Study on the Structure, Thermodynamic property, and Fluorescence of Pyridin-2-ylmethyl-tert-butylamine Dimethyl aluminum complex

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Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex with a planar five-membered ring was synthesized and characterized by elemental analysis, UV-Vis spectra, TG/DSC, ¹H NMR, and ¹³C NMR. Through single-crystal diffraction, it is proved that the structure of the alkyl aluminum complex is a planar five-membered ring. By comparison the crystal data of 11 kinds of five-membered ring dialkyl aluminum complexes, we found that the planar five-membered ring dialkyl aluminum

Introduction

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Bidentate nitrogen ligand complexes have a widespread application in the fields of catalysis,^[1] atomic layer deposition and chemical vapor deposition precursors,^[2,3] and organometal-lic chemistry.^[4] Four-membered rings, five-membered rings, and six-membered rings are common ring-forming forms of bidentate nitrogen ligand complex chelates.^[5] The five-membered ring configuration has a planar configuration and a non-planar configuration. More and more attention has been paid to the β -hydrogen elimination of non-planar five-membered ring configurations such as pyrrole and indole-functionalized secondary amines complexes^[6] and the redox conversion of planar five-membered ring a-diimine.^[7]

Aluminum is a heavy main group metal.^[8] The major metal complexes can also exhibit transition metal compounds' properties under specific ligands' action with the development of organometallic chemistry.^[9] Research on bidentate nitrogen ligand five-membered ring dialkyl aluminum complexes has been widely reported in recent years. For example, α -diimine and 8-Anilide-5,6,7-trihydroquinoline dialkyl aluminum complexes are used as highly active catalysts in the ring-opening polymerization cyclic esters;^[12,19] α -diimine and 2-imino pyridine dialkyl aluminum are used to study redox ligands.^[10] The properties of planar five-membered ring dialkyl aluminum complexes are valuable to study. However, a planar bidentate

is formed when there is at least one unequal sp² hybrid nitrogen in the ligand. TG/DSC study of the compound's thermodynamic properties showed the thermal decomposition temperature of complex 7 was determined to be 210°C. The rigid plane structure of the product was proved by fluorescence analysis. When the excitation wavelength was 380 nm, the emission wavelength was 478 nm.

nitrogen ligand five-membered ring dialkyl aluminum complex containing $\beta\text{-hydrogen}$ has not been reported.

Pyridin-2-ylmethyl-substituted amine is a ligand similar to α -aminoaldimine, which is partially replaced by pyridine. This ligand retains β -hydrogen relative to α -aminoaldimine. The complexes of nickel, cobalt, and copper with pyridin-2-ylmethyl-substituted amine have been used in ethylene polymerization and optical properties.^[11] Bidentate nitrogen ligand fivemembered ring dialkyl aluminum complexes have been extensively studied. However, few studies have been reported on the alkyl aluminum complexes based on pyridin-2-ylmethyl-substituted amine. Only two studies have investigated similar structures, including 5,6,7-trihydroguinolyl and guinolin-8amine derivatives.^[12] Previous studies did not consider β-hydrogen. Therefore, we have prepared the pyridin-2-ylmethyl-tertbutylamine dimethyl aluminum complex, obtained the crystal structure, and studied the optical properties and thermodynamics. To study the formation conditions of planar bidentate nitrogen ligand five-membered ring dialkyl aluminum complex, we further analyzed the structural characteristics of several kinds of five-membered ring dialkyl aluminum complexes from the inner ring angle and intra-ring bond length and the effects of different N-donor on the configuration of the corresponding five-membered rings complexes.

Results and Discussion

As seen in Scheme 1, the reaction of AlMe₃ with one equiv. of ¹BuHNCH₂ (o-C₆H₅N) in hexane at -30 °C afforded dimethyl aluminum complex (Scheme 1) in high yield. Compound 7 was obtained as solid in good yield and purified through crystallization at -30 °C in *n*-hexane after extraction of ether-removed residue. Both elemental and NMR spectra of complex 7 were consistent with the proposed monomeric structure, implying the formation and purity. When the ligand's substituent is

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Scheme 1. Synthesis of Pyridin-2-ylmethyl-tert-butylamine and Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex.

