第 33 卷第 1 期
2017 年 1 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.33 No.1
169-174

2-苯亚胺官能化吲哚基钕胺基配合物与芳基取代甲脒的反应性

冯志君*,[1,2] 崔巧玉[1] 韦 芸[2] 周双六[2] 吴运军[1] 王少印[1]

([1]皖南医学院医用基础化学教研室,芜湖 241002)

([2]功能分子固体教育部重点实验室,安徽师范大学化学与材料科学学院分子材料实验室,芜湖 241000)

摘要: 2-(苯亚胺基次甲基)吲哚钕胺基配合物[η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]$_2$Eu[N($SiMe_3$)$_2$] (**1**)与二芳基取代甲脒(2,6-$R_2C_6H_3N$=CHNH($C_6H_3R_2$-2,6)(R=^{i}Pr (**2**), Me (**3**))经过配体交换反应,分别得到了含吲哚基脒基钕配合物[η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]Eu[(η^3-2,6-$^i Pr_2C_6H_3$)N=CHN($C_6H_3{}^iPr_2$-2,6)][N($SiMe_3$)$_2$] (**4**)和含脒基的稀土钕配合物[(η^3-2,6-$Me_2C_6H_3$)N=CHN($C_6H_3Me_2$-2,6)]$_2$Eu[N($SiMe_3$)$_2$] (**5**)。结果表明,脒基的位阻显著影响了吲哚基稀土金属胺基配合物与二芳基取代甲脒的配体交换反应。配合物 **4** 和 **5** 通过 IR、元素分析和 X 射线单晶衍射分析进行了表征。

关键词: 稀土金属; 钕; 吲哚基配体; 胺基配合物

中图分类号: O614.33+8 **文献标识码**: A **文章编号**: 1001-4861(2017)01-0169-06

DOI: 10.11862/CJIC.2017.006

Reactivity of 2-Phenylimino-Functionalized Indolyl Europium Amide with Diaryl-Substitued Formamidines

FENG Zhi-Jun*,[1,2] CUI Qiao-Yu[1] WEI Yun[2] ZHOU Shuang-Liu[2] WU Yun-Jun[1] WANG Shao-Yin[1]

([1]*Department of Chemistry, Wannan Medical College, Wuhu, Anhui* 241002, *China*)

([2]*Key Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui* 241000, *China*)

Abstract: Reactions of structurally well-defined europium(Ⅲ) amido complex having 2-(phenyliminomethine) indolyl ligands [η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]$_2$Eu[N($SiMe_3$)$_2$] (**1**) with formamidines (2,6-$R_2C_6H_3N$=CHNH($C_6H_3R_2$-2,6) (R=^{i}Pr (**2**), Me (**3**)) afforded the formamidinato indolyl-ligated europium complex [η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]Eu[(η^3-2,6-$^i Pr_2C_6H_3$)N=CHN($C_6H_3{}^iPr_2$-2,6)][N($SiMe_3$)$_2$] (**4**) and formamidinato complex [(η^3-2,6-$Me_2C_6H_3$)N=CHN($C_6H_3Me_2$-2,6)]$_2$Eu[N($SiMe_3$)$_2$] (**5**), respectively. Results showed that the steric hindrance of formamidines has a great influence on the reactivity of the imino-functionalized indolyl rare-earth metal amido complex with diaryl-substitued formamidines. The complexes **4** and **5** were characterized by IR spectra, elemental analyses and X-ray crystallographic diffraction study. CCDC: 1496184, **4**; 1496185, **5**.

