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Dinuclear niobium(III) and tantalum(III) complexes with thioether and selenoether ligands [{$M^{III}X_2(L)$}$_2$(μ-X)$_2$(μ-L)] (M = Nb, Ta; X = Cl, Br; L = R_2S, R_2Se): Syntheses, structures, and the optimal conditions and the mechanism of the catalysis for regioselective cyclotrimerization of alkynes

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ABSTRACT

A series of dinuclear niobium(III) and tantalum(III) halide complexes with chalcogen donors [{$M^{III}X_2(L)$}$_2$(μ-X)$_2$(μ-L)] (M = Nb; X = Cl, Br; L = R_2S, R_2Se) (M = Ta; X = Cl, Br; L = R_2S) have been prepared by the reaction of dimetal(V) decahalide (M_2X_{10}) with magnesium and L. The structures of five of those new complexes were determined by X-ray crystallography to have a M–M double bond. It is evidenced that the solvent and the temperature play important roles in achieving high yield and regioselectivity for cyclotrimerization of alkynes. The reaction of the niobium(III) chloride complexes (L = dimethyl sulfide (Me_2S), tetrahydrothiophene (C_4H_8S, THT, thiolane)) with phenylacetylene at room temperature in toluene gave both head-to-tail cycloadded trimers of alkyne, 1,3,5-$(Ph)_3$-2,4,6-$(H)_3$-benzene and head-to-head cycloadded 1,2,4-$(Ph)_3$-3,5,6-$(H)_3$-benzene, in high yields. The smaller the thioether ligands, the higher the catalytic activity. The niobium(III) chloride complexes with selenoether (L = dimethyl selenide (Me_2Se), tetrahydroselenophene (C_4H_8Se, THSe, selenolane) have higher rates for the reaction with alkynes, but low activity for the cyclotrimerization. Tantalum(III) chloride complexes (L = Me_2S, THT, tetrahydrothiopyran ($C_5H_{10}S$, THTP, thiane)) have lower catalytic activities than the niobium(III) ones, because the Ta–S(μ-L) bond lengths are shorter than those of niobium analogs. The stability of the precursor complexes toward the first oxidative addition depends on the M–S(μ-L) bond strength, and controls the concentration of catalytic active species. The niobium(III) bromide complexes (L = Me_2S, THT) and the tantalum(III) bromide one (L = Me_2S) react with alkynes to give head-to-tail compounds regioselectively, but are less catalytically active than those of chloride complexes.

1. Introduction

During the last six decades, numerous studies have revealed that many transition metal complexes catalyze the cyclotrimerization of alkynes, but even now it is a major challenge for synthetic chemistry to develop methods and conditions with high regio- and chemoselectivity in the cyclotrimerization of a wide variety of alkynes [1]. The development of early transition metal complexes as catalysts has been focused on those of Ti [2], Zr [3], Mo [4], *etc.*, while the catalytic activity of the lower oxidation states of Nb and Ta in discrete complexes remains relatively unexplored. It has been reported that the mononuclear Nb and Ta complexes, [$NbCl_3$(DME)] and [$TaCl_3$(DME)] (DME = 1,2-dimethoxyethane), respectively, have catalytic activity to let alkynes cyclotrimerize [5,6]. These catalytic reactions always gave a mixture of 1,3,5- and 1,2,4-cyclotrimers, which are formed through head-to-tail and head-to-head additions, respectively, and the yields generally do not depend on the properties of the substituent on the alkynes.

On the other hand, the dinuclear Nb and Ta complexes [{$M^{III}X_2(L)$}$_2$(μ-X)$_2$(μ-L)] ([$Nb_2Cl_6(Me_2S)_3$] (**1a**) (Me_2S = dimethyl

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sulfide), $[Nb_2Cl_6(THT)_3]$ (**1b**) (THT = tetrahydrothiophene (C_4H_8S, thiolane)), $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), and $[Ta_2Cl_6(THT)_3]$ (**2b**)) are well known to act as a starting materials for synthesizing other dinuclear and multinuclear complexes (Scheme 1) [7–9]. Especially, reactions of $[Nb_2Cl_6(THT)_3]$ (**1b**) and $[Ta_2Cl_6(THT)_3]$ (**2b**) with alkynes give various products including polymers, cyclotrimers, and complexes with η^2-alkene depending upon the sort of alkyne [10–14]. Recently, we have found that the reaction of $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) and $[Nb_2Cl_6(THT)_3]$ (**1b**) with various alkynes ($R_1C{\equiv}CR_2$) gave cycloadded trimer, 1,3,5-$(R_1)_3$-2,4,6-$(R_2)_3$-benzene regioselectively in high yields, even at room temperature in CH_2Cl_2. We have also suggested a plausible mechanism for the cyclotrimerization (Scheme 2) [15]. The reaction mechanism consists of three consecutive processes. In the first step, after leaving of the bridging sulfur in the precursor complex, the oxidative addition of the alkynes to the metal center takes place to give $[\{M^VX_2(L)(\eta^2\text{-}R_1C{=}CR_2)\}_2(\mu\text{-}X)_2]$. The addition of the second alkyne to form a five-membered metallacycle is the second step, and it is the source of the regioselectivity. The third step forms metalla–heptacyclic complex. This step is also regioselective. On reaction of the complex with a new alkyne, the original catalytically-active complex is reproduced.

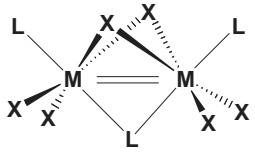
We still do not know the determining factors for such high regioselectivity and high yields. It will be necessary to examine the influences of the sort of central metal, the electronic state and steric bulkiness of the sulfur and selenium donor and the halide, and environments such as temperature and solvent, to verify the optimal conditions for the catalytic reaction.

As one step towards this goal we report here on the syntheses and structures of the new complexes of the type $[\{M^{III}X_2(L)\}_2(\mu\text{-}X)_2(\mu\text{-}L)]$: $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) (Et_2S = diethyl sulfide), $[Nb_2Cl_6(THTP)_3]$ (**1d**) (THTP = tetrahydrothiopyran ($C_5H_{10}S$, thiane)), $[Nb_2Cl_6(Me_2Se)_3]$ (**1e**) (Me_2Se = dimethyl selenide), $[Nb_2Cl_6(THSe)_3]$ (**1f**) (THSe = tetrahydroselenophene (C_4H_8Se, selenolane)), $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Ta_2Cl_6(THTP)_3]$ (**2d**), and $[Ta_2Br_6(Me_2S)_3]$ (**2g**), and on the reaction of all these complexes (**1a**–**1h**, **2a**, **2b**, **2d**, and **2g**) with phenylacetylene under various conditions to reveal optimal conditions.