isopropyl or *n*-propyl, the oily product is obtained, but it can not be separated, purified, and characterized. The products with substituent TMS can be distilled to obtain reliable products with low melting-point, but after exposure, the products quickly change from colorless solid to purple oily liquid, and the peak shape is disorderly detected by nuclear magnetic hydrogen spectroscopy. It is judged that the Pyridin-2-ylmethyl-substituted amine dimethyl aluminum complex is sensitive to light, and only a *tert*-butyl product is obtained. The crystal data and crystallographic data of Compound7 are shown in Figure 1, Table 1 and Table 5. The sum of the inner angles of the fivemembered ring $C_5-C_6-N_2-Al_1-N_1$ is 540°, which is a plane.

Eleven five-membered ring dialkyl aluminum complexes in Scheme 2 and Scheme 3are used as the five-membered ring structure's research objects. According to the degree of saturation in the ring, compounds 1 and 2 are ethylenediamine derivative dimethyl aluminum, and there is no double bond in the ring. The ring of the compound (3, 4a–b, 5a–c, 6, 7, and 9a–c) contains an unsaturated bond, the unsaturated bonds are introduced by imine, pyridine, pyrrole, benzene ring, and cyclohexene; α -diimine and 2- iminopyridine are redox ligands. Radical anionic and derived anionic are redox states of ligands in compounds (10a, 11a) and compounds (10b, 11b).^[20,21]

As shown in Table 2, the sum of the inner ring angles of compounds 1 and 2 is $517-519^{\circ}$ ($<540^{\circ}$), a non-planar

Table 1. Selected Bond Lengths (Å) and Angles (deg) (Summary of Data CCDC 1538588). AI₁-N₁ 1.98 $C_6 - C_5$ 1 4 7 9 $AI_1 - N_2$ 1.838 $C_4 - H_4$ 0.929 $AI_1 - C_{10}$ 1.964 0.93 $C_1 - H_1$ $N_1 - C_5$ 1 3 4 5 1 364 $C_1 - C_2$ 1.448 1.551 $N_2 - C_6$ 2₇-C₈ $N_2 - C_7$ 1.446 C7–C₀₄ 1.496 $C_6 - H_{6A}$ 0.97 $N_2 - AI_1 - C_{10}$ 121.30 (11) $C_{10} - AI_1 - C_{10A}$ 109.30 (2) $N_2 - AI_1 - N_2$ 84.76 (14) $C_{10} - AI_1 - N_1$ 107.53 (12) $C_5 - N_1 - AI_1$ 113.0 (3) $C_7 - N_2 - C_6$ 116.5 (3) $C_6 - N_2 - AI_1$ 115.9 (3) $N_2 - C_6 - C_5$ 111.0 (3) $N_1 - C_5 - C_6$ 115.3 (3)



Scheme 2. Selected five-membered ring dialkyl aluminum complexes (1–9a).



Scheme 3. Selected five-membered ring dialkyl aluminum complexes (9b–11b).

structure. Ethylenediamine derivatives (saturated structure) react with alkyl aluminum to form non-planar five-membered ring dialkyl aluminum complexes. The sum of the inner angles of the ring of the compounds (8, 10a, 10b, 11a, and 11b) is 540°, which is a plane structure. Redox ligands (α -diimine and



Figure 1. Molecular structure of Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex in the crystal.

Table 2. Selected Bond Angles (deg).						
	N ₂ —AI—N ₁	Al-N ₂ -C ₂	$C_1 - C_2 - N_2$	$C_2 - C_1 - N_1$	C ₁ –N ₁ –AI	Σ
1	86.77-86.85	100.34-100.83	109.75–109.76	107.18–108.40	113.52–114.16	~517.5
2	87.13	99.52	110.34	107.49	115.24	519.6
3	85.62	109.83	115.98	115.13	101.62	528.2
4a	84.2	111.0	115.4	115.8	112.6	539.0
4b	85.9	113.3	119.5	114.7	106.0	539.4
5a–5c	84.84-85.58	107.63	109.08	117.66	114.32	~ 533.0
		103.04	107.38	115.21	112.80	
6	85.18	109.90	115.9	115.4	113.50	539.9
7	84.76	115.9	111.0	115.3	113.0	540.0
8	83.30	115.3	113.1	113.1	115.3	540.0
9a-9c	84.01-84.68	113.6-113.80	107.4-108.52	117.4–117.7	116.99–116.42	540.0
10a	85.28	110.37	115.73	116.5	111.17	540.0
10b	83.64	113.86	115.1	112.4	114.99	540.0
11a	84.31	111.27	115.13	115.16	114.01	540.0
11b	83.88	111.98	115.21	111.93	116.87	540.0

