Inorganic Chemistry

Lithium Aluminate Complexes and Alumoles from 1,4-Dilithio-1,3-Butadienes and AlEt₂Cl

Yongliang Zhang,[†] Junnian Wei,[†] Wen-Xiong Zhang,[†] and Zhenfeng $Xi^{*,\dagger,\ddagger}$

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, Shanghai 200032, China

S Supporting Information

ABSTRACT: A series of lithium aluminate complexes and alumoles were synthesized from 1,4-dilithio-1,3-butadienes 1 and AlEt₂Cl. Their structures were characterized using single-crystal X-ray structural analysis and NMR spectroscopy. The structure of the lithium aluminate complex 2-TMEDA showed that the Al atom adopted a tetracoordinated mode bonded with two butadienyl C_{sp2} atoms and two ethyl C_{sp3} atoms. The lithium cation was located above the alumole ring. The structure of **3a** revealed a dimeric 1-ethylalumole in the solid state. Diffusion ordered spectroscopy NMR spectra showed that **3a** was also a dimer in C_6D_6 solvent. However, in tetrahydrofuran (THF) solution, the dimeric **3a** dissociated into the 1-ethylalumole–THF adduct. The lithium aluminate complex **2** transformed into **3a**-THF when treated with 1.0 equiv of AlEt₂Cl. Preliminary reaction chemistry and synthetic applications of the lithium aluminate complex were also investigated.



■ INTRODUCTION

Organoaluminum chemistry is an important research field in organometallic chemistry.¹ Organoaluminum reagents are widely used as homogeneous polymerization catalysis,² Lewis acid reagents,³ and organic synthons.⁴ Among all these compounds, aluminum ate complexes, especially the alkali metal aluminum ate complexes, have been widely used as metalation reagents. Because of their mixed-metal synergistic effect, these aluminum ate complexes can display special regioselectivity and excellent functional group tolerance.^{5,6}

Aluminacyclopentadienes (alumole) are also useful organometallic compounds.⁷ They are proposed as intermediates in organoaluminum-mediated reactions.⁸ Recently, Tokitoh and co-workers reported the formation and crystal structure of the Lewis-base free alumole⁹ and its analogues such as 1bromoalumole¹⁰ and 1-aminoalumole.¹¹ However, due to the limitation of synthetic methods, the synthesis of alumoles is still challenging.

We have been interested in the synthetic applications of multiply substituted 1,4-dilithio-1,3-butadienes 1 (dilithio reagents for short).¹² By transmetalation of dilithio reagents, various novel organometallic compounds could be obtained and characterized, such as organocopper(I) aggregates,¹³ heavy alkaline earth complexes,¹⁴ dimagnesiabutadiene compounds,¹⁵ and lutetacyclopentadienes.¹⁶

Herein, we report the synthesis and crystal structures of the lithium aluminate complex 2 and 1-ethylalumoles 3 through the reaction of dilithio reagents 1 with $AlEt_2Cl$. Structural transformations between the compounds 1a, 2, and 3a-THF (THF = tetrahydrofuran) were observed by *in situ* NMR.

Preliminary reaction chemistry and synthetic applications of the lithium aluminate complex 2 and 1-ethylalumole 3a were also investigated.

RESULTS AND DISCUSSION

Synthesis and Structures of Lithium Aluminate Complexes. Treatment of dilithio reagent 1a with 1.0 equiv of AlEt₂Cl in benzene at room temperature for 3 h afforded the lithium aluminate complex 2 as white solids in 90% isolated yield (Scheme 1). The compound 2, soluble in benzene, toluene, and many polar solvents, was characterized by NMR spectroscopy in THF- d_8 (see Supporting Information for details). Its ¹³C NMR spectrum showed that the chemical shift of the sp² carbons in alumole ring were 129.1 ppm (C1, C4) and 160.4 ppm (C2, C3), respectively. When 1.0 equiv of tetramethylethylenediamine (TMEDA) was added into the

Scheme 1. Synthesis of Lithium Aluminate Complex 2 and Its TMEDA-Coordinated Complex 2-TMEDA



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benzene solution of 2, the corresponding TMEDA-coordinated complex 2-TMEDA was quantitatively obtained (detected by *in situ* NMR, see Supporting Information for details), which was stable under inert atmosphere.

