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Study of small oligomers based on Ru₂(DMBA)₄ and meta-phenylene diethynylene

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1. Introduction

Preparation of metal- σ -alkynyl compounds has been an active area of research since the 1950s [1,2]. Extensive efforts in the recent years revealed many intriguing and useful attributes of metalalkynyl species, which include interesting electronic structures and novel topologies [3], their applications as nonlinear optical materials [4-6], OLED and photovoltaic materials [7-9], and active species for molecular electronics [10-13]. The possibility of forming $[M-C=C-Y-C=C-]_n$ type oligomers/polymers was recognized from the beginning of metal-alkynyl chemistry [1,14], where M is one of either coinage metals or platinum group metals and Y is an aromatic group. During the ensuing decades, the Osaka group led by Hagihara and Takahashi reported many Pd/Pt based polymers based on the original $[M-C=C-Y-C=C-]_n$ motif [14], while the Cambridge group led by Lewis produced similar polymers based on mono-nuclear Pt and Ru species [15,16]. More recently, Wong and coworkers have developed many Pt-based metal-alkynyl polymers with an emphasis on optoelectronic applications [17–21]. Though

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ABSTRACT

The reactions between Ru_2 (DMBA)₄(NO₃)₂ (DMBA = *N*,*N*'-dimethylbenzamidinate) and *meta*-phenylene diethynylenes bearing 5-ester substituents (-CO₂ⁱPr, L1; -CO₂Bn, L2) in the presence of Et₂NH afforded a series of oligomeric compounds with meta-phenylene diethynylene bridge, namely L-[Ru₂ (DMBA)₄L]_m with *m* as integers. With L1, the compounds with m = 1-3 (**1a**, **2a** and **3a**) were separated and fully characterized. With L2, only the compound with m = 1 (1b) was successfully isolated. In addition to routine spectroscopic characterizations, the structures of both compounds 1b and 2a were determined using single crystal X-ray diffraction. For the series of 1a, 2a and 3a, both the voltammetric and absorption spectroscopic characteristics bear close resemblance to those of simple Ru₂ (DMBA)₄(C₂R)₂ compounds, indicating the absence of significant inter-unit electronic couplings in the oligomers.

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much of the aforementioned successes on metal- σ -alkynyls are based on 4d and 5d metals, chemistry of σ -alkynyls based on 3d metal complexes of polyaza-macrocycles has received considerable interest [22-27]. Besides σ -alkynyl species, another interesting avenue of metal-alkynyl chemistry is the formation of the Pauson-Khand type adducts (η^2 -C=C) between oligoynes and mono-/oligometallic species [28-32].

A major focus area of our laboratory is the diruthenium alkynyl chemistry, where the charge mobility along the Ru_2 - σ -alkynyl backbone has been demonstrated in both bulk solution [33–38] and nano-scale devices [39–43]. It is worth noting that the development of diruthenium and triruthenium alkynyl chemistry has also benefited from key contributions from the laboratories of Cotton [44], Bear and Kadish [45-47], Lehn [48] and Peng [49]. Among several families of diruthenium alkynyl compounds developed in our laboratory, those based on the DMBA (DMBA is *N*,*N*'-dimethylbenzamidinate) supporting ligand are unique in the formation of Ru2-alkynyl bond under weak base conditions (Scheme 1) [36,50-52]. In addition to affording symmetric bisalkynyl species under mild conditions such as ambient atmosphere and room temperature, the weak base protocol enables the one-pot synthesis of novel unsymmetric bisalkynyl species exhibiting voltammetric characteristic consistent with a molecular diode [53]. In

2

ARTICLE IN PRESS

J.-W. Ying et al. / Journal of Organometallic Chemistry xxx (2017) 1-6

$$Ru_2(DMBA)_4(NO_3)_2 + 2 HC_2R \xrightarrow{R_3N} Ru_2(DMBA)_4(C_2R)_2$$

Scheme 1. Ru₂-alkylnylation under Weak Base Conditions.

the aforementioned studies, ligation of mono-ethynes was the focus. We became intrigued by the *meta*-phenylene diethynylene type ligands, based on which hexagon and helical supramolecules were realized in the laboratories of Moore and others [54–56]. Reported herein are the reactions between Ru₂ (DMBA)₄(NO₃)₂ and *meta*-phenylene diethynylene ligands under aerobic weak base conditions, and the identification of resultant oligomers.