2-imino pyridine) react with alkyl aluminum to form planar fivemembered ring dialkyl aluminum complexes. Unlike dialkyl aluminum complexes with saturated structure and redox ligands, the sum of compound's (3-7 and 9a-c) five-membered interior angles is 528–540°. The presence of unsaturated bonds in the ring makes the dialkyl aluminum complex closer to forming a planar five-membered ring. A five-membered ring dimethyl aluminum complex with an unsaturated bond has both planar and non-planar results. 1,2-diamino benzenes dimethyl aluminum (3), imino-amide dialkyl aluminum, and Mono-anionic pyrrolyl dimethyl aluminum (5a-c) are non-planar five-membered rings. Quinolin-8-amine derivatives dimethyl aluminum (6), α -diimine dimethyl aluminum (alkylation product, 9a-c), and pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum (7) are planar five-membered rings. Compound 4a, b has a structure similar to that of the compound 9a-c, has a fivemembered ring close to the plane (the sum of the ring's inner angles is 539°). When the unsaturated bond is opposite to the center of aluminum (3), it tends to form a non-planar fivemembered ring. When pyrrole nitrogen is bonded with aluminum, it cannot form a planar structure. However, the

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coordination bonds formed by pyridine and imine with aluminum center can form a planar structure. Imine nitrogen and pyridine nitrogen are non-isotropic sp² hybrids, while pyrrole nitrogen is isotropic sp² hybridizing. When the N–C–C–N ligand containing unequal sp² hybrid nitrogen reacts with alkyl aluminum, it tends to form a planar five-membered ring dialkyl aluminum complex. The sum of the combined N–Al–N angles and the ring's inner angles has a similar rule: the higher the structure's conjugate degree, the sharper the angle.

As shown in Table 3, the N–C–C–N bond length of the planar five-membered ring (7–11) is shorter than that of the N–C–C–N of the non-planar five-membered ring (1,2,5a–c). Because of the introduction of benzene (3, 6) and cyclohexene (4a, b), the bond length of C_1 – C_2 is considerably shortened (1.348–1.434 Å), which makes the bond length of N–C–C–N relatively shorter, so it is not suitable to participate in the comparison. Because of the N–C–C–N bond length's contraction, under a similar bond length of Al–N, the N–Al–N angle is sharper than that of the saturated structure. The coordination bond (Al–N₂) length (2.003–2.049 Å) of the non-planar five-membered ring dialkyl aluminum complex (1–3, 4b,5a–c) is

Table 3. Selected Bond Lengths (Å).						
	AI ₁ -N ₁	Al ₁ -N ₂	C ₁ C ₂	C ₁ N ₁	C ₂ –N ₂	$\Sigma_{\rm (N1-C1-C2-N2)}$
1	1.865–1.876	2.016-2.043	1.519–1.524	1.465-1.467	1.489–1.495	4.473-4.486
2	1.836	2.049	1.520	1.455	1.501	4.476
3	1.865	2.023	1.411	1.378	1.477	4.266
4a	1.897	1.968	1.434	1.344	1.333	4.111
4b	1.856	2.045	1.348	1.494	1.395	4.237
5a–5c	1.878-1.888	2.003-2.027	1.494-1.500	1.372-1.382	1.499-1.502	4.365–4.384
6	1.880	1.985	1.418	1.385	1.382	4.185
7	1.838	1.980	1.479	1.448	1.345	4.272
8	1.915	1.915	1.496	1.337	1.337	4.170
9a–9c	1.839–1.845	1.984-1.988	1.502-1.518	1.286-1.295	1.467-1.477	4.255-4.290
10a	1.914	1.935	1.391	1.375	1.390	4.156
10b	1.874	1.956	1.485	1.381	1.295	4.161
11a	1.906	1.963	1.430	1.386	1.383	4.199
11b	1.871	1.988	1.492	1.379	1.360	4.231