Single crystals of the complex 2-TMEDA suitable for X-ray diffraction was obtained via recrystallization from hexane at room temperature. The structure of the complex 2-TMEDA demonstrated that the Al atom adopted a tetracoordinated mode bonded with two C_{sp2} atoms and two ethyl C_{sp3} atoms (Figure 1). The TMEDA-coordinated lithium cation was



Figure 1. Diamond drawing of 2-TMEDA with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1-C2 1.358(4), C2-C3 1.529(4), C3-C4 1.355(4), Al1-C1 2.029(3), Al1-C4 2.034(3), C1-Li1 2.343(6), C2-Li1 2.354(6), C3-Li1 2.372(6), C4-Li1 2.375(6); C1-Al1-C4 87.23(13), C2-C1-Al1 104.7(2), C1-C2-C3 118.1(3), C4-C3-C2 118.0(3), C3-C4-Al1 104.8(2).

located above the alumole ring. The dihedral angle (25.086°) between the plane formed by C1, C2, C3, and C4 and that formed by C1, C4, and Al1 in 2-TMEDA indicated that the alumole ring was not coplanar. The dihedral angle was much larger than that in lithium 1,1-diaminoalumoluide (1.642°) reported by Tokitoh and co-workers,¹¹ probably because of the steric effect of the TMEDA-coordinated lithium cation. The butadiene moiety of the alumole ring exhibited clear bond alternation, which was similar to the structure of the lithium 1,1-diaminoalumoluide.¹¹ The angle of C1–Al–C4 is 87.23(13), which is smaller than the classic C–Al–C angles in usual tetracoordinated aluminum compounds [e.g., Al₂Me₆: C–Al–C, 104.3(1)–123.2(1) Å¹⁷].

Synthesis and Structures of 1-Ethylalumoles. We recently reported the synthesis of 1,4-dimagnesia-1,3-butadienes.¹⁵ These dimagnesia compounds were afforded by the reaction of dilithio reagents with 2.0 equiv of isopropylmagnesium chloride. With the aim of forming 1,4-dialumina-1,3butadienes, we treated dilithio reagent 1a with 2.0 equiv of $AlEt_2Cl$ in hexane/ Et_2O (3/1) at room temperature for 3 h. However, instead of the target compounds, 1-ethylalumole 3a was afforded in 70% isolated yield (Scheme 2). In a similar procedure, compounds 3b and 3c could be prepared.

Scheme 2. Synthesis of 1-Ethylalumoles



Single crystals of compound **3a** suitable for X-ray diffraction were obtained via recrystallization from hexane at room temperature as colorless crystals. Single-crystal X-ray structural analysis revealed that **3a** exists as a dimeric structure (Figure 2). The dimeric form was similar to that of the 1-bromoalumole reported by Tokitoh and co-workers.^{10a} The whole molecule of **3a** was disordered (see Supporting Information for details).



Figure 2. Diamond drawing of **3a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. The whole molecule of **3a** was disordered. The major part was shown above. Selected bond lengths (Å) and angles (deg): Al1–C1 1.975(3), Al1–C4 2.082(6), C1–C2 1.345(5), C2–C3 1.500(5), C3–C4 1.401(7), Al1–C9 2.264, Al2–Al1 2.5603(12), Al2–C4 2.124(3), Al2–C9 2.033(2), C9–C10 1.356(3), C10–C10' 1.503(4). C1–Al1–C4 91.3(2), C2–C1–Al1 106.4(2), C1–C2–C3 118.5(3), C4–C3–C2 122.1(3), C3–C4–Al1 98.7(2), C1–Al1–Al2 102.24(11), C4–Al1–Al2 53.26(10), C9–Al2–C91 90.26(12), C10–C9–Al2 103.27(14), C9–C10–C10' 120.56(12).