2. Results and discussion

2.1. Syntheses of $[\{M^{III}X_2(L)\}_2(\mu\text{-}X)_2(\mu\text{-}L)]$

We have previously adopted Tsunoda's method, which uses magnesium as a reductant, to prepare $[\{Nb^{III}Cl_2(L)\}_2(\mu\text{-}Cl)_2(\mu\text{-}L)]$ [15,16]. It is highly useful due to the convenience of treatment and high yields to prepare $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) and $[Nb_2Cl_6(THT)_3]$ (**1b**) rather than using Na/Hg or Na/K [17]. We therefore employed Mg for synthesizing other complexes **1c**–**1h**, $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), $[Ta_2Cl_6(THT)_3]$ (**2b**), $[Ta_2Cl_6(THTP)_3]$ (**2d**), and $[Ta_2Br_6(Me_2S)_3]$ (**2g**). All these complexes were provided by the reaction of dimetal(V) decahalide (M_2X_{10}) with Mg and L in a mixture of CH_2Cl_2 or toluene with diethyl ether (Et_2O) for several days as shown in Scheme 3. All the prepared complexes are air-unstable solids. Single crystals were obtained for the new complexes $[Nb_2Cl_6(Et_2S)_3]$ (**1c**), $[Nb_2Cl_6(THTP)_3]$ (**1d**), $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Ta_2Cl_6(THTP)_3]$ (**2d**) and $[Ta_2Br_6(Me_2S)_3]$ (**2g**). The ^1H and ^{13}C NMR spectra in $CDCl_3$ for all the complexes suggest that the molecular structures in the solid state (*see below*) remain unchanged in solution. The diamagnetism of these complexes is rationalized by the formation of a M–M double bond, although M in the oxidation number +3 has d^2 electron configuration.



1a (M = Nb, X= Cl, L = Me_2S)
1b (M = Nb, X= Cl, L = THT)
1c (M = Nb, X= Cl, L = Et_2S)
1d (M = Nb, X= Cl, L = THTP)
1e (M = Nb, X= Cl, L = Me_2Se)
1f (M = Nb, X= Cl, L = THSe)
1g (M = Nb, X= Br, L = Me_2S)
1h (M = Nb, X= Br, L = THT)

2a (M = Ta, X= Cl, L = Me_2S)
2b (M = Ta, X= Cl, L = THT)
2d (M = Ta, X= Cl, L = THTP)
2g (M = Ta, X= Br, L = Me_2S)

Scheme 1. Dinuclear Nb and Ta complexes $[\{M^{III}X_2(L)\}_2(\mu\text{-}X)_2(\mu\text{-}L)]$ (**1a**–**2g**).

2.2. Molecular structure of the catalyst $[\{M^{III}X_2(L)\}_2(\mu\text{-}X)_2(\mu\text{-}L)]$

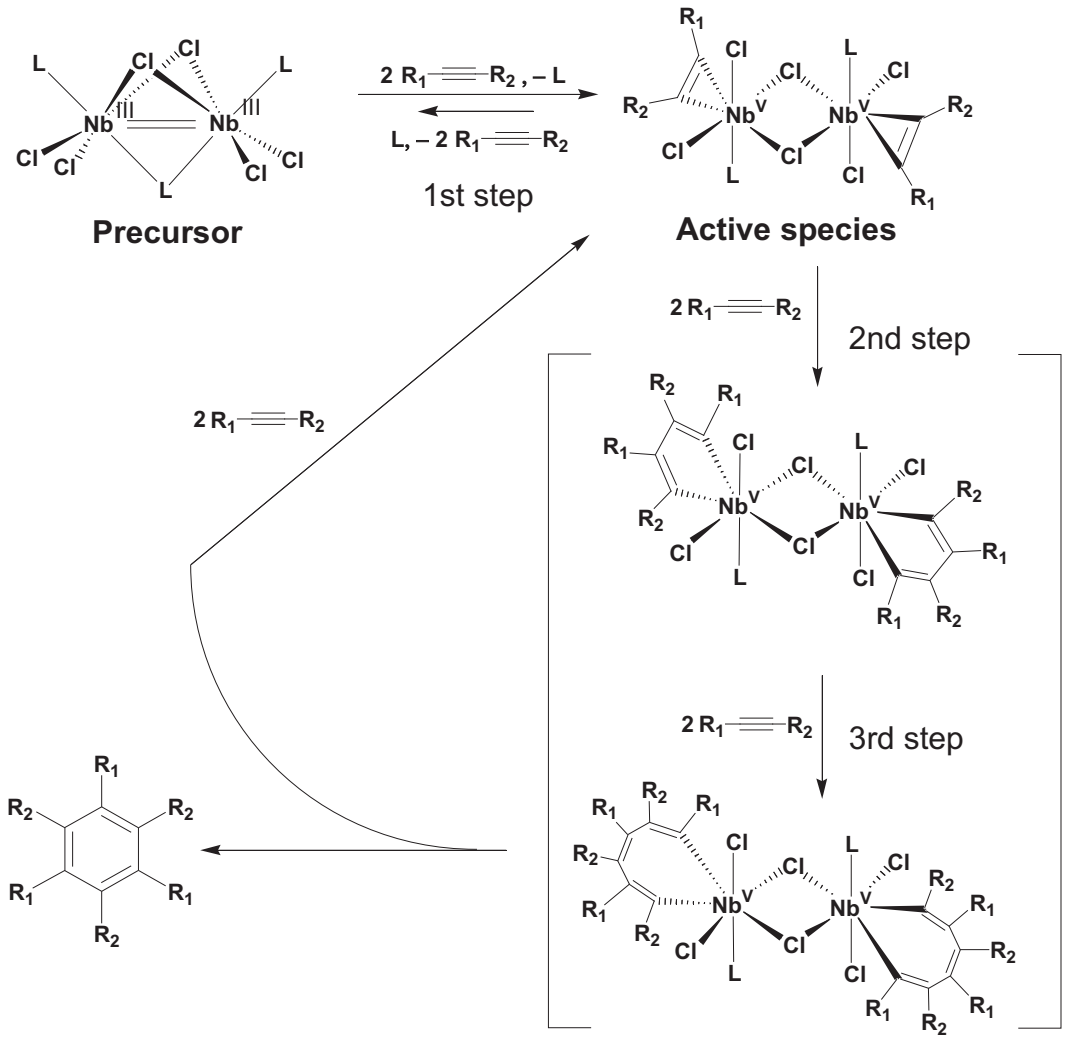
Molecular structures were determined by the single crystal X-ray crystallographic analyses for the new complexes $[Nb_2Cl_6(Et_2S)_3]$ (**1c**), $[Nb_2Cl_6(THTP)_3]$ (**1d**), $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Ta_2Cl_6(THTP)_3]$ (**2d**) and $[Ta_2Br_6(Me_2S)_3]$ (**2g**). The ORTEP drawing and selected bond lengths and angles of **1c** are shown in Fig. 1 and Table 1, respectively, and those of others are collected in Fig. S1, and Tables S3 and S4, respectively. We have reanalyzed the molecular structures of two known complexes $[Nb_2Br_6(THT)_3]$ (**1h**) and $[Ta_2Cl_6(Me_2S)_3]$ (**2a**) [18,19] (shown in Fig. S1), and used those results for the discussion about the influences of the M–M double bond and coordination bonds. The above mentioned five new complexes have very similar structures with those of known ones [15,18–20].