2. Results and discussion

2.1. Syntheses

Syntheses of *meta*-arylene diethynylene ligands were based on the Sonogashira type cross coupling reactions as outlined in Scheme 2 [57,58], and the experimental details are provided in the supplementary content. Trimethylsilyl (TMS) was retained as the protecting group of terminal ethyne owing to its chemical stability over the free ethyne. In order to optimize the solubility of the resultant L-[Ru₂ (DMBA)₄-L]_m type compounds, two side chains, isopropyl (ⁱPr) and benzyl (Bn), on the aromatic ring of the organic spacer were introduced through esterification, as shown in Scheme 2. Typical desilylation of L1TMS₂ and L2 TMS₂ using K₂CO₃ in MeOH would lead to transesterification of the ester group [59]. Hence, the desilylation of L1TMS₂ and L2 TMS₂ was achieved in excellent yield with TBAF (containing 5% of water) in THF.

While the preparation of the symmetric Ru_2 (DMBA)₄(C₂R)₂ type compounds using LiC_2R was successful and expedient [50], the presence of an ester group in both L1 and L2 prevents the use of lithiation method. Hence, the weak base assisted reaction is the ideal alternative for the Ru₂ (DMBA)₄ compounds based on L1 and L2, as shown in Scheme 3. Generally, the reactions between Ru₂ $(DMBA)_4(NO_3)_2$ and excess L1/L2 in the presence of diethylamine (Et₂NH) afforded a mixture of Ln-[Ru₂ (DMBA)₄-Ln]_m as monitored by TLC. Typically, overnight reaction gave the Ru₂ based monomer (m = 1) as the major product when three equiv of Ln was used. Reducing the equivalents of Ln to two, the reaction under similar conditions resulted in significant amounts of dimer, trimer and higher oligomers in addition to the monomer. These oligomers were readily identified on TLC as their R_f values decrease with the increasing degree of oligomerization. Using flash column chromatography, we were able to obtain usable quantities of compounds 1a-3a and 1b, which were characterized by ESI-MS (Figs. S2-S5), ¹H NMR and elemental analysis. All compounds in solid state are indefinitely stable under ambient conditions.

2.2. Molecular structures

Single crystals of X-ray quality were successfully grown for compounds **1b** and **2a** from THF/hexanes solution (**1b**) and THF/



Conditions: (i) Bu₄NF, THF; (ii) Ru₂(DMBA)₄(NO₃)₂, Et₂NH, THF

Scheme 3. Reaction between Ru₂-(DMDA)₄(NO₃)₂ and *m*-phenylene diethynylene.

ether solution (**2a**). The structural plots of **1b** and **2a** are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles listed in the captions. The asymmetric unit of the crystal of **1b** contains only one half of the diruthenium molecule, which is related to the other half via a crystallographic 2-fold axis passing through the midpoint of Ru1- Ru1' bond. The Ru1- Ru1' bond length in **1b** (2.4675 (7) Å) is comparable to those previously determined for the Ru₂ (DMBA)₄(C₂Ar)₂ type compounds (2.45–2.46 Å) [51–53] and consistent with the existence of a Ru-Ru single bond and a ground state configuration of $\pi^4\delta^2\pi^{*4}$. The Ru1-C1 bond is short (1.998 (6) Å), reflecting the formation of a strong σ (Ru-C) bond at the expense of σ (Ru-Ru) bond [50]. It is clear from the structural parameters that there is a significant deviation from an idealized lantern structure in the first coordination sphere of the



Fig. 1. Molecular structure of **1b**. The half of the molecule is related to the other half by a crystallographic axis passing through the Ru1-Ru1' bond. Selected bond lengths (Å) and angles (deg): Ru1-Ru1', 2.4675 (7); Ru1-C1, 1.998 (6); Ru1-N1, 2.001 (4); Ru1-N2, 2.119 (4); Ru1-N3, 1.995 (4); Ru1-N4, 2.073 (4); Ru1'-Ru1-C1, 166.0 (2).