The NMR spectra of 1-ethylalumole 3a were analyzed (Figure 3, see Supporting Information for details). The ¹H



Figure 3. ¹H NMR Spectra of 1-ethyloalumole 3a in C_6D_6 and THF- d_8 .

NMR spectra of **3a** could be considered as similar to that of the 1-bromoalumole at -60 °C reported by Tokitoh and coworkers,⁹ indicating that the dimeric form of **3a** was retained in C₆D₆. However, in THF, dissociation of the dimer afforded a different ¹H NMR spectra. Variable temperature NMR spectra of **3a** have been conducted (see Supporting Information for details). The ¹H NMR spectra showed hardly no difference at -50, 30, and 90 °C, indicating that the dimeric form could be kept in a wide range of temperatures. The effect of ethyl group (our case) and Br atom (Tokitoh's case) toward the stability was different. Besides, the TMS groups may also enhance the stability of **3a**. To further confirm this dimeric form, diffusion ordered spectroscopy (DOSY) NMR experiments were carried

out. DOSY has been used as an efficient method to estimate the degree of aggregation and molecular weight of compounds by measuring the diffusion coefficient, D.¹⁸ A DOSY NMR spectrum (see Supporting Information for details) confirmed that **3a** existed in C₆D₆ as a dimer, giving a calculated estimated molecular weight of 578, which is about 3% error from the theoretical value [M_w of alumole dimer = 561].

Addition of excess amount of THF to the C_6D_6 solution of 3 at room temperature quantitatively afforded 1-ethylalumole-THF adduct 3-THF (Scheme 3). The corresponding NMR spectra proved these results.





^{*a*}Yields were Determined by ¹H NMR Spectroscopy.

Single crystals of compound 3c-THF suitable for X-ray diffraction were obtained via recrystallization from hexane/ THF (10/1) at room temperature as colorless crystals. The single-crystal X-ray structure analysis revealed a coplanar AlC4 ring skeleton by the sum of the internal bond angles of 540° and the dihedral angle of 0.387° between the plane formed by C1, C2, C3, and C4 and that formed by C1, C4, and Al1 (Figure 4). The lengths of the two Al–C bonds are 1.985(2) Å



Figure 4. Diamond drawing of **3c**-THF with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1–C1 1.985(2), Al1–C4 1.986(2), C1–C2 1.347(3), C2–C3 1.523(3), C3–C4 1.359(3); C1–Al1–C4 91.91(10), C2–C1–Al1 104.74(17), C1–C2–C3 119.6(2), C4–C3–C2 119.3(2), C3–C4–Al1 104.40(16).

and 1.986(2) Å, respectively, which were comparable with the classic Al–C bonds [e.g., Al₂Me₆: Al–C, 1.949(2)–2.606(2) Å¹⁷]. The Lewis-base free alumole reported by Tokitoh and co-workers was stable because of the protection of the bulky Mes* group.⁹ In the structure of **3c**-THF, the TMS group may enhance the stability of **3c**-THF due to the α -anion-stabilizing effect of silicon.¹⁹

Structural Transformations. Transformation between compounds **1a**, **2**, and **3a** were investigated by *in situ* NMR (Scheme 4). When 1.0 equiv of $AlEt_2Cl$ was reacted with **1a** in C_6D_6 , the reaction afforded **2** as the sole product. When 2.0 equiv of $AlEt_2Cl$ was used, **3a** could be observed as the major product in THF- d_8 . According to the literature reports,²⁰ alkali metal tetraorgano aluminates could be converted into trialkylaluminum compounds when treated with 1.0 equiv of

Scheme 4. Structural Transformations Between 1a, 2, and 3a as Detected by NMR Spectroscopy



dialkylaluminum chloride. Thus, we treated 2 with 1.0 equiv of AlEt₂Cl in THF- d_8 . Results showed that 2 transformed into 3a completely with the concomitant loss of AlEt₃. Dialumina compound 4 was assumed to be the intermediate in this progress. When reacted with excess EtLi in THF- d_8 , 3a transformed into 2.