2.2.1. Presence of M–M double bond

Each metal center has a pseudo-octahedral environment with a shared trigonal face consisting of one sulfur donor ligand and two halides, the coordination of which is completed by terminal two halides and one sulfur donor. Formation of the metal–metal bonding is obvious from the M–M distance, *e.g.*, Nb–Nb 2.6888(4) Å in $[Nb_2Cl_6(THTP)_3]$ (**1d**); Ta–Ta 2.6730(5) Å in $[Ta_2Cl_6(THTP)_3]$ (**2d**), and the former is longer than the latter. This trend is clearly seen for other pairs of Nb and Ta complexes, *i.e.* $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) *vs.* $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), and $[Nb_2Cl_6(THT)_3]$ (**1b**) *vs.* $[Ta_2Cl_6(THT)_3]$ (**2b**) [15,18,20]. Those distances lie within the range of usual atomic distances of Nb^{III}–Nb^{III} and Ta^{III}–Ta^{III} double bonds, 2.61–2.94 Å and 2.51–2.84 Å, respectively [7,21].

A further indication of the strong metal–metal attraction is the displacement of the metal centers toward one another away from the center of the idealized octahedral coordination sphere. Averages of deviations of the metal center from the *Cl*$_4$ plane Cl(1)–Cl(2)–Cl(3)–Cl(4) or Cl(3)–Cl(4)–Cl(5)–Cl(6) in each coordination sphere are 0.167 Å and 0.181 Å in $[Nb_2Cl_6(THTP)_3]$ (**1d**) and $[Ta_2Cl_6(THTP)_3]$ (**2d**), respectively. Averages of deviations of the metal center from the *Br*$_4$ plane Br(1)–Br(2)–Br(3)–Br(4) or Br(3)–Br(4)–Br(5)–Br(6) are 0.187 Å and 0.204 Å in $[Nb_2Br_6(Me_2S)_3]$ (**1g**) and $[Ta_2Br_6(Me_2S)_3]$ (**2g**), respectively. Deviations in the complexes with Br are similar with those in the corresponding complexes with Cl, and the trend is common for Nb and Ta complexes: deviations are larger in Ta complexes than that in Nb ones, and in complexes with Br than in complexes with Cl. The tendency may be due to the more enhanced covalency of M–M and M–μ-S bonds in Ta complexes than that of Nb complexes.

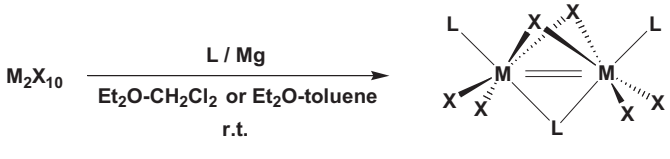
The influence of the thioether ligand on the Nb–Nb and Ta–Ta bonds is little, since the complexes of the same metal center and the same halide have very similar M–M distances despite the thioether



Scheme 2. Plausible mechanism for the cyclotrimerization.

ligands, such as for Nb and Cl, $[Nb_2Cl_6(Me_2S)_3]$ (**1a**), $[Nb_2Cl_6(THT)_3]$ (**1b**), $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) and $[Nb_2Cl_6(THTP)_3]$ (**1d**), and $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), $[Ta_2Cl_6(THT)_3]$ (**2b**) and $[Ta_2Cl_6(THTP)_3]$ (**2d**), respectively.

On the other hand, influence of the halide is obvious. The M–M bonding is shorter in the complexes with Cl than in ones with Br, and the trend is common for Nb and Ta complexes. Comparison of the structures of complexes with Me_2S having chloride bridges, $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) 2.6880(3) Å and $[Ta_2Cl_6(Me_2S)_3]$ (**2a**) 2.6785(8) Å, with those having bromide bridges, $[Nb_2Br_6(Me_2S)_3]$ (**1g**) 2.7253(4) Å and $[Ta_2Br_6(Me_2S)_3]$ (**2g**) 2.7072(8) Å, reveals the trend, and which holds for the complexes with THT [19]. The ionic radius of the bromide ion, 1.96 Å, is larger than that of chloride ion



1a (88%) **2a** (60%)
1b (64%) **2b** (56%)
1c (88%) **2d** (53%)
1d (84%) **2g** (75%)
1e (92%)
1f (63%)
1g (51%)
1h (69%)

Scheme 3. Syntheses of dinuclear Nb and Ta complexes, $[\{M^{III}X_2(L)\}_2(\mu\text{-}X)_2(\mu\text{-}L)]$ (**1a**–**2g**).

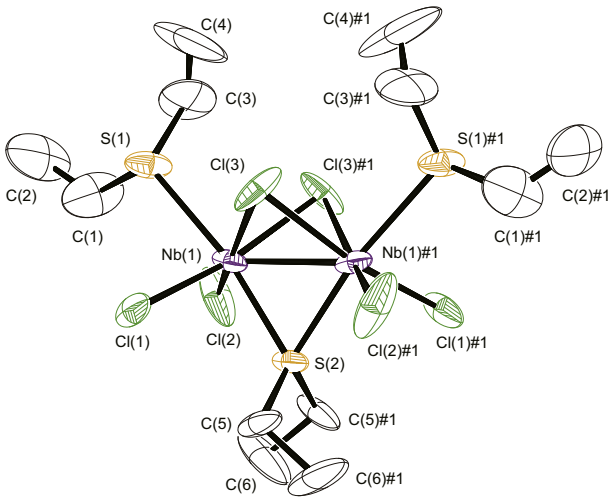


Fig. 1. The ORTEP drawings of **1c** with the numbering scheme. Ellipsoids are drawn at their 50% probability level; hydrogen atoms were omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (deg) for $[Nb_2Cl_6(Et_2S)_3]$ (**1c**).

$[Nb_2Cl_6(Et_2S)_3]$ (**1c**)[a]			
Nb(1)–Nb(1)#1	2.6903(18)	Cl(1)–Cl(2)	3.6613 (41)
Nb(1)–Cl(1)	2.381(2)	Cl(3)–Cl(3)#1	3.0976 (53)
Nb(1)–Cl(2)	2.369(3)		
Nb(1)–Cl(3)	2.513(2)	Nb(1)–Cl(3)–Nb(1)#1	65.39(7)
Nb(1)–Cl(3)#1	2.468(2)	Nb(1)–S(2)–Nb(1)#1	67.78(10)
Nb(1)–S(1)	2.628(3)	S(1)–Nb(1)–S(2)	170.42(8)
Nb(1)–S(2)	2.412(3)	S(2)–Nb(1)–Nb(1)#1	56.11(5)
Nb1–Cl(1)–Cl(2)–Cl(3)–Cl(3)#1	0.1610 (19)	C(1)–S(1)–C(3)	103.8(8)
S(1)–S(1)#1	6.1659 (56)	C(5)–S(2)–C(5)#1	103.3(9)

[a] Symmetry transformations used to generate equivalent atoms:#1 *y*, *x*, −*z*.