Scheme 2. Preparation of *m*-diethylnylbenzene ligands.

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J.-W. Ying et al. / Journal of Organometallic Chemistry xxx (2017) 1–6



Fig. 2. Molecular structure of **2a**. Acetylenic carbons are labeled and shown as ellipsoids. Selected bond lengths (Å) and angles (deg): Ru1-Ru2, 2.462 (1); Ru3-Ru4, 2.456 (1); Ru1-C14, 1.958 (11); Ru2-C51, 2.019 (11); Ru3-C64, 1.963 (10); Ru4-C101, 1.953 (11); (Ru-N_{long/av}.2.005 [9], (Ru-N_{short/av}, 2.091 [9]; Ru2-Ru1-C14, 165.5 (3); Ru1-Ru2-C51, 164.6 (3); Ru4-Ru3-C64, 169.0 (3); Ru3-Ru4-C101, 167.6 (3).

Ru₂ core: the two short (Ru1-N1 and Ru1-N3) and two long (Ru1-N2 and Ru1-N4) Ru-N bonds, and the non-linear Ru1'-Ru1-C1 angle (166.0 (2)). As discussed in detail initially for the Ru₂ (DArF)₄(C_2Ar)₂ type compounds [60], the structural distortion observed herein is attributed to a second order Jahn-Teller effect.

The structure of compound 2a is shown in Fig. 2, where the main feature is the formation of the dimer of dimer through simultaneous axial ligation of L1 to two Ru₂ (DMBA)₄ units. There are many structural examples of two mononuclear units ([M]) bridged by 1,3diethynylbenzene, such as $[M] = RuCl(dppm)_2$ [61], Pt $(P^{i}Pr_{3})_{2}(C_{2}Ph)$ [62], $Cp^{*}Fe$ (dppe) [63], heterometallic Ru/Re [64], Pt (PEt₃)₂I [65] and Co(cyclam)Cl [25]. Compound **2a** is the only example of two dinuclear units linked by 1,3-diethynylbenzene to the best of our knowledge. It is worth noting that the Re₂ (DMBA)₄ type compounds are also apt in forming linear coordination polymers with either ditopic oxoanions or di-carboxylates as the linker [66,67]. Clearly, the M_2 (DMBA)₄ type compounds are excellent synthons for metallo olgomers/polymers through axial ligation. Close examination of metric parameters listed in the captions of Figs. 1 and 2 reveals a strong resemblance in the geometry of the first coordination sphere between 1b and 2a.

2.3. Electrochemistry

Rich redox activity has been the hallmark of diruthenium alkynyl compounds, and the *trans*-Ru₂ (DMBA)₄(C₂R)₂ type compounds often undergo two reversible 1e⁻ processes: an oxidation and a reduction [11]. These characteristics are retained in the compounds reported here (Table 1), and the presence of at least two 1e⁻ couples is clear in the cyclic voltammograms (CV) of compounds **1a** –**3a** shown in Fig. 3. The CV of **1a** constitutes of a reversible oxidation (**A**) and two successive quasi-reversible reductions (**B** and **C**). The $E_{1/2}(\mathbf{A})$ of **1a** is about 0.09 V more positive than that reported for Ru₂ (DMBA)₄(C₂Ph₂ (0.52 V vs. Ag/AgCl)