greater than 2.0 Å; the coordination bond $(AI-N_2)$ length (1.915–1.988 Å) of the planar five-membered ring dialkyl aluminum complex (6-11) is less than 2.000 Å. The bond lengths of the two types of aluminum-nitrogen bonds in the compound (8, 10a, 11a) are the most similar because the ligand's redox state is radical-anionic. When the compound is converted from radical-anionic to derived anionic, the bond length of Al-N₁ of compound decreases, and the bond length of Al-N₂ of compound increases. The bond lengths of the two aluminum-nitrogen bonds of α -diimine and 2-iminopyridine derived anionic dialkyl aluminum complex (10b, 11b) are close to compound 6. The Al-N bond length of the compound (7, 9a-c) is similar, and the Al-N₁ bond length is shorter than that of the compound (10b, 11b). The sum of intra-ring bond lengths of planar five-membered rings (< 8.1 Å). The sum of intra-ring bond lengths of non-planar five-membered rings (8.246-

Table 4. Selected Al–C Lengths (Å).				
	AI–C		AI–C	
1	1.966	7	1.964	
2	1.970	8	1.969	
3	1.962	9a–9c	1.963–1.969	
4a	1.965	10a	1.981	
4b	1.966	10b	1.961	
5a–5c	1.950-1.959	11a	1.984	
6	1.962	11b	1.969	

Table 5. Crystallographic data and refinement details for com-				
pound 7.				
Compound	7			
Formula	$C_{12}H_{21}AIN_2$			
M _w	220.29			
Color	colorless			
Crystal system	Monoclinic			
Space group	P 21/m			
a/Å	7.9104 (15)			
b/Å	7.5465 (14)			
<i>c</i> /Å	12.127 (2)			
$\alpha/^{\circ}$	90			
β/°	107.824 (4)			
$\gamma/^{\circ}$	90			
V/Å ³	689.2 (2)			
Z	2			
$D_{\rm c}/\rm{gcm}^{-3}$	1.062			
μ/mm^{-1}	0.122			
F (000)	240			
Crystal size/mm	0.36×0.25×0.14			
2θ range/°	2.327–22.174			
Index range	$-10 \le h \le 10$			
	-9≦k≦9			
	-15≦l≦13			
No.of reflns	6135			
collected No. of indep. reflns. (<i>R</i> _{int})	1715 (0.0497)			
$R, WR_2 (I > 2\sigma (I))$	0.0653, 0.1870			
R , w R_2 (all data)	0.1073, 0.2154			
Goodness of fit, F ²	1.061			
Data/restraints/params.	1715/15/93			
Largest diff. peak, hole/e A ³	0.518, -0.537			

8.405 Å). The planar five-membered ring is contractible relative to the non-planar five-membered ring structure.

As shown in Table 4, the average Al–C length of alkyl aluminum is between 1.950–1.984 Å. The compound's average Al–C bond length (10a, 11a) is longer than the compound (10b, 11b). The change of the state of redox ligand affects the length of Al–C bonds. Under non-redox ligands' action, the range of bond length of five-membered ring dialkyl aluminum complexes is small (1.950–1.969 Å). Planar five-membered rings or non-planar five-membered rings have little influence on the length of Al–C.

It is worth noting that 7 is a planar five-membered ring dialkyl aluminum complex containing β -H, compared with a non-planar five-membered ring dialkyl aluminum complexes (1,2, 5a-c) containing β -H. The bond length of C-H of 7 is 0.97 Å, while C-H of five-membered ring dialkyl aluminum complexes (1,2, 5a-c) is 0.99 Å.

Ethylenediamine dialkyl aluminum complexes have low thermal stability, and thermal decomposition ocurs around 150 °C,^[3a] commonly used as the precursor of chemical vapor deposition. A non-planar five-membered ring structure may lead to thermal decomposition of ethylenediamine dialkyl aluminum complexes at elevated temperatures. Compared with ethylenediamine dimethyl aluminum complex, compound 7 is a planar five-membered ring dimethyl aluminum complex with β –H. If the plane structure has better thermal stability under a similar structure, it can provide a new idea for chemical vapor deposition and atomic layer deposition precursors.