1.81 Å [22]. Bromide having bigger ionic radius compared with chloride may lead to the elongation of the metal–halide bond (2.63 Å for Br, 2.50 Å for Cl), and the decreased angle of metal–halide–metal (62° for Br, 65° for Cl). We do not know whether these changes in geometry may cause or result of the elongation of M–M bonding.

The results of the X-ray crystallography explain that M–M bonding is shorter in the chloride complexes than in the bromide ones. Quantum chemical calculations, Natural Bond Orbital (NBO) Analysis, were carried out for assessing the electronic effect on the M–M bonding. The occupancy of electrons on the Nb–Nb bonding in $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) is larger than that in $[Nb_2Br_6(Me_2S)_3]$ (**1g**). The larger occupancy on the Nb–Nb bonding leads to the shorter bond lengths. Therefore, the elongation of M–M bonding in bromide-bridged complexes are understandable from the viewpoint of electronic factors (Tables S7 and S9).

2.2.2. Coordination bonds to sulfur atoms and halides

The influence of the sort of the thioether ligand on the Nb–S and Ta–S bonds is little, since Nb complexes with chloride, such as $[Nb_2Cl_6(Me_2S)_3]$ (**1a**), $[Nb_2Cl_6(THT)_3]$ (**1b**), $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) and $[Nb_2Cl_6(THTP)_3]$ (**1d**), and Ta complexes with chloride $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), $[Ta_2Cl_6(THT)_3]$ (**2b**) and $[Ta_2Cl_6(THTP)_3]$ (**2d**), have very similar M–S lengths with each other, respectively. However the difference in bond length is seen among metal-to-bridging thioether (μ-S) bonding: the bond length of Ta–S in $[Ta_2Cl_6(THTP)_3]$ (**2d**) (2.389 Å) is shorter than that of Nb–S in $[Nb_2Cl_6(THTP)_3]$ (**1d**) (2.423 Å), while the length of Ta to the terminal thioether (η-S) bonding (2.624 Å) is almost the same as Nb–η-S (2.639 Å). The similar trend is seen for other pairs of Nb and Ta complexes, *i.e.* $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) *vs.* $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), and $[Nb_2Cl_6(THT)_3]$ (**1b**) *vs.* $[Ta_2Cl_6(THT)_3]$ (**2b**) [15,18,20].

If the metal–sulfur bond were purely ionic, the distance should coincide with the sum of ionic radii of metal (0.72 Å for six-coordinate Nb^{III} and Ta^{III}) and sulfide (1.84 Å) to be 2.56 Å. The distance to the bridging ligand is fairly shorter, and that to the terminal ligand (η-S) is longer, than this value. This suggests that the interaction of μ-S with metal center is much stronger than that of η-S. The difference is due to the influence of the covalency of the metal–sulfur interactions.

The trend in M–S bond length is common for Nb and Ta complexes, in spite of the chloride and bromide complexes. We reveal that the size of the triangular shape which consists of two terminal and one bridging sulfurs (η-S–μ-S–η-S) on each metal center remains similar even if the halide alternates. The distance of η-S–η-S in the chloride complex $[Nb_2Cl_6(Me_2S)_3]$ (**1a**): 6.233 Å is similar with that in the bromide complex $[Nb_2Br_6(Me_2S)_3]$ (**1g**): 6.197 Å. Since the lengths of both Nb–μ-S and Nb–η-S in $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) are similar with those of $[Nb_2Br_6(Me_2S)_3]$ (**1g**), respectively, the sort of halide influences little on the triangular shape.

We have already discussed the difference in the bond nature between Nb–S and Nb–Cl from the incorporation of the 3d orbital [15], but the treatment seems incorrect. In this study, we did the NBO calculations and revealed that the σ*(Nb–μ-S) consists of the $sp^{3.24}d^{4.06}$ hybrid of Nb and the $sp^{2.23}$ hybrid of μ-S (Table S8). The extent of the stabilization of the complex resulting from the existence of one bridging sulfur donor ligand Me_2S (1042 kJ mol^{-1}) is larger than that from the existence of two bridging chlorides (297 kJ mol^{-1}). Although there is an obvious difference in interactions of μ-S with Nb–Nb bonding from those of μ-Cl with Nb–Nb bonding, no incorporation of d orbitals of μ-S in those interactions.

2.3. Active species

Our previous paper suggests that the catalytic active intermediate retains the dinuclear structure throughout the reaction, and that the structure is essential for regioselectivity [15]. The latter is rationalized from the catalytic abilities of analogous catalysts $[NbCl_3(DME)]$ and $[Mo_2Cl_6(THT)_3]$ [4a,5]. Quantum chemical calculations may also help the understanding on the difference in the stabilities of dinuclear and mononuclear complex.

It has been reported that the mononuclear Nb complex, $[NbCl_3(DME)]$ has catalytic activity to let alkynes cyclotrimerize [5]. This catalytic reaction always gave a mixture of 1,3,5- and 1,2,4-cyclotrimers, which are formed through head-to-tail and head-to-head additions, respectively. The yields of both cyclotrimers generally do not depend on the properties of the substituent on the alkynes. The reaction of $[NbCl_3(DME)]$ with $R_1C{\equiv}CR_2$ (R_1 = Ph, Et, Me_3Si. R_2 = H, Ph.) gave complexes with metallacyclopropene $[NbCl_3(\eta^2\text{-}R_1C{=}CR_2)]$ [5]. For the analogous Ta complexes, the reaction of $[TaCl_3(\eta^2\text{-}R_1C{=}CR_2)]$ (R_1, R_2 = Et, *etc*), as well as $[TaCl_3(DME)]$, with alkyne gave cyclotrimerized products [6]. Therefore, in the Nb case it is reasonable that an intermediately generated $[NbCl_3(\eta^2\text{-}R_1C{=}CR_2)]$ has a catalytically active species. The dinuclear Mo complex $[Mo_2Cl_6(THT)_3]$ has the same skeletal structure as $[Nb_2Cl_6(THT)_3]$ (**1b**). However, for the former Mo complex, the feature of the catalytic activity is entirely different, *i.e.* exhibiting linear oligomerization, cyclotrimerization, and polymerization, from those of the latter, and a mononuclear catalytically active species $[MoCl_2(THT)_2(\eta^2\text{-}R_1C{=}CR_2)]$ (R_1 = Me, Et. R_2 = Ph) is generated from the reaction with alkynes [4a]. For example, the reaction of $[Mo_2Cl_6(THT)_3]$ with alkynes $R_1C{\equiv}CR_2$ (R_1 = Me, Et, H. R_2 = Ph, *n*-Bu, *n*-Pr) gave a mixture of 1,3,5- and 1,2,4-cyclotrimers. Although the authors claimed the steric bulkiness of the alkyne plays a dominant role in giving a regioselectivity for the cyclotrimers. We tend to think the difference in catalytic activity between $[Nb_2Cl_6(THT)_3]$ and $[Mo_2Cl_6(THT)_3]$ comes from the structure of active species. Cotton and coworkers reported that the $[M_2Cl_6(THT)_3]$ (M = Nb (**1b**), Ta (**2b**)) with alkynes $R_1C{\equiv}CR_2$ (R_1 = Ph, R_2 = Ph; R_1 = *t*-Bu. R_2 = Me) gave

[{MCl_2(THT)(η^2-$R_1C{=}CR_2$)}$_2$(μ-Cl)$_2$] which retains the dinuclear structure without cleaving of M–μ-Cl bonds. We also confirmed the generation of this dinuclear complex with η^2-alkene from the reaction of 2-hexyne with 1/6 equiv of [Nb_2Cl_6(THT)$_3$] (**1b**) in $CDCl_3$ (0.4 mL) by monitoring with ^{1}H NMR at room temperature [15]. In conclusion, it was thought that the intermediate is in the dinuclear structure throughout the reaction, and the structure is essential for regioselectivity.