[52], consistent with the electron deficient nature of L1 compared to phenylacetylide. The appearance of successive reductions **B** and **C** was not observed previously for the Ru_2 (DMBA)₄(C₂Ar)₂ type compounds [52]. It is possible that one of the two L1 ligands dissociates upon the first reduction (**B**) to yield a neutral Ru_2 (DMBA)₄ (L1), and further reduction of the latter yields couple C. The CV of 2a is very similar to that of **1a**, other than slight broadening of the couple A. Clearly, the two Ru₂ (DMBA)₄ units in 2a do not interact across the µ-L1 bridge, unlike the cases of two Ru₂ units bridged by linear oligoyn-diyls [33,34,36–38]. Finally, the CV of 3a consists of two quasi-reversible couples A and B that are somewhat broader than those of 1a and 2a. Yet, there is no clear evidence for inter-unit couplings in 3a. Curiously, there is only one reduction for 3a, implying that the trimer molecule remains intact on reduction. Presently, we do not have a good rationale for the contrast in the voltammetric behavior of 3a with those of 1a and 2a. Similar electronic properties were observed for the benzyl series.

3

2.4. Electronic absorption spectra

The Vis-NIR spectra of compounds **1a**, **2a** and **3a** are shown in Fig. 4, and all three compounds display two intense absorptions at *ca*. 500 and 880 nm. The overall pattern of the Vis-NIR spectra is very similar to those of Ru_2 (DMBA)₄(C=CAr)₂ type compounds reported in literature [11], which all display two major absorptions at 500–503 nm and 874–881 nm. According to an early TD-DFT

Table 1Electrode potentials for compounds 1a, 2a and 3a.

Compd	E _{1/2} (A)/V	E _{1/2} (B)/V	E _{1/2} (C)/V
1a	0.61	-0.88	-1.01
2a	0.57	-0.89	-1.04
3a	0.62	-0.90	n/a

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J.-W. Ying et al. / Journal of Organometallic Chemistry xxx (2017) 1-6



Fig. 3. Cyclic voltammograms of compounds 1a, 2a and 3a recorded in 0.20 M (n-Bu)₄NPF₆ THF solution at a scan rate of 0.10 V/s. The concentration of compounds is such that [Ru₂] is always 1.0 mM.



Fig. 4. Visible-NIR absorption spectra of compounds 1a, 2a and 3a recorded in THF solution.

study of the Ru₂ (DMBA)₄(C_{2n}Fc)₂ type compounds [35], the lower energy absorption can be attributed to the $\pi^*(Ru_2) \rightarrow \delta^*(Ru_2)$ transition, where the axial alkynyl ligand contributes through the antibonding overlap between $\pi(C\equiv C)$ and $\pi^*(Ru_2)$. The absorption around 510 nm is due to a mixture of both the L(N) $\rightarrow \delta^*(Ru_2)$ and $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transitions. It is clear from Fig. 4 that the intensity of both bands increase linearly with the increasing degree of oligomerization, and there is no discernible new feature associated with the dimer (2a) or trimer (3a) when compared with the monomer (1a). Hence, the interunit electronic couplings are insignificant, consistent with the conclusion drawn from voltammetric data.

3. Conclusions

We presented a successful strategy in preparing a unique series of Ru₂-based oligomers, and fully characterized lower members (n = 1-3) of the series based on L1. The structural features of the first coordination sphere of Ru₂ center in compounds **1b** and **2a** are very similar to those of previously studied Ru₂ (DMBA)₄(C₂R)₂ type compounds. The electrochemical and spectroscopic features of oligomers with n = 2 and 3 are very similar to those of n = 1, indicating a minimal interunit electronic coupling.

4. Experimental

4.1. General procedure and materials

3-Bromo-5-iodobenzoic acid was purchased from Alfa Aesar, potassium carbonate, benzyl bromide, and isopropyl bromide from Aldrich, diethylamine, triethylamine, tetrabutylammonium fluoride, and 3-bromo-5-iodobenzoic acid from ACROS, trimethylsilyl acetylene from GFS, and silica gel from Merck. Ru₂ (DMBA)₄(NO₃)₂ was prepared according to literature procedure [68]. THF was obtained either from the distillation over Na/benzophenone under an N₂ atmosphere prior to use or obtained from a solvent purification system (Innovative Technology Inc.). Elemental analysis was performed by Atlantic Microlab, Norcross, GA. ¹H NMR spectra were recorded on a Varian Mercury 200 NMR spectrometer with chemical shifts (δ) referenced to the residual CHCl₃ in CDCl₃, respectively. UV-vis spectra were obtained with a Cary 50 UV-Vis-NIR spectrophotometer. Mass spectra were recorded on a Bruker Autoflex[®] MALDI-TOF Mass Spectrometer. Mass spectra were collected on a TripleTOF 5600 System (Sciex, Concord, Ontario, Canada) using nano-electrospray ionization. Both cyclic voltammograms (CVs) were recorded in $0.2 \text{ M} (n-Bu)_4 \text{NPF}_6$ solution (THF, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of diruthenium species was always 1.0 mM.