TGA evaluated compound 7 under the Ar atmosphere's thermal properties at a heating rate of 10°C/min from 30 to 800°C. As shown in Figure 2, it can be noticed that the weight loss curve is divided into two stages of weight loss curve, and the weight loss rate changes obviously near 210°C, which can be inferred to be the thermal decomposition point of the product. After taking out the thermogravimetric crucible, it is found that the bottom of the crucible has a black metallic luster, but there is no apparent reaction in hydrochloric acid,



Figure 2. Thermogravimetric analysis (TGA) and Differential Scanning Calorimeter (DSC) of Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex at atmospheric pressure and 60 mL/ min Ar purge gas at a 10 °C/min heating rate.

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and the decomposition product may be a mixture of carbon, nitrogen, and aluminum. The structure's thermal decomposition temperature is about 210 °C, higher than that of ethylenediamine methyl aluminum.^[3a]

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The TG curve's inflection point appears at about 210 °C, and similar to the DSC curve, there is also an upward trend of the DSC curve at this position, corresponding to the exothermic process of thermal decomposition. It shows that compound 7 presents evaporation before 210 °C and endothermic decomposition after this 210 °C.

Vapor pressure-temperature plot was obtained to understand better TGA analysis's thermal properties, which is according to the Langmuir and Antoine equation's theoretical basis, choosing benzoic acid as a standard.^[22] As shown in Figure 3, compound 7 can provide sufficient vapor pressure under below 200 °C. From the above thermal studies, it is clear that compound 7 was appropriate for CVD precursors. Combined with the thermogravimetric curve and saturated vapor pressure curve, compound 7 can produce enough vapor pressure in the range of 100–200 °C, and the thermal decomposition temperature is above 210 °C. The volatilization process and thermal decomposition process are carried out separately, so compound 7 has a potential application prospect in chemical vapor deposition and atomic layer deposition.

As shown in Figure 4, the maximum absorption wavelength of compound 7 is 380 nm, and the emission wavelength is 478 nm (Under the emission wavelength of 480 nm, the maximum excitation wavelength is 374 nm). The ligand has only one pyridine ring, the ligand does not have fluorescence properties, and the rigid plane structure formed by coordination with alkyl aluminum has fluorescence properties. The complexes' fluorescence properties also show that the N–C–C–N–Al five-membered rings of alkyl aluminum complexes are in the same plane, consistent with the crystal data.



Figure 3. Vapor pressure-temperature curves for Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex.



Figure 4. UV-Vis spectra and Fluorescence spectra of Pyridin-2ylmethyl-tert-butylamine dimethyl aluminum complex dissolved in hexane.

Conclusions

Compared with 11 five-membered ring dimethyl aluminum complexes with different configurations, the ligands forming planar five-membered rings contain at least one unequivalent sp² hybrid nitrogen (imine, pyridine). Compared with ethylenediamine dimethyl aluminum, the thermal decomposition temperature of the planar methyl aluminum complex formed by the introduction of pyridine is increased to 210 °C. Pyridin-2ylmethyl-tert-butylamine dimethyl aluminum complex can be used as both atomic layer deposition precursors and chemical vapor deposition precursors due to the increase of decomposition temperature. Pyridin-2-ylmethyl-tert-butylamine dimethyl aluminum complex has fluorescence properties (excitation wavelength 380 nm, emission wavelength 478 nm, cyan light), consistent with the single crystal's rigid plane results.

Experimental Section

General Considerations: All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Hexane dried over Na/benzophenone ketyl and distilled before use. Complexes L1 were synthesized according to the previous literature. ¹H and ¹³C NMR spectra were recorded on Bruker AVANCE III HD 400 MHz spectrometer, and the chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. All NMR spectra have been determined at 25 °C. X-ray data were collected with Bruker D8 Venture. The TG curve was obtained with an STA 449 F3 analyzer at atmospheric pressure and 60 mL/min Ar purge gas at a 10 °C/min heating rate. From 30 to 800 °C. Photoluminescence spectra were recorded on CARY Eclipse.