The DFT calculations suggest that the "catalytically active species" has a dinuclear structure. We have carried out calculations on [{$NbCl_2(Me_2S)(\eta^2$-$CH_3C{=}CCH_3)$}$_2$(μ-Cl)$_2$], and mononuclear complex [$NbCl_3(Me_2S)(\eta^2$-$CH_3C{=}CCH_3)$] generated from the cleavage of the bond to bridging Cl (Scheme S1). We first characterized optimized geometries as potential minima on the potential energy surface. The mononuclear complex has a distorted trigonal bipyramidal structure (Fig. S4). We obtained the total energy of each complex, and calculate the total energy difference between dinuclear and mononuclear complexes (*see Supporting information*). One molecule of dinuclear complex is more stable than two molecules of mononuclear complexes by 148 kJ mol^{-1}.

2.4. Optimal conditions for Nb complexes

The reaction of [$Nb_2Cl_6(Me_2S)_3$] (**1a**) and [Nb_2Cl_6(THT)$_3$] (**1b**) with phenylacetylene has been reported to give head-to-tail cycloadded trimers of alkyne, 1,3,5-(Ph)$_3$-2,4,6-(H)$_3$-benzene (**3**) regioselectively in CH_2Cl_2 at room temperature, and these complexes act as catalysts to give cycloadded products regioselectively [15]. It is important to understand the mechanism and limiting factors for this regioselective cyclotrimerization in high yields. Therefore, we investigated the reaction under various conditions, particularly of the temperature and the solvent, in order to disclose the influence on the catalytic activity and the regioselectivity. In our experiments, depending upon the conditions, a cyclotrimer through the head-to-head addition 1,2,4-(Ph)$_3$-3,5,6-(H)$_3$-benzene (**4**) was found in addition to **3** in product mixtures. These products were identified by ^{1}H NMR spectra.

To confirm the effects of temperature on the product, we checked the reaction [$Nb_2Cl_6(Me_2S)_3$] (**1a**) in $CHCl_3$ or toluene at lower and higher temperatures than room temperature (10–18 °C). The system generated **3** highly regioselectively in both the solvents at 0 °C, while the regioselectivity disappears in CH_2Cl_2 at 40 °C. The higher temperature in toluene, the regioselectivity becomes inverted, *i.e.* the predominant product was switched from 1,3,5-isomer to 1,2,4-isomer. The same tendency was observed for [Nb_2Cl_6(THT)$_3$] (**1b**). Thus, temperature is a more important factor than the solvent for emerging the regioselectivity for 1,3,5-isomer. We carried out the experiments for checking the stability of [$Nb_2Cl_6(Me_2S)_3$] (**1a**) both at 40 °C and room temperature in CD_2Cl_2, and obtained results that the complex is decomposed faster at higher temperature (Table S6). This lower stability at high temperature may be responsible for the lower yield at 40 °C than at room temperature.

The second step, addition of the second alkyne to form a η^2-butadiene moiety, is the rate-determining and the key step for the regioselectivity. The carbon–carbon bond should be formed between incoming and coordinated alkynes in the head-to-tail fashion to give 1,3,5-isomer at low temperature. On the other hand, at higher temperature, the insertion of the second alkyne into the Nb–C bond becomes possible, since the thermal motion provides space which accommodates the incoming ligand, and leads to the binding to the metal center. The reason for the inverted regioselectivity is still uncertain, but the differences of thermal stabilities of isomeric form in the product of the second step, dinuclear five-membered metallacycles, may be responsible (Scheme 2, [15]).

All of the complexes dealt in the present study are easily decomposed in highly polar solvents, *i.e.* CH_3CN, EtOH *etc*. In the presence of excess amount of electron pair donor, such as THF, terminal sulfur donor ligands are substituted, although the bridging sulfur-based ligand did not dissociate from the metal center [7r,s]. Thus we examined the catalytic reaction of the complexes in non-polar solvents. [$Nb_2Cl_6(Me_2S)_3$] (**1a**) reacted with phenylacetylene to give cycloadded trimers in various solvents shown in Table 2. As seen in Table 2, the solvent plays an important role for determining the regioselectivity and the yield of the cyclotrimers. The catalytic activity was decreased in $CHCl_3$, CCl_4, toluene and benzene. In these solvents oxidation and/or the dissociation of ligands of the catalyst precursor complex was not observed. The ^{1}H and ^{13}C NMR spectra were monitored [$Nb_2Cl_6(Me_2S)_3$] (**1a**) in CCl_4 at room temperature for 4 h. The signal intensities of free ligands did not increase. Therefore, the low activity these solvents may be due to the local elevation of the temperature despite enough stirring and sufficient cooling, since the system seems to produce some heat during the reaction in these solvents. The regioselective production of **3** catalyzed by [$Nb_2Cl_6(Me_2S)_3$] (**1a**) took place in CH_2Cl_2, THF, and C_6H_5Cl. The system is kept under mild conditions because the reaction is less exothermic in these solvents, and gives 1,3,5-isomer regioselectively. The improvement of the selectivity in haloarenes is a general tendency (entry 6 and 12), while haloalkanes except CH_2Cl_2 are not suitable for solvents. Eventually, the optimal conditions in the solvent and temperature were disclosed to be CH_2Cl_2 and below 40 °C, respectively.

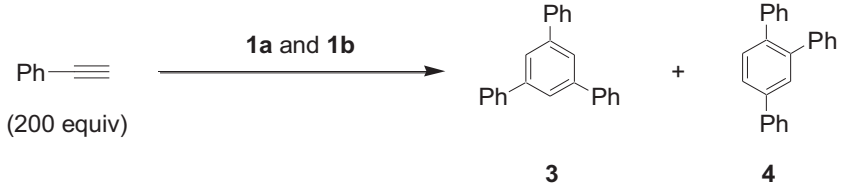
2.5. Influence of the metal center on the catalytic activity

We investigated the influence of the metal center on the catalytic ability. Data shown in Table 3 suggest that Ta complexes have lower activity towards phenylacetylene than Nb ones. It is reasonably supposed that the higher the electron density at the M–M double bond which is back-donated to the bridging sulfur-donor ligand, the lower the concentration of catalytically active species in the first step. Since the M–(μ-S)–M interaction is stronger in the Ta complexes than in the Nb ones, the concentration of the catalytically active species is lower in the Ta system than the Nb ones to decrease the catalytic activity in the first step.