Preliminary reactivity of lithium aluminate complex 2 and 1ethylalumole 3 were also investigated (Scheme 5). Lithium

Scheme 5. Reaction Chemistry of 2 and 3a



aluminate complex 2 reacted with dimethyl acetylenedicarboxylate (DMAD) to give the hexa-substituted benzene 5 in 54% isolated yield. Treatment of 2 with excess sulfur afforded the corresponding thiophene compound 6 in 85% isolated yield. However, the corresponding reactions of 1-ethylalumole 3a either afforded a much lower yield of products or no products at all under the same condition. 3a could not react with S₈ in THF. The reaction of 3a and 1.2 equiv of DMAD in THF afforded the corresponding hexa-substituted benzene 5 in 44% yield.

According to the work of Tokitoh and co-workers,^{10b} we proposed the following reaction mechanism (Scheme 6). In this reaction, DMAD would insert into an Al–C bond of **2** to afford the alumacycloheptatriene 7, which would then undergo reductive elimination to generate the final product **5**. A similar reaction mechanism would be considered for the reaction between **2** and S_8 .

Scheme 6. Proposed Reaction Mechanism from 2 to 5



In summary, we have synthesized and structurally characterized several lithium aluminate complexes and alumoles. The structures were determined by NMR spectra and single-crystal X-ray structural analysis. 1-Ethylalumoles **3** exists as a dimer in the crystalline state. DOSY NMR spectra of **3a** in C_6D_6 confirmed this dimeric structure. Addition of an excess amount of THF to the solution of **3** afforded 1-ethylalumole-THF adduct **3**-THF. Structural transformations between compounds **1a**, **2**, and **3a** were investigated by *in situ* NMR. Preliminary reaction chemistry and synthetic applications of **2** and **3a** were investigated.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under a slightly positive pressure of dry and oxygen-free argon by using standard Schlenk line techniques or under an argon atmosphere in a Mikrouna Super (1220/750) Glovebox. The argon in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. ¹H and ¹³C NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) or Bruker-500 spectrometer (FT, 500 MHz for ¹H; 126 MHz for ¹³C) at 30 °C.

Synthesis of Lithium Aluminate Complex 2 and 2-TMEDA. To a benzene solution (5 mL) of 1,4-dilithio-1,3-butadiene (119 mg, 0.5 mmol), 1.0 equiv of $AlEt_2Cl$ (60 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was dissolved in benzene and filtered. The filtrate was reduced under a vacuum, affording the lithium aluminate complex 2 as white solid. Then 1.0 equiv of TMEDA (12 mg, 0.1 mmol) was added to the benzene solution of 2 (32 mg, 0.1 mmol) and stirred for another 1 h at room temperature. The solution was concentrated and stored at room temperature to afford 2-TMEDA as a colorless solid.

2, white solid, isolated yield 90% (84 mg). ¹H NMR (500 MHz, THF- d_8) δ : -0.39 (q, J = 8.0 Hz, 4H, CH₂), 0.00 (s, 18H, CH₃), 0.89 (t, J = 8.0 Hz, 6H, CH₃), 2.02 (s, 6H, CH₃). ¹³C NMR (126 MHz, THF- d_8) δ : 2.8 (6 CH₃), 12.7 (2 CH₃), 24.7(2 CH₃), 129.1 (2 quat. C), 160.4 (2 quat. C). Anal. Calcd (%) for **2**: C, 60.71; H, 10.83. Found: C, 60.25; H, 10.66.