Experimental Details

 $tBuHNCH_2$ (o-C₆H₅N) (L): tBuHNCH2 (o-C₆H₅N) A 30 mL solution of ethanol that contained 2-pyridine carboxaldehyde (2.40 mL, 25 mmol) and *t*-butylamine (2.65 mL, 25 mmol) was stirred with the presence of 4 Å activated molecular sieves at 20 °C for 24 h. Added

excess NaBH₄ (1.00 g, 26 mmol) to the reaction solution. The reaction was stirred overnight at 25 °C, then quenched by water and extracted into dichloromethane. After the solvent was removed under reduced pressure, the residue was distilled to give a yellow liquid product in 60 %. ¹H NMR (400 MHz, CDCl₃): 8.51 (d, 1H, Py *H*), 7.61 (m, 1H, Py *H*), 7.30 (d, 1H, Py-*H*), 7.11 (m, 1H, Py *H*), 3.86 (s, 2H, Py-CH₂N), 1.69 (s, 1H, NHC (CH₃)₃). 1.17 (s, 9H, NC (*CH*₃)₃).

tBuNCH₂ (*o*-C₆H₅N)AlMe₂ (7): A solution of AlMe₃ in 2.27 mL hexane (3.88 mmol) was added to tBuHNCH2 (*o*-C₆H₅N) (0.63 g, 3.88 mmol) in hexane (30 mL) at -30 °C. The solution was warmed to room temperature to give a green solution and stirred for 12 h. After removal of all volatiles under vacuum, the product was obtained as a yellow crystal. M.P.: 28.8–34.5 °C, Anal. (calcd, %): C 63.4 (63.2), H 10.2 (10.2). N 13.5 (13.5); ¹H NMR (400 MHz, C₆D₆) δ 7.38 (m, 1H, Py H), 6.72 (m, 1H, Py H), 6.44 (m, 1H, Py H), 6.27 (m, 1H, Py H), 4.08 (br, 2H, Py-CH₂N), 1.39 (s, 9H, NC (*CH₃*)₃), -0.53 (s, 6H, AlMe₂); ¹³C NMR (101 MHz, C₆D₆) δ 165.3 (s, Py), 143.9 (s, Py), 138. 7 (s, Py), 123.1 (s, Py), 122.6 (s, Py), 52.0 (s,Py-CH₂N), 51.3 (s, C (CH₃)₃), 31.3 (s, C (*CH₃*)₃), -5.8 (s, AlMe₂).

Supporting Information:

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CCDC 1538588 contains the supplementary crystallographic data for 7. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk. The ¹H NMR, ¹³C NMR spectra of compound 7, and crystallographic data are available from the supporting information.

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Keywords: Bidentate nitrogen ligand · methyl aluminum complex · structure · thermodynamic properties · planar five-membered ring

- a) Z. Chen, M. Brookhart, Acc. Chem. Res. 2018, 51, 1831–1839;
 b) W. Chen, H. Song, J. Li, Angew. Chem. Int. Ed. 2020, 59, 2365–2369;
 c) Z. Feng, Z. Huang, S. Wang, Dalton Trans. 2019, 48, 11094–11102;
 d) Y. Zhao, Y. Liu, B. Wu, Dalton Trans. 2015, 44, 13671–13680.
- [2] a) X. Lou, H. Zhou, S. B. Kim, *Nano Lett.* 2016, *16*, 7650–7654;
 b) S. Seppälä, J. Niinistö, T. Blanquar, *Chem. Mater.* 2016, *28*, 5440–5449; c) S. B. Kim, C. Yang, T. Powers, *Angew. Chem. Int. Ed.* 2016, *55*,10228–10233; *Angew. Chem.* 2016, *128*, 10384–10389; d) P. Dröse, S. Blaurock, C. G. Hrib, *Z. Anorg. Allg. Chem.* 2011, *637*, 186–189; e) P. Tutacz, N. Harmgarth, F. Zörner, *Z. Anorg. Allg. Chem.* 2018, *644*, 1653–1659.