Keywords: rare-earth metal; europium; indolyl ligand; amido complex

During the course of lanthanide chemistry studies, novel reactivity of rare-earth metal complexes has been one of the most important research fields[1-3], because such kinds of reactions are usually the basis for lots of important catalytic procedures, organic transformations and proposed pathway for the formation of lanthanide compounds. To date, much effort has been devoted to study the reactivity of rare-

收稿日期:2016-08-14。收修改稿日期:2016-11-02。

皖南医学院博士科研启动基金(No.rcqd201613)和国家级大学生创新训练项目(No.201510368021)资助。

*通信联系人。E-mail:fengzhijun73@163.com

earth metal complexes[4-15], which involves a number of small molecular substrates including H_2[4], CO[5], CO_2[6-9], alkane[10], alkene[8,11], alkyne[11], amine[9], carbodiimide[12], silane[4,13], phosphine[14], nitrile[7-8], isocyanate[8-9], amidine[13], carbonyl compound[7,11], heterocyclic compound[11] and so on[15]. Among them, amidines, used as ligands or substrates for reactivity studies[16-18], have drawn much attention due to being easily prepared and tuned sterically and electronically. Amidines have played an important role in the investigation on the influence of spatial hindrance and electronic effect on the synthesis, bonding modes, structures and performances of rare-earth metal complexes. Thus, reactivity studies between indolyl rare-earth metal amido complexes with formamidines are still the interesting work.

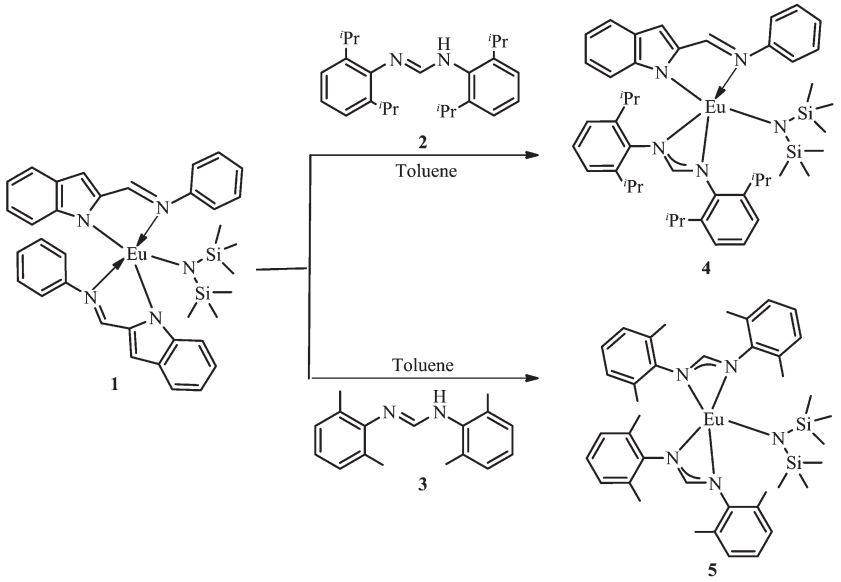
Recently, we have reported the reactivity of 2-(2, 6-diisopropylphenylaminomethine)indolyl europium (Ⅱ) amido complex with formamidines having different spatial hindrance afforded novel complexes incorporating indolyl ligands bonded with metal in novel μ-η^3:η^1:η^1 and μ-η^2:η^1:η^1 bonding manners[19], respectively. In addition, we have also reported the reactivities of rare-earth metal monoalkyl complexes incorporating bidentate indolyl ligands with $PhSiH_3$ or amidine, and have obtained the first example of trivalent rare-earth metal complexes having an amido-functionalized indolyl ligand bonded to a metal in the μ-η^6:η^1:η^1 fashions[20].

Continuing our investigation on the amino, imino-functionalized indolyl ancillary ligand system, we have synthesized europium (Ⅲ) amido complex having 2-(phenyliminomethine)indoly ligands[21]. Encouraged by above-mentioned results, we further investigated the reactivity of the indolyl europium (Ⅲ) amide with formamidines, as shown in Scheme 1. According to our experimental results, when treating of europium(Ⅲ) complex containing imino-functionalized indolyl groups and $N(SiMe_3)_2$ group as ancillary ligands with formamidines, the attack occurs primarily onto the Eu-N bonds between indolyl ligand and central metal. Moreover, the results also made it clear that the reactivity of europium (Ⅲ) amido complex having the functionalized indolyl ligands and the structures of the resultants are significantly dependent on the steric hindrance of formamidines. Herein, we will report these results and structural studies of new complexes.