2-TMEDA, colorless solid. ¹H NMR (400 MHz, C_6D_6) δ : 0.30 (q, J = 8.0 Hz, 4H, CH₂), 0.39 (s, 18H, CH₃), 1.41 (t, J = 8.0 Hz, 6H, CH₃), 1.47(s, 4H, CH₂), 1.75 (s, 12H, CH₃), 2.23 (s, 6H, CH₃). ¹³C NMR (100 MHz, C_6D_6) δ : 2.2 (6 CH₃), 11.5 (2 CH₃), 24.1 (2 CH₃), 45.7 (4, CH₃), 56.7 (2, CH₂), 164.0 (2 quat. C), 165.6 (2 quat. C). IR: 2950 (s), 2884 (s), 2846 (s), 2796 (m), 1521 (w), 1464 (s), 1361 (w), 1289 (w), 1242 (s), 1185 (w), 1104 (m), 1070 (w), 1020 (m), 945 (m), 838 (s), 752 (m) cm⁻¹. Anal. Calcd (%) for 2-TMEDA: C, 61.06; H, 11.65; N, 6.47. Found: C, 60.32; H, 11.40; N, 6.30.

Synthesis of Alumoles 3. To a hexane/ $Et_2O(3/1)$ solution (5 mL) of 1,4-dilithio-1,3-butadiene (0.5 mmol), 2.0 equiv of Al Et_2CI (121 mg, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced

pressure, and the residue was dissolved in hexane. The filtrate was reduced under a vacuum, and the residue was resolved with hexane and stored at room temperature to afford 3 as a colorless solid.

3a, colorless solid, isolated yield 75% (169 mg). ¹H NMR (400 MHz, C_6D_6) δ : 0.18 (s, 18H, CH₃), 0.38 (s, 18H, CH₂), 0.52 (q, *J* = 8.3 Hz, 4H, CH₂), 1.04 (t, *J* = 8.2 Hz, 6H, CH₃), 1.98 (s, 6H, CH₃), 2.19 (s, 6H, CH₃). ¹³C NMR (100 MHz, C_6D_6) δ : 0.9 (6 CH₃), 3.2 (2 CH₂), 3.6 (6 CH₃), 10.9 (2 CH₃), 23.6 (2 CH₃), 29.3 (2 CH₃), 126.9 (2 quat. C), 164.3 (2 quat. C), 174.1 (2 quat. C), 205.2 (2 quat. C). IR: 3026 (w), 2993 (m), 2949 (m), 2898 (w), 2863 (w), 2799 (w), 1526 (w), 1543 (m), 1432 (m), 1246 (s), 1216 (w), 1104 (m), 1012 (m), 976 (w), 895 (m), 836 (s), 787 (m), 752 (m) cm⁻¹.

3b, colorless solid, isolated yield 80% (196 mg). ¹H NMR (400 MHz, C_6D_6) δ : 0.22 (s, 18H, CH₃), 0.40 (s, 18H, CH₂), 0.53 (q, J = 8.2 Hz, 4H, CH₂), 1.05 (t, J = 8.2 Hz, 6H, CH₃), 1.38–1.45 (m, 4H, CH₂), 1.56–1.68 (m, 4H, CH₂), 2.39–2.47 (m, 2H, CH₂), 2.58–2.69 (m, 4H, CH₂), 2.77–2.84 (m, 4H, CH₂). ¹³C NMR (100 MHz, C_6D_6) δ : 1.5 (6 CH₃), 3.3 (2 CH₂), 3.7 (6 CH₃), 11.0 (2 CH₃), 22.3 (2 CH₂), 34.2 (2 CH₂), 39.8 (2 CH₂), 124.9 (2 quat. C), 167.0 (2 quat. C), 172.4 (2 quat. C), 206.8 (2 quat. C). IR: 2941 (s), 2895 (m), 2864 (m), 1527 (w), 1456 (m), 1246 (s), 1100 (m), 953 (s), 838 (s), 771 (m) cm⁻¹. Anal. Calcd (%) for **3b**: C, 62.68; H, 10.19. Found: C, 61.76; H, 9.92.