It is reported that Nb and Ta complexes [Nb_2Cl_6(THT)$_3$] (**1b**) and [Ta_2Cl_6(THT)$_3$] (**2b**) gave different products from each other in the reaction with 1,2-bis(diphenylphosphino)ethane (dppe). In those systems [Nb_2Cl_6(THT)$_3$] (**1b**) allows the bridging sulfur donor to leave, and the original face-sharing bioctahedral structure changes into an edge-sharing ones with two bridging chlorides [{$NbCl_2$(dppe)}$_2$(μ-Cl)$_2$]. On the other hand, the face-sharing bioctahedral structure remains in [Ta_2Cl_6(THT)$_3$] (**2b**) due to the inertness or stability of the bridging sulfur donor, even though two [Ta_2Cl_6(THT)$_3$] (**2b**) dimerize to give a tetranuclear complex [{Ta_2(μ-Cl)$_2$(μ-THT)Cl_4}$_2$(μ-dppe)$_2$] [7p]. In the present work, we checked the bond lengths of the complexes closely, and reveal that the Ta complexes have a slightly shorter coordination bonds than Nb complexes. This feature leads to the less "labile" Ta complexes than the Nb ones.

We also tested reactions of [$Ta_2Cl_6(Me_2S)_3$] (**2a**) with phenylacetylene relevance to the solvent and temperature (Table 3). We have found that [$Ta_2Cl_6(Me_2S)_3$] (**2a**) maintains regioselectivity even if the solvent is altered or the temperature is elevated. For Nb complexes the solvent and temperature affect the activity and regioselectivity remarkably (*see above*). The conditions under 40 °C in CH_2Cl_2 are necessary for Nb complex [$Nb_2Cl_6(Me_2S)_3$] (**1a**) to give 1,3,5-benzene derivatives regioselectively, but these conditions are not necessary for Ta complex **2a**. This may arise from the robustness of the precursor complex [$Ta_2Cl_6(Me_2S)_3$] (**2a**), and the catalyst

Table 2
Cyclotrimerization of phenylacetylene catalyzed by $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) and $[Nb_2Cl_6(THT)_3]$ (**1b**) under various conditions.



Entry	Catalyst	Duration (h)	Solvent	*T* (°C)	Isomer ratio[a]		Yield (%)
					3	**4**	
1[b]	**1a**	4	CH_2Cl_2	r.t.	>99:1		96
2	**1a**	4	Toluene	r.t.	48	52	67
3	**1a**	4	$CHCl_3$	r.t.	51	49	78
4	**1a**	4	CCl_4	r.t.	60	40	30
5	**1a**	4	Benzene	r.t.	44	56	64
6	**1a**	4	C_6H_5Cl	r.t.	87	13	56
7	**1a**	4	THF	r.t.	86	14	15
8	**1a**	4	CH_2Cl_2	40	51	49	40
9	**1a**	4	Toluene	40	36	64	78
10	**1a**	4	Toluene	60	34	66	73
11	**1a**	4	Toluene	70	33	67	54
12	**1b**	1	$C_6H_4Cl_2$	r.t.	>99:1		5
13	**1b**	1	CH_2Cl_2	40	72	28	14
14	**1b**	1	Toluene	40	55	45	31
15	**1b**	1	Toluene	50	42	58	42
16	**1a**	4	Toluene	0	96	4	6
17	**1a**	4	$CHCl_3$	0	88	12	33

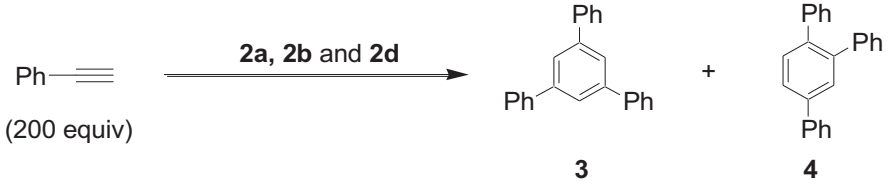
[a] From the intensity ratio of ^{1}H NMR.
[b] Ref. [15].

activating temperature range of Ta complexes becomes higher than that of Nb ones.

$[Ta_2Cl_6(THTP)_3]$ (**2d**) is so inert toward phenylacetylene in CH_2Cl_2 that phenylacetylene is recovered from the reaction mixture, and **2d** itself is gradually decomposed with the residual O_2 and H_2O in solution. In this study, we refer to the influences of the metal and thioether ligands on the catalytic activity. Ta complexes have lower catalytic activity than Nb ones, and $[Nb_2Cl_6(THTP)_3]$ (**1d**) has lowest catalytic activity among the Nb complexes and scarcely gave cyclotrimerized products (*see below*). Therefore, it seems reasonable that $[Ta_2Cl_6(THTP)_3]$ (**2d**) has no catalytic activity in CH_2Cl_2 (Table 3). Meanwhile, the catalytic activity of $[Ta_2Cl_6(Me_2S)_3]$ (**2a**) is more enhanced in toluene than in CH_2Cl_2. The reaction of $[Ta_2Cl_6(THTP)_3]$ (**2d**) with phenylacetylene in 200-fold equivalent in toluene-d_8 was followed by ^{1}H and ^{13}C NMR spectra for 4 h. Cyclotrimerized product **3** scarcely generated in this reaction (**3**:phenylacetylene = 1:200).

The above mentioned experimental results may suggest that the contributions of the μ-S ligand and the M–M bonding are more significant in Ta complexes than in Nb complexes. Eventually, the influence of the difference in metal center in $[\{M^{III}Cl_2(L)\}_2(\mu\text{-}Cl)_2(\mu\text{-}L)]$ on the catalytic activity may be due to the concentration of the catalytically active species produced in the first step, which depends on the strength of the back-donation from metal–metal bond to the bridging sulfur donor in the precursor complexes.

Table 3
Cyclotrimerization of phenylacetylene catalyzed by $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), $[Ta_2Cl_6(THT)_3]$ (**2b**), and $[Ta_2Cl_6(THTP)_3]$ (**2d**) under various conditions.



Entry	Catalyst	Duration (h)	Solvent	*T* (°C)	Isomer ratio[a]		Yield (%)
					3	**4**	
1	**2a**	4	CH_2Cl_2	r.t.	>99:1		8
2	**2a**	4	CH_2Cl_2	40	76	24	77
3	**2a**	4	Toluene	r.t.	95	5	42
4	**2a**	4	Toluene	40	96	4	44
5	**2a**	4	Toluene	60	92	8	50
6	**2b**	1	CH_2Cl_2	r.t.	>99:1		15
7	**2d**	46	CH_2Cl_2	r.t.	–	–	0

[a] From the intensity ratio of ^{1}H NMR peaks.