1 Experimental

1.1 Materials and methods

All manipulations of air- and moisture-sensitive materials were performed using Schlenk techniques or in a glovebox under an atmosphere of purified argon. Toluene and hexane were refluxed and freshly distilled over sodium benzophenone ketyl under argon



Scheme 1

prior to use. [2-(C_6H_5NH=CH)C_8H_5N]$_2$Eu[N($SiMe_3$)$_2$] (**1**)[21] and 2,6-$R_2C_6H_3N$=CHNH($C_6H_3R_2$-2,6) (R=^{i}Pr (**2**), Me (**3**))[22] were prepared according to the literature methods. Elemental analyses data were obtained on a Perkin-Elmer 2400 Series Ⅱ elemental analyzer and analyses were carried out in the microanalytical laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. IR spectra were run on a Shimadzu FTIR-8400s spectrometer (KBr pellet). Melting points were determined in sealed capillaries and are uncorrected.

1.2 Syntheses of complexes

1.2.1 Synthesis of [η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]Eu[(η^3-2,6-$^i Pr_2C_6H_3$)N=CHN($C_6H_3{}^iPr_2$-2,6)][N($SiMe_3$)$_2$] (**4**)

A Schleck flask was charged with complex **1** (0.90 g, 1.20 mmol), 2,6-$^i Pr_2C_6H_3N$=CHNH($C_6H_3{}^iPr_2$-2,6) (**2**) (0.43 g, 1.20 mmol) and toluene (30 mL). The reaction mixture was stirred at 70 ℃ for 16 h. The red-brown solution was evaporated to dryness and extracted with *n*-hexane (14 mL). Orange-red crystals that were suitable for X-ray diffraction were obtained upon crystallization from hexane at 0 ℃ after a few days (0.59 g, 55%). m.p. 187 ℃. Anal. Calcd. for $C_{46}H_{65}N_5Si_2Eu$ (%): C, 61.65; H, 7.31; N, 7.81. Found (%): C, 61.16; H, 7.63; N, 8.22. IR (KBr pellet, cm^{-1}): 2 959 (w), 2 865 (w), 1 660 (s), 1 614 (s), 1 589 (s), 1 483 (m), 1 445 (m), 1 423 (m), 1 298 (w), 1 194 (w), 1 065 (w), 957 (w), 908 (w), 872 (w), 800 (m), 767 (m), 753 (m), 737 (m), 695 (s).

1.2.2 Synthesis of [(η^3-2,6-$Me_2C_6H_3$)N=CHN($C_6H_3Me_2$-2,6)]$_2$Eu[N($SiMe_3$)$_2$] (**5**)

The synthesis of complex **5** was same to that of complex **4** except that 2,6-$Me_2C_6H_3$N=CHNH($C_6H_3Me_2$-2,6) (**3**) (0.60 g, 2.40 mmol) was used instead of compound **2**. Yield: 0.55 g, 56%. m.p. 205 ℃. Anal. Calcd. for $C_{40}H_{58}N_5Si_2Eu$(%): C, 58.80; H, 7.16; N, 8.57. Found(%): C, 58.38; H, 7.42; N, 8.68. IR (KBr pellet, cm^{-1}): 2 961 (w), 2 854 (w), 1 661 (s), 1 613 (s), 1 589 (s), 1 483 (m), 1 444 (m), 1 425 (m), 1 298 (w), 1 195 (w), 1 066 (w), 955 (w), 906 (w), 870 (w), 799 (m), 765 (m), 750 (m), 737 (m), 696 (s).