- [3] a) J. Khanderi, D. Rische, H. W. Becker, J. Mater. Chem. 2004, 14, 3210–3214; b) E. S. Beh, L. Tong, R. G. Gordon, Organometallics 2017, 36, 1453–1456.
- [4] a) B. E. Cole, J. P. Wolbach, W. G. Dougherty Jr, *Inorg. Chem.* 2014, *53*, 3899–3906; b) F. Z. Yang, Y. H. Wang, M. C. Chang, *Inorg. Chem.* 2009, *48*, 7639–7644.
- [5] M. Asay, C. Jones, M. Driess, Chem. Rev. 2011, 111, 354–396.
- [6] a) Z. Feng, Z. Huang, S. Wang, *Dalton Trans.* 2019, 48, 11094–11102; b) Z. Feng, X. Zhu, S. Wang, *Inorg. Chem.* 2013, 52, 9549–9556.
- [7] Y. Bai, W. Chen, J. Li, Coordin. Chem. Rev. 2019, 383, 132–154.
- [8] P. P. Power, Nature 2010, 463, 171-7.
- [9] T. W. Myers, N. Kazem, S. Stoll, J. Am. Chem. Soc. 2011, 133, 8662–8672.
- [10] a) C. C. Lu, D. B. George, T. Weyhermüller, Angew. Chem. Int. Ed. 2008, 47, 6384–6387; Angew. Chem. 2008, 120, 6484–6487; b) A. A. Trifonov, E. A. Fedorova, I. A. Borovkov, Organometallics 2007, 26, 2488–2491; c) C. C. Lu, E. Bill, T. Weyhermüller, J. Am. Chem. Soc. 2008, 130, 3181–3197; d) A. A. Trifonov, I. D. Gudilenkov, J. Larionova, Organometallics 2009, 28, 6707–6713; e) P. J. Chirik, Inorg. Chem. 2011, 50, 9737–9740; f) S. Dai, C. Chen, Angew. Chem. 2016, 128, 13475–13479; Angew. Chem. Int. Ed. 2016, 55, 13281–13285.
- [11] a) C. Zuccaccia, V. Busico, R. Cipullo, Organometallics 2009, 28, 5445–5458; b) F. Z. Yang, Y. C. Chen, Y. F. Lin, Dalton Trans. 2009, 7, 1243–1250; c) X. Zhang, S. Zhou, X. Fang, Inorg. Chem. 2020, 59, 9683–9692; d) Y. C. Lin, K. H. Yu, Y. F. Lin, Dalton Trans. 2012, 41, 6661–6670; e) H. Golchoubian, M. Tarahomi, E. Rezaee, Polyhedron 2015, 85, 635–642.
- [12] a) M. Shen, W. Zhang, K. Nomura, *Dalton Trans.* 2009, 41, 9000–9009; b) S. Liu, J. Zhang, W. Zuo, *Polymer* 2017, 9, 83.
- [13] M. L. Hlavinka, J. R. Hagadorn, Chem. Commun. 2003, 21, 2686–2687.
- [14] R. Kretschmer, M. Dehmel, M. Bodensteiner, Eur. J. Inorg. Chem. 2017, 5, 965–970.
- [15] J. P. Bezombes, B. Gehrhus, P. B. Hitchcock, Dalton Trans. 2003, 9, 1821–1829.
- [16] D. Pappalardo, C. Tedesco, C. Pellecchia, Eur. J. Inorg. Chem. 2002, 3, 621–628.
- [17] a) W. Y. Huang, S. J. Chuang, N. T. Chunag, *Dalton Trans.* 2011, 40, 7423–7433; b) C. C. Zhou, C. H. Hung, J. H. Huang, J. Chin. Chem. Soc. 2006, 53, 1297–1302; c) C. F. Tsai, H. J. Chen, J. C. Chang, *Inorg. Chem.* 2004, 43, 2183–2188.
- [18] H. V. R. Dias, W. Jin, R. E. Ratcliff, *Inorg. Chem.* **1995**, *34*, 6100–6105.
- [19] L. Xiao, Y. Zhao, S. Qiao, Dalton Trans. 2020, 49, 1456–1472.
- [20] J. Li, K. Zhang, H. Huang, Organometallics 2013, 32, 1630–1635.
- [21] T. W. Myers, L. A. Berben, Inorg. Chem. 2012, 51, 1480–1488.
- [22] a) G. V. Kunte, S. A. Shivashankar, A. M. Umarji, *Meas. Sci. Technol.* 2008, *19 (2)*, 025704; b) S. F. Wright, D. Dollimore, J. G. Dunn, K. Alexander, *Thermochim. Acta* 2004, *421*, 25–30; c) J. Selvakumar, V. S. Raghunathan, K. S. Nagaraja, *J. Phys. Chem. C* 2009, *113*, 19011–19020.

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