2.6. Influence of the chalcogen donor and halide on the catalytic activity

At first we discuss about the catalytic activities of Nb complexes with sulfur donors. As shown in Table 4, $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) acts as a catalyst to give **3** regioselectively with lower activity than $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) and $[Nb_2Cl_6(THT)_3]$ (**1b**). The complex with THTP $[Nb_2Cl_6(THTP)_3]$ (**1d**) scarcely gave cyclotrimerized products, although the regioselectivity is sustained (79:21). The low yields (0.5%) suggest that $[Nb_2Cl_6(THTP)_3]$ (**1d**) reacts with alkynes as a reactant, not as a catalyst. Judging from the yield of the product, $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) has a highest catalytic activity among various $[Nb_2Cl_6L_3]$ for the cyclotrimerization of alkynes, and a sequence of the decreasing activity is,

$[Nb_2Cl_6(Me_2S)_3]$ (**1a**) > $[Nb_2Cl_6(THT)_3]$ (**1b**) > $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) > $[Nb_2Cl_6(THTP)_3]$ (**1d**). The smaller the thioether ligands, the higher the catalytic activity.

For the complexes with acyclic saturated thioethers, the reactivity is probably associated with the stability of the active species, which is mainly governed by the bulkiness of the hydrocarbon moiety. $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) with ethyl group is extremely unstable compared with $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) with methyl group. Other Nb complexes with di-*t*-butyl sulfide and with *t*-butyl methyl sulfide have not been synthesized, after many trials to prepare those complexes. On the other hand for the complexes with cyclic saturated thioethers, the inertness of the complex to give active species may be responsible for the low catalytic activity. Although $[Nb_2Cl_6(THT)_3]$ (**1b**) with a less bulky thioether has a higher catalytic activity than $[Nb_2Cl_6(THTP)_3]$ (**1d**) with bulky ones, the former is not so extremely stable as the latter. The steric bulkines is therefore not the determining factor but the electronic properties. The donor ability of $[Nb_2Cl_6(THT)_3]$ (**1b**) may be slightly higher than $[Nb_2Cl_6(THTP)_3]$ (**1d**), which leads to the dissociation of the bridging thioether ligand bound to the complex with π-back donation-based bonds. The exception is trimethylene sulfide. We have tried to synthesize the complex having trimethylene sulfide by the reaction of $NbCl_5$ with trimethylene sulfide, and a purple solution indicating the generation of $[Nb_2Cl_6L_3]$ was obtained. However the complex is extremely unstable to decompose at higher temperature than −18 °C even in solution. The reason for the unstableness is speculated to be reactivity of trimethylene sulfide with Nb center inside the complex, just as is seen for ethylene sulfide, which does not form complexes but leads to decomposition.

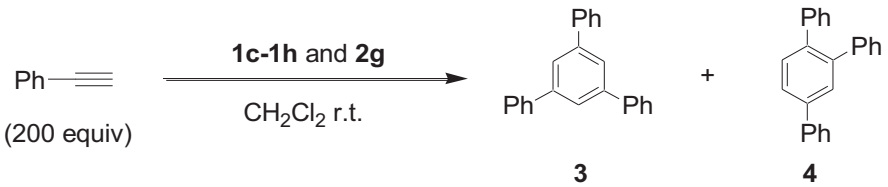
In addition, we tried to synthesize the Nb complex with thiophene having conjugate π-systems, but have not obtained any proof of generation of complexes. This may be due to the low donating ability of cyclic unsaturated thioether ligands.

The trend which the catalytic activity depends on the size of thioether ligands is applicable to the case of the complexes with selenoether ligands $[Nb_2Cl_6(Me_2Se)_3]$ (**1e**) and $[Nb_2Cl_6(THSe)_3]$ (**1f**). We have already determined the structure of the $[Nb_2Cl_6(Me_2Se)_3]$ (**1e**) analog $[\{NbCl_2(Me_2Se)\}_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)]$ which has dimethyl selenide at the terminal positions [23]. The bond lengths of the complex in terminal positions are longer than $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) probably due to the difference in the ionic radius of Se^{2-} (1.98 Å) from that of S^{2-}, while the donating ability of Se^{2-} is larger than that of S^{2-}. We disclosed that the Nb complexes with selenoethers, $[Nb_2Cl_6(Me_2Se)_3]$ (**1e**) and $[Nb_2Cl_6(THSe)_3]$ (**1f**), exhibit higher rates in catalytic reaction than those with sulfur donors, but have the lower activities, for which the higher sensitivity to air (*e.g.*; O_2, H_2O) compared with $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) and $[Nb_2Cl_6(THT)_3]$ (**1b**) is responsible. Therefore, $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) with dimethyl sulfide having eventually smallest size in our series of sulfur donors has highest activity.

For the effect of the halide on the catalytic reaction, it is suggested that the bromide complexes, $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Nb_2Br_6(THT)_3]$(**1h**) and $[Ta_2Br_6(Me_2S)_3]$ (**2g**) give **3** regioselectively. However the catalytic activities of the complexes are lower than the chloride ones, *i.e.* $[Nb_2Cl_6(Me_2S)_3]$ (**1a**), $[Nb_2Cl_6(THT)_3]$ (**1b**) and $[Ta_2Cl_6(Me_2S)_3]$ (**2a**), respectively (Table 4). It is quite reasonable that the deviation of the metal center from the X_4 plane is more significant for complexes with Br than ones with Cl (*see above*), since the steric bulkiness of the Br is higher than Cl. The enhanced effect of bromide on preventing alkynes from approaching to the coordination vicinity compared with chloride allows to the catalytic activities decrease in Nb complexes. Therefore, steric factor plays a significant role in controlling the catalytic behavior.

Furthermore, NBO analysis revealed the lower electron density around the metal center in $[Nb_2Br_6(Me_2S)_3]$ (**1g**) than in $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) (*see above*). Thus the lability of precursor to give catalytically active species decreases in complexes with Br, and consequently the complex has a lower catalytic activity. The trend is common for Nb and Ta complexes, probably because the M−μ-S

Table 4
Cyclotrimerization of phenylacetylene catalyzed by $[Nb_2Cl_6(Et_2S)_3]$ (**1c**), $[Nb_2Cl_6(THTP)_3]$ (**1d**), $[Nb_2Cl_6(Me_2Se)_3]$ (**1e**), $[Nb_2Cl_6(THSe)_3]$ (**1f**), $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Nb_2Br_6(THT)_3]$ (**1h**), and $[Ta_2Br_6(Me_2S)_3]$ (**2g**) in CH_2Cl_2 at room temperature.



Entry	Complex	Duration (h)	Isomer ratio[a]		Yield (%)
			3	**4**	
1	**1c**	1	>99:1		10
2	**1d**	1	79	21	0.5
3	**1e**	1	>99:1		20
4	**1f**	0.17	>99:1		15
5	**1g**	4	91	9	16
6	**1h**	1	90	10	11
7	**2g**	4	97	3	2

[a] Determined by ^1H NMR.

bond lengths for Nb are very similar with those of Ta for each of complexes with Cl or Br.