1.3 X-ray crystallographic analyses

Single crystals of complexes **4** and **5** suitable for X-ray diffraction studies were sealed in thin-walled glass capillaries under argon. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). An empirical absorption correction was applied using the SADABS program[23]. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package[24]. All hydrogen atoms were refined using a riding model. A summary of the crystallographic data and selected experimental information are listed in Table 1, while the selected bond lengths and angles are summarized in Table 2.

CCDC: 1496184, **4**; 1496185, **5**.

Table 1　Crystallographic data and structure refinement for complexes 4 and 5

Complex	4	5
Empirical formula	$C_{46}H_{64}EuN_5Si_2$	$C_{40}H_{56}EuN_5Si_2$
Formula weight	895.16	815.04
Temperature / K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*C*2/*c*
a / nm	1.137 2(3)	2.373 39(13)
b / nm	1.223 5(3)	1.154 60(6)
c / nm	1.818 7(5)	1.995 10(10)
α / (°)	92.508(3)	90
β / (°)	95.407(3)	128.622(6)
γ / (°)	109.134(3)	90

Continued Table 1

V / nm^3	2.372 5(11)	4.271 4(4)
Z	2	4
D_c / (g·cm^{-3})	1.253	1.267
μ / mm^{-1}	1.407	1.556
F(000)	932	1 688
Crystal size / mm	0.16×0.15×0.13	0.18×0.15×0.13
θ range / (°)	1.77~27.42	2.06~27.61
Limiting indices (h, k, l)	−13~14, −15~15, −23~23	−30~30, −15~15, −25~24
Reflections collected, unique	19 700, 10 417	18 166, 4 943
R_{int}	0.068 5	0.029 9
Data, restraints, parameters	10 417, 0, 501	4 943, 0, 225
Goodness-of-fit on F^2	1.019	1.029
Final R indices [$I>2\sigma(I)$]	R_1=0.062 7, wR_2=0.122 7	R_1=0.027 6, wR_2=0.060 6
R indices (all data)	R_1=0.132 0, wR_2=0.151 0	R_1=0.038 0, wR_2=0.064 6
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	1 725, −1 607	394, −286

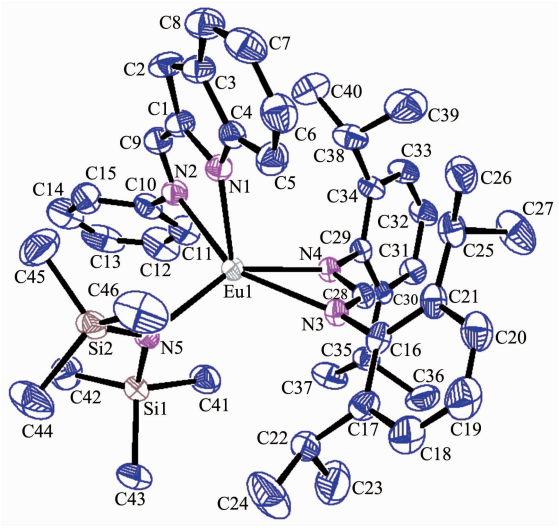
Table 2 Selected bond lengths (nm) and angles (°) for complexes 4 and 5