4.2. Preparation of compounds 1a, 2a and 3a

a 100 mL round bottom flask, isopropyl-3,5-In bis(trimethylsilylethynlene)benzoate (0.438 mmol. 0.156 g) (L1TMS₂) was desilylated with TBAF in 20 mL THF solution. The reaction was stirred at room temperature for 20 min and then was filtered through a 2 cm silica gel pad. The filtrate was added into a suspension of (0.218 mmol, 0.200 g) of Ru₂ (DMBA)₄(NO₃)₂ in 50 mL THF and 10 mL of Et₂NH. The reaction mixture was stirred at room temperature overnight and filtered through a celite pad. The solvents were removed on rotovap and the residue was dried under vacuum. The residue was purified by column chromatography and eluted with THF/hexanes (1/5, v/v). Several fractions were collected. The first fraction was identified as monomer **1a** (yield: 28% based on Ru). Data for 1a: ¹H NMR: 7.72 (d, 4H, aromatic), 7.67–7.38 (m, 14H, aromatic), 7.27–7.01 (m, 8H, aromatic), 5.19 (m, 2H, -COOCH-), 3.29 (s, 24H, CH₃N-), 3.03 (s, 2H, HC≡C-), 1.30 (m, 12H, CH₃-). MS-FAB (m/z, based on ¹⁰¹Ru): 1213 [M⁺ – H]. ToF-MS (m/z, based on ¹⁰¹Ru) 1214 [M⁺]. Electrochemistry, E_{1/2}/V, Δ E_p/V, *i*_{backward}/*i*_{forward}: **A**, 0.613, 0.058, 0.926; **B**, -0.876, 0.185, 0.927; Anal. Found (calcd) for C₆₄H₆₆N₈O₄Ru₂ · 0.5hexane: C, 64.10 (64.04); H, 5.74 (5.86); N, 8.83 (8.92).

The second fraction was identified as the dimeric compound **2a** (yield 12% based on Ru). Data for **2a**: ¹H NMR: 7.63 (*d*, 4H, aromatic), 7.41–7.27 (*m*, 27H, aromatic), 6.96 (*m*, 18H, aromatic), 5.12 (*m*, 3H, -COOCH-), 3.21 (*s*, 30H, CH₃N-), 3.18 (*s*, 18H, CH₃N-), 2.95 (*s*, 2H, HC≡C-), 1.33–1.20 (*m*, 18H, CH₃-); HRMS (MALDI)

(C₁₁₄H₁₂₀N₁₆O₆Ru₄) calcd 2216.5890 [M⁺], found 2216.5913 [M⁺]; MALDI (m/z), based on ¹⁰¹Ru): 2216 [M⁺]; ToF-MS (m/z), based on ¹⁰¹Ru) 2214 [M⁺]. Electrochemistry, $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{forward}$: A, 0.572, 0.100, 0.978; B, -0.885, 0.163, 0.394.

The third fraction was identified as the trimeric compound **3a** (vield 5% based on Ru). Data for **3a**: ¹H NMR: 7.67 (*d*, 2H, aromatic), 7.42-7.28 (m, 39H, aromatic), 6.97 (s, 31H, aromatic), 5.21-5.04 (m, 4H, -COOCH-), 3.27 (m, 72H, CH₃N-), 3.02 (s, 2H, HC=C-), 1.34-1.25 $(m, 24H, CH_3-)$; MALDI $(m/z, based on {}^{101}Ru)$: 3216 $[M^+]$; HRMS (MALDI) (C₁₆₄H₁₇₄N₂₄O₈Ru₆) calcd 3216.8380 [M⁺], found 3216.8389 [M⁺]; ToF-MS (*m*/*z*, based on ¹⁰¹Ru) 3219 [M⁺].