3a-THF. ¹H NMR (400 MHz, THF- d_8) δ : 0.00 (q, J = 8.1 Hz, 2H, CH₂), 0.05 (s, 18H, CH₃), 0.98 (t, J = 8.0 Hz, 3H, CH₃), 2.10 (s, 6H, CH₃). ¹³C NMR (100 MHz, THF- d_8) δ : 0.9 (1 CH₂), 1.9 (6 CH₃), 9.4 (1 CH₃), 24.2 (2 CH₃), 146.5 (2 quat. C), 168.0 (2 quat. C).

3b-THF. ¹H NMR (400 MHz, THF- d_8) δ : 0.01 (q, \overline{J} = 8.2 Hz, 2H, CH₂), 0.05 (s, 18H, CH₃), 1.00 (t, J = 8.2 Hz, 3H, CH₃), 1.61 (m, 4H, CH₂), 2.58 (m, 4H, CH₂). ¹³C NMR (100 MHz, THF- d_8) δ : 1.0 (1 CH₂), 2.0 (6 CH₃), 9.5 (1 CH₃), 24.9 (2 CH₂), 35.9 (2 CH₂), 144.4 (2 quat. C), 170.1 (2 quat. C).

3c-THF, colorless solid, isolated yield 36% (679 mg). ¹H NMR (400 MHz, C_6D_6) δ : 0.06 (s, 18H, CH₃), 0.40 (q, J = 8.0 Hz, 2H, CH₂), 1.12–1.18 (m, 4H, CH₂), 1.50 (t, J = 8.0 Hz, 3H, CH₃), 3.60–3.66 (m, 4H, CH₂), 6.84–6.90 (m, 2H, CH), 6.94–7.04 (m, 8H, CH). ¹³C NMR (100 MHz, C_6D_6) δ : 1.0 (1 CH₂), 1.8 (6 CH₃), 9.6 (1 CH₃), 25.2 (2 CH₂), 70.9 (2 CH₂), 125.4 (2 quat. C), 127.2 (4 CH), 129.1 (4 CH), 147.8 (2 quat. C), 150.6 (2 quat. C), 172.1 (2 quat. C). IR: 3058 (w), 3014 (w), 2947 (m), 2891 (m), 1594 (w), 1528 (m), 1462 (w), 1237 (m), 1068 (m), 993 (w), 917 (m), 838 (s), 767 (m) cm⁻¹. Anal. Calcd (%) for 3c-THF: C, 70.54; H, 8.67. Found: C, 69.64; H, 8.64.

A Typical Procedure for the Reaction of 2. Under an atmosphere of nitrogen, compound 2 (95 mg, 0.3 mmol) and Et₂O (5 mL) was added into 25 mL Schlenk tube. Then 1.2 equiv of DMAD (51 mg, 0.36 mmol) or 0.5 equiv of S_8 (38 mg, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and workup; the residue was purified by column chromatography to give products 5 and 6. Compounds S^{21} and 6^{22} are known compounds, whose NMR spectra are consistent with literature reports.

X-ray Crystallographic Studies. Single crystals of 2-TMEDA and 3a suitable for X-ray analysis were grown in hexane at room temperature for about 2 days. Single crystals of 3c-THF suitable for Xray analysis were grown in hexane/THF (10/1) at room temperature for about 2 days. Data collections for 2-TMEDA, 3a, and 3c-THF were performed at 180 K on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structure of 2-TMEDA, 3a, and 3c-THF were solved with the Olex2 solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using least squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1400964 (2-TMEDA), CCDC-1400965 (3a), CCDC-1400966 (3c-THF). These data can be obtained free of charge from the Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01551.

DOSY NMR spectrum of 3a in C_6D_6 , NMR data, further experimental details and spectra for all new compounds (PDF)

Crystallographic data for 2-TMEDA, 3a and 3c-THF (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: zfxi@pku.edu.cn.

Notes

The authors declare no competing financial interest.

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