		4			
Eu(1)-N(1)	0.234 3(6)	Eu(1)-N(4)	0.243 6(5)	C(28)-N(3)	0.132 0(8)
Eu(1)-N(2)	0.251 0(6)	Eu(1)-N(5)	0.225 0(5)	C(28)-N(4)	0.131 0(7)
Eu(1)-N(3)	0.240 2(5)	N(2)-C(9)	0.129 6(9)		
N(2)-C(9)-C(1)	123.0(7)	N(1)-Eu(1)-N(3)	104.65(19)	N(5)-Eu(1)-N(2)	96.80(19)
N(5)-Eu(1)-N(1)	110.20(19)	N(5)-Eu(1)-N(4)	137.97(18)	N(3)-Eu(1)-N(2)	148.81(19)
N(5)-Eu(1)-N(3)	113.13(19)	N(1)-Eu(1)-N(4)	111.82(18)	N(4)-Eu(1)-N(2)	95.57(18)
		5			
Eu(1)-N(1)	0.240 16(19)	Eu(1)-N(1)^i	0.240 16(19)	C(9)-N(2)^i	0.132 0(3)
Eu(1)-N(2)	0.242 4(2)	Eu(1)-N(2)^i	0.242 4(2)	N(2)-C(9)^i	0.132 1(3)
Eu(1)-N(3)	0.223 1(3)	C(9)-N(1)^i	0.131 3(3)	N(1)-C(9)^i	0.131 3(3)
N(3)-Eu(1)-N(2)^i	103.84(5)	N(1)^i-Eu(1)-N(2)	107.74(7)	N(3)-Eu(1)-N(1)	122.32(5)
N(3)-Eu(1)-N(1)^i	122.32(5)	N(1)-Eu(1)-N(2)^i	107.75(7)	N(3)-Eu(1)-N(2)	103.84(5)
N(1)-Eu(1)-N(1)^i	115.35(9)	N(2)-Eu(1)-N(2)^i	152.33(10)	N(1)-Eu(1)-N(2)	55.91(6)

Symmetry codes: ^{i} $-x+1$, y, $-z+1/2$ for **5**

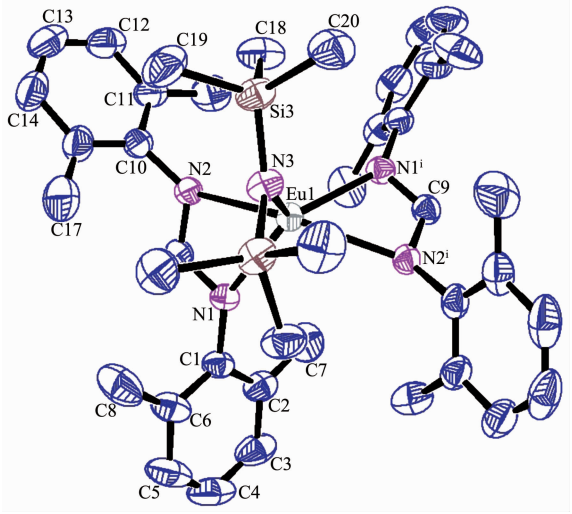
2 Results and discussion

As shown in Scheme 1, reaction of europium complex **1** with the sterically bulky formamidine [(2,6-^{i}Pr$_2$C$_6$H$_3$)NCHNH(C$_6$H$_3{}^i$Pr$_2$-2,6)] (**2**) gave europium complex formulated as [η^1:η^1-2-(C$_6$H$_5$NH=CH)C$_8$H$_5$N]Eu[(η^3-2, 6-^{i}Pr$_2$C$_6$H$_3$)N=CHN(C$_6$H$_3{}^i$Pr$_2$-2, 6)][N(SiMe$_3$)$_2$] (**4**), containing an indolyl ligand and an formamidinato ligand via ligand exchange process. Treatment of europium complex **1** with the less bulky formamidine 2,6-Me$_2$C$_6$H$_3$N=CHNH(C$_6$H$_3$Me$_2$-2,6) (**3**) afforded europium complex formulated as [(η^3-2,6-Me$_2$C$_6$H$_3$)N=CHN(C$_6$H$_3$Me$_2$-2,6)]$_2$Eu[N(SiMe$_3$)$_2$] (**5**), only incorporating formamidinato ligands and N(SiMe$_3$)$_2$. Complexes **4** and **5** are extremely sensitive to air and moisture. They were characterized by spectroscopic and elemental analyses, and their structures were further elucidated by X-ray diffraction study. The structures of **4** and **5** are individually displayed in Fig.1 and 2, while selected bond lengths and angles are given in Table 2.