4.3. Preparation of compounds 1b

In а 100 mL round bottom flask, benzyl-3,5bis(trimethylsilylethynyl)benzoate $(L2TMS_2)$ (0.329 mmol. 0.133 g) was desilylated with TBAF in 20 mL THF solution. The reaction was stirred at room temperature for 20 min and then was filtered through a 2 cm silica gel pad. The filtrate was added into a suspension of Ru₂ (DMBA)₄(NO₃)₂ (0.164 mmol, 0.150 g) in 50 mL THF and 30 mL of Et₂NH, and the reaction mixture was stirred at room temperature overnight. The progress of the reaction was monitored by TLC. Upon the complete consumption of Ru₂ (DMBA)₄(NO₃)₂, several more polar but less abundant products were present besides the dominant product 1b. The reaction mixture was filtered through a celite pad, and the volatiles were removed on rotovap. The residue was purified by column chromatography with THF/hexanes (1/5, v/v). While clean separation of more polar fractions failed, compound 1b was obtained in a yield of 25%. Data for **1b**: ESI (*m*/*z*, based on ¹⁰¹Ru): 1260 [M⁺-2, C=CH]; ¹H NMR: 7.67 (d, 4H, aromatic), 7.48–7.39 (m, 24H, aromatic), 7.00 (d, 10H, aromatic), 5.21–5.15 (m, 2H, -COOCH₂-), 3.29 (s, 24H, MeN-), 3.02 (s, 2H, C=CH-); Electrochemistry, $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{for-}$ ward: A, 0.615, 0.057, 0.879; B, -0.903, 0.144, 0.551; Anal. Found (calcd) for $C_{72}H_{66}N_8O_4Ru_2 \cdot 2H_2O$: C, 63.79 (64.27); H, 5.66 (5.24); N, 8.61 (8.33).

4.4. Structure determination of compounds 1b and 2a

Single crystals of **1b** were obtained by slow evaporation of a hexanes-THF solution, and those of 2a from an ether-THF solution. X-ray intensity data were measured on a Nonius-Kappa CCD X-ray diffractometer using MoK α ($\lambda = 0.71073$ Å). Structures were solved and refined using the Bruker SHELXTL[©] (Version 5.1) software package. Crystallographic data are given in Table 2.

Table 2

Crystallographic parameters for compounds 1b and 2a.

	1b	2a
Formula	C72H66N8O4Ru2	C122H140N16O8Ru4
Fw	1309.52	2362.86
Space group	C2/c	P1
a (Å)	18.3996 (3)	10.5615 (3)
b (Å)	14.0424 (2)	19.9650 (5)
<i>c</i> (Å)	28.8534 (6)	31.7100 (10)
α(°)	90	76.224 (12)
β(°)	101.097 (7)	81.988 (12)
γ(°)	90	77.64 (2)
Volume (Å ³)	7315.6 (2)	6316.1 (3)
Z	4	2
$d_{\rm calc}$. (gcm ⁻³)	1.189	1.242
$\mu (mm^{-1})$	0.451	0.515
Radiation	Μο Κα (0.71073)	Μο Κα (0.71073)
T (K)	150 (1)	150 (1)
<i>R</i> 1, w <i>R</i> 2 ($I > 2\sigma(I)$)	0.062, 0.178	0.092, 0.212

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Appendix A. Supplementary data

Synthesis and characterizations of ligands L1TMS₂ and L2TMS₂ (PDF); ESI-MS, ¹H NMR and FT-IR spectra for compounds **1a/1b/1c**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 1518596 and 1518597 for compounds 1b and 2a, respectively. Copies of this information may be obtained free of charge from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or www: http://ccdc. cam.ac.uk).

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2017.03.011.

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6

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J.-W. Ying et al. / Journal of Organometallic Chemistry xxx (2017) 1-6

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