans.* **1990**, 1161–1172; b) C. Jones, C. H. L. Kennard, C. L. Raston, G. Smith, *J. Organomet. Chem.* **1990**, *396*, C39.

[4] B. J. Deelman, M. F. Lappert, H. K. Lee, T. C. W. Mak, W. P. Leung, P. R. Wei, *Organometallics* **1997**, *16*, 1247–1252.

[5] a) P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc., Chem. Commun.* **1994**, 2637–2638; b) M. F. Lappert, D.-S. Liu, *J. Organomet. Chem.* **1995**, *500*, 203–217; c) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3066; d) C. F. Caro, M. F. Lappert, P. G. Merle, *Coord. Chem. Rev.* **2001**, *219*, 605–663.

[6] a) X. Chen, C. X. Du, J. P. Guo, X. H. Wei, D. S. Liu, *J. Organomet. Chem.* **2002**, *655*, 89–95; b) X. Chen, L. Wang, J. P. Guo, S. P. Huang, D. S. Liu, *Mendeleev Commun.* **2005**, *15*, 160–161.

[7] W.-P. Leung, H. Cheng, H. L. Hou, Q.-C. Yang, Q.-G. Wang, T. C. W. Mak, *Organometallics* **2000**, *19*, 5431–5439.

[8] W.-P. Leung, Q. W. Y. Ip, T.-W. Lam, T. C. W. Mak, *Organometallics* **2004**, *23*, 1284–1291.

[9] a) W.-P. Leung, C.-W. So, K.-H. Chong, K.-W. Kan, H.-S. Chan, T. C. W. Mak, *Organometallics* **2006**, *25*, 2851–2858; b) W.-P. Leung, K.-H. Chong, Y.-S. Wu, C.-W. So, H.-S. Chan, T. C. W. Mak, *Eur. J. Inorg. Chem.* **2006**, 808–812; c) W.-P. Leung, C.-W. So, Y.-S. Wu, H.-W. Li, T. C. W. Mak, *Eur. J. Inorg. Chem.* **2005**, 513–521.

[10] W.-P. Leung, K.-W. Kan, K.-H. Chong, *Coord. Chem. Rev.* **2007**, *251*, 2253–2265.

[11] B. J. Deelman, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, H.-K. Lee, T. C. W. Mak, *Organometallics* **1999**, *18*, 1444–1452.

[12] R. J. Bowen, M. A. Fernandes, M. Layh, *J. Organomet. Chem.* **2004**, *689*, 1230–1237.

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[13] M. J. Henderson, R. I. Papasergio, C. L. Raston, A. H. White, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1986**, 672–674.

[14] a) L. M. Engelhardt, U. Kynast, C. L. Raston, A. H. White, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 681–682; b) L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston, A. H. White, *J. Chem. Soc., Chem. Commun.* **1988**, 336–338.

[15] X. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998–1999.

[16] J. T. York Jr, V. G. Young, W. B. Tolman, *Inorg. Chem.* **2006**, *45*, 4191–4198.

[17] J. D. Farwell, P. B. Hichcock, M. F. Lappert, A. V. Protchenko, *J. Organomet. Chem.* **2007**, *692*, 4953–4961.

[18] N. W. Aboelella, B. F. Gherman, L. M. R. Hill, J. T. York, N. Holm Jr, V. G. Young, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2006**, *128*, 3445–3458.

[19] H. Dietrich, W. Mahdi, R. Knorr, *J. Am. Chem. Soc.* **1986**, *108*, 2462–2464.

[20] D. Colgan, R. I. Papasergio, C. L. Raston, A. H. White, *J. Am. Chem. Soc.* **1984**, *106*, 1708.

[21] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc., Chem. Commun.* **1994**, 1699–1702.

[22] H. Gornitzka, D. Stalke, *Organometallics* **1994**, *13*, 4398–4405.

[23] L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1988**, 1011–1020.

[24] T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1984**, 822–824.

[25] B. S. Lim, A. Rahtu, J.-S. Park, R. G. Gordon, *Inorg. Chem.* **2003**, *42*, 7951–7959.

[26] Z. Li, T. S. Barry, R. G. Gordon, *Inorg. Chem.* **2005**, *44*, 1728–1735.

[27] X. Jiang, J. C. Bollinger, M.-H. Baik, D. Lee, *Chem. Commun.* **2005**, 1043–1045.

[28] S. Maier, W. Hiller, J. Strahle, C. Ergezinger, K. Dehnicke, *Z. Naturforsch., Teil B* **1988**, *43*, 1628–1632.

[29] P. B. Hitchcock, M. F. Lappert, M. Layh, *J. Chem. Soc., Dalton Trans.* **1998**, 1619–1624.

[30] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc., Chem. Commun.* **1994**, 1699–1700.

[31] a) Z. Li, S. T. Barry, R. G. Gordon, *Inorg. Chem.* **2005**, *44*, 1728–1735; b) A. R. Sadique, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **2001**, *40*, 6349–6355.

[32] a) K. C. Jayaratne, L. R. Sita, *J. Am. Chem. Soc.* **2000**, *122*, 958–959; b) A. Littke, N. Sleiman, C. Bensimon, D. S. Richeson, G. P. A. Yap, S. J. Brown, *Organometallics* **1998**, *17*, 446–451; c) W.-H. Sun, P. Hao, S. Zhang, Q.-S. Shi, W.-W. Zuo, X.-B. Tang, *Organometallics* **2007**, *26*, 2720–2734.

[33] G. M. Sheldrick, *Correction Software*, University of Göttingen, Göttingen, Germany, **1996**.

[34] G. M. Sheldrick, *Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

[35] *Program for Crystal Structure Refinement*, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, **1998**.

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