All hydrogen atoms are omitted for clarity

Fig.1　Molecular structure of **4** with 30% thermal ellipsoids



All hydrogen atoms are omitted for clarity; Symmetry codes: ^{i} $-x+1$, y, $-z+1/2$

Fig.2　Molecular structure of **5** with 30% thermal ellipsoids

Complex **4** crystallizes in a triclinic crystal system with space group $P\bar{1}$. X-ray analyses revealed that **4** is five-coordinated mononuclear complex. As shown in Fig.1, the central Eu^{3+} is coordinated by a bidentate indolyl ligand in η^1:η^1 hapticities, an formamidinato ligand in an η^3 fashion and $N(SiMe_3)_2$ ligand adopting a distorted trigonal bipyramid configuration similar to that of complex **1**[21]. The C(28)-N(3) length of 0.132 0(8) nm and C(28)-N(4) of 0.131 0(7) nm has become average and close to the value between carbon-carbon length of single bond and that of double bond, showing the characteristic of delocalized bond and indicating that the formamidinato ligand is bonded to the Eu^{3+} with an η^3 manner. Among the Eu-N lengths in complex **4**, the Eu(1)-N(2) length of 0.251 0(6) nm of the appendant arm is significantly longer than the others (Eu(1)-N(1) 0.234 3(6) nm, Eu(1)-N(3) 0.240 2(5) nm, Eu(1)-N(4) 0.243 6(5) nm, Eu(1)-N(5) 0.225 0(5) nm), and close to the corresponding value of 0.252 5(3) nm in complex **1** and that of 0.256 5(2) nm in complex [2-(^{t}BuN=CH)C_8H_5N]Eu[$N(SiMe_3)_2$]$_2$[21], indicating coordination nature of the N2 atom. The bond angles of N(5)-Eu(1)-N(1), N(5)-Eu(1)-N(3), N(1)-Eu(1)-N(3), N(1)-Eu(1)-N(4) and N(5)-Eu(1)-N(2) are respectively 110.20(19)°, 113.13(19)°, 104.65(19)°, 111.82(18)° and 96.80(19)°.

Complex **5**, crystallizing in a monoclinic crystal system with space group *C*2/*c*, is also five-coordinated. Differently, the coordination environment of the central metal is completed by two formamidino groups and one -$N(SiMe_3)_2$ ligand as a centrosymmetric tetragonal pyramid arrangement, in which N3 atom of -$N(SiMe_3)_2$ group occupies the vertex, as shown in Fig. 2. Given that the C(9)-N(1)^i, N(1)-C(9)^i lengths of 0.131 3(3) nm, C(9)-N(2)^i of 0.132 0(3) nm and N(2)-C(9)^i of 0.132 1(3) nm, the bonding mode of formamidino ligand bonded to Eu^{3+} is described as an η^3 fashion. The Eu(1)-N(1)^i length of 0.240 16(19) nm or Eu(1)-N(2)^i length of 0.242 4(2) nm is in accordance with the corresponding Eu(1)-N(1) length of 0.240 16(19) nm or Eu(1)-N(2) length of 0.242 4(2) nm, indicating a centrosymmetric geometry. Moreover, the centrosymmetric structure is also deduced by the bond angles of N(3)-Eu(1)-N(2)^i of 103.84(5)°, N(3)-Eu(1)-N(1)^i of 122.32(5)°, N(3)-Eu(1)-N(1) of 122.32(5)° and N(3)-Eu(1)-N(2) of 103.84(5)°. Thus, the result suggested that imino-functionalized indolyl ligands in complex **1** are completely replaced by the less bulky formamidino groups, while the geometry of the resultant complex **5** is obviously different from that of complex **1**.

3　Conclusions

In summary, we have studied the reactivity of

europium(Ⅲ) amido complex having 2-(phenylimino-methine)indoly ligands [2-(C_6H_5NH=CH)C_8H_5N]$_2$Eu[N($SiMe_3$)$_2$] (**1**) with formamidines. Reaction of **1** with the sterically bulky formamidine [(2,6-^{i}Pr$_2$C$_6$H$_3$)NCHNH($C_6H_3{}^iPr_2$-2,6)] or the less bulky formamidine 2,6-$Me_2C_6H_3N$=CHNH($C_6H_3Me_2$-2,6) gave complexes [η^1:η^1-2-(C_6H_5NH=CH)C_8H_5N]Eu[(η^3-2,6-^{i}Pr$_2$C$_6$H$_3$)N = CHN($C_6H_3{}^iPr_2$-2,6)][N($SiMe_3$)$_2$] (**4**) and [(η^3-2,6-$Me_2C_6H_3$)N=CHN($C_6H_3Me_2$-2,6)]$_2$Eu[N($SiMe_3$)$_2$] (**5**), respectively. The results showed that the steric hindrance of organic molecular substrates have significantly effects on the reactivity of rare-earth metal amido complexes containing imino-functionalized indolyl ligands and the structures of the resultant new lanthanide complexes. Further study on the reactivity of the rare-earth metal compounds with the related indolyl ligands is in progress in our laboratory and will be reported soon.

References:

[1] Bochkarev M N. *Chem. Rev.*, **2002**,**102**:2089-2117

[2] Edelmann F T, Freckmann D M M, Schumann H. *Chem. Rev.*, **2002**,**102**:1851-1896

[3] Li T S, Kaercher S, Roesky P W. *Chem. Soc. Rev.*, **2014**,**43**:42-57

[4] Fegler W, Venugopal A, Kramer M, et al. *Angew. Chem. Int. Ed.*, **2015**,**54**:1724-1736

[5] Shima T, Hou Z. *J. Am. Chem. Soc.*, **2006**,**128**:8124-8125

[6] LeBlanc F A, Piers W E, Parvez M. *Angew. Chem. Int. Ed.*, **2014**,**53**:789-792

[7] Xu L, Wang Y C, Xi Z F, et al. *Chem. Eur. J.*, **2015**,**21**:6686-6689

[8] Chu J X, Lu E L, Chen Y F, et al. *Angew. Chem. Int. Ed.*, **2011**,**50**:7677-7680

[9] Hong J Q, Zhang L X, Zhou X G, et al. *Organometallics*, **2013**,**32**:7312-7322

[10]Cole M L, Deacon G B, Junk P C, et al. *Organometallics*, **2013**,**32**:1370-1378

[11]Arnold P L, McMullon M W, Rieb J, et al. *Angew. Chem. Int. Ed.*, **2015**,**54**:82-100

[12]Xu L, Wei J N, Xi Z F, et al. *Chem. Eur. J.*, **2015**,**21**:15860-15866

[13]Chu J X, Lu E L, Chen Y F, et al. *Organometallics*, **2013**,**32**:1137-1140

[14]Wang K, Luo G, Zhang L X, et al. *Angew. Chem. Int. Ed.*, **2014**,**53**:1053-1056

[15]Rong W, He D, Cui D M, et al. *Chem. Commun.*, **2015**,**51**:5063-5065

[16]Edelmann F T. *Chem. Soc. Rev.*, **2009**,**38**:2253-2268

[17]Yao S, Chan H S, Lee H K, et al. *Inorg. Chem.*, **2009**,**48**:9936-9946

[18]Cole M L, Deacon G B, Junk P C, et al. *Chem. Eur. J.*, **2013**,**19**:1410-1420

[19]Feng Z J, Zhu X C, Wang S W, et al. *Inorg. Chem.*, **2013**,**52**:9549-9556

[20]Zhang G C, Wang S W, Zhou S L, et al. *Organometallics*, **2015**,**34**:4251-4261

[21]Feng Z J, Wei Y, Wang S W, et al. *Dalton Trans.*, **2015**,**44**:20502-20513

[22]Hirano K, Urban S, Wang C, et al. *Org. Lett.*, **2009**:1019-1022

[23]Sheldrick G M. *SADABS, A Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.

[24]Sheldrick G M. *SHELXTL* 5.10 *for Windows NT, Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Inc., Madison, WI, **1997**.