2.7. Efficiency as a catalyst

We have calculated overall turnover frequencies for overall cyclotrimerization products (TOF) and turnover numbers (TON), which are collected in Tables S15 and S16, respectively. The efficiency as a catalyst is discussed based on those data. $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) in CH_2Cl_2 at room temperature shows the most highest TON. The most effective factor on TON is the alkyl chain in thioether ligands than other factors, such as metal, halide and chalcogen. On the other hand, five-membered cyclic sulfur donor ligands have an advantage for high TOF in both Nb and Ta complexes. It seems that TOF mainly depends both on the formation constant of catalytically active species in the first step, which is closely related to the stability of the precursor complex, and the rate of conversion into the five-membered metallacycle species. Furthermore, the decrease in the stability of the active species makes TON lower due to the retardation in the yield of recovery of active species after the catalytic cycle.

Among Nb complexes, TON is higher for that with dimethyl chalcogenides than for those with five-membered cyclic chalcogen donors, while the TOF exhibits a reverse relationship. These phenomena can be understood by the stabilities of active species and precursor, respectively. For example, $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) with chalcogen donor Et_2S shows 1/3 of TOF and 1/12 of TON compared with those of $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) with Me_2S. This means that $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) is more stable by three times in precursor and less stable by 36 times in the active species than those of $[Nb_2Cl_6(Me_2S)_3]$ (**1a**). On the other hand, $[Nb_2Cl_6(THT)_3]$ (**1b**) with THT shows 9 times of TOF and 9 times of TON compared with those of $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) with Et_2S. Cyclic chalcogen donor makes both TOF and TON higher.

3. Conclusion

The structures of Nb and Ta complexes $[Nb_2Cl_6(Et_2S)_3]$ (**1c**), $[Nb_2Cl_6(THTP)_3]$ (**1d**), $[Nb_2Br_6(Me_2S)_3]$ (**1g**), $[Ta_2Cl_6(THTP)_3]$ (**2d**), and $[Ta_2Br_6(Me_2S)_3]$ (**2g**) were determined by X-ray crystallography. A dinuclear structure with a M^{III}–M^{III} double bond is common for all the complexes.

In the reaction with phenylacetylene to give the 1,3,5-cyclotrimerized product, $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) exhibits the highest performance both in the catalytic activity and in the regioselectivity. The optimal conditions are: $[Nb_2Cl_6(Me_2S)_3]$ (**1a**) in CH_2Cl_2 at room temperature (<40 °C). The dinuclear framework of the complex with chalcogen donors and halides seems essential to give rise to the regioselectivity for the 1,3,5-trimer, while the activity varies with each of the central metal and chalcogen donors and halides. On the other hand, both activity and regioselectivity depends strongly upon the external conditions such as the temperature and the solvent. This behavior is seen in the following observations. The difference in the central metal gives little influence on the regioselectivity, but significant influence on the activity: the regioselective catalysis is observed below 40 °C for Nb complexes, while even over 40 °C for Ta complexes. Furthermore, the difference in chalcogen donor and halide affects strongly on the activity, but weakly on the regioselectivity.

Trials for isolation of the reaction intermediate in each step, and the catalytic reaction with other alkynes are in progress for the purpose of clarifying the mechanism.

4. Experimental

4.1. General

All the reactions were carried out under a dry argon atmosphere by using standard Schlenk tube techniques. All the solvents were dehydrated and purified by distillation: Et_2O and toluene were refluxed over sodium benzophenone ketyl and distilled, CH_2Cl_2, $CHCl_3$ and *n*-hexane were refluxed over CaH_2 and distilled. These purified solvents were stored under a dry argon atmosphere. Other reagents employed were in the reagent grade and used as received without further purification.

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400, DRX-400, AVANCE500 NMR spectrometer. For ^1H and ^{13}C NMR measurements, Me_4Si was used an internal standard ($\delta = 0$).

Elemental analyses were carried out using FISONS EA 1112 at the Comprehensive Analysis Center for Science, Saitama University. Crystals of $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) (CCDC 923586), $[Nb_2Cl_6(THTP)_3]$ (**1d**) (CCDC 923585), $[Nb_2Br_6(Me_2S)_3]$ (**1g**) (CCDC 923588), $[Nb_2Br_6(THT)_3]$ (**1h**) (CCDC 923587), $[Ta_2Cl_6(Me_2S)_3]$ (**2a**) (CCDC 923582), $[Ta_2Cl_6(THTP)_3]$ (**2d**) (CCDC 923583), and $[Ta_2Br_6(Me_2S)_3]$ (**2g**) (CCDC 923584) were grown in CH_2Cl_2–hexane (C_6H_{14}) at room temperature or at −18 °C and submitted for X-ray crystallography measurements. The X-ray diffraction data for all the compounds were collected on Bruker SMART APEX diffractometer and BRUKER APEX II Ultra diffractometer equipped with CCD area detector. Crystallographic data and structure refinement for $[Nb_2Cl_6(Et_2S)_3]$ (**1c**) are shown in Table 5, and those of others are shown in Tables S1 and S2, respectively. The frame data were acquired with the *SMART-W2K/NT* software using Mo Kα radiation (λ = 0.71073 Å) from a fine-focus tube. The observed frames were processed using the *SAINT-WK2/NT* software to give the *hkl* data set. The crystals used for the diffraction measurements show no decomposition during the data collection. Absorption correction was performed using the *SADABS* program [24]. The structures are solved by the direct method [25] or Patterson method [26] and refined by least-squares method on F^2 using *SHELEx-97* incorporated in *SHELxTL-NT* program [27]. All non-hydrogen atoms for all the complexes were refined anisotropically. Hydrogen atoms were included and refined using a riding model for all the complexes.

Table 5
Crystallographic data of $[Nb_2Cl_6(Et_2S)_3]$ (**1c**).

Compound	**1c**
Empirical formula	$C_{12}H_{30}Cl_6Nb_2S_3$
Formula weight	669.06
Temperature (K)	150(2)
Crystal system	Tetragonal
Space group	$P\,4_12_12$
a (Å)	8.3794(6)
b (Å)	8.3794(6)
c (Å)	35.899(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2520.6(4)
Z	4
$D_{calcd.}$ (Mg/m^3)	1.763
Crystal size (mm)	0.12 × 0.06 × 0.06
Index ranges	$-10 \le h \le 9$ $-10 \le k \le 10$ $-45 \le l \le 40$
Goodness-of-fit on F^2	1.036
Final R indices	$R_1 = 0.0632$
$[I > 2\sigma(I)]$	$wR_2 = 0.1185$

4.2. Syntheses of [{$MX_2(L)$}$_2$(μ-X)$_2$(μ-L)] (**1a**–**2g**)

4.2.1. Preparation of [{$NbCl_2(Me_2S)$}$_2$(μ-Cl)$_2$(μ-Me_2S)] (**1a**)

The complex was prepared by the method proposed in the literature [15]. Diniobium decachloride Nb_2Cl_{10} (2.3 g, 4.3 mmol), Mg (0.57 g, 23.4 mmol) were suspended in CH_2Cl_2 (76 mL), then dimethyl sulfide (C_2H_6S, Me_2S, 1.7 mL, 23 mmol) was add to the mixture, and finally Et_2O (12 mL) at room temperature. The mixture was stirred for 4 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (2.2 g, yield 88%). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.33 (6H, bridge-Me_2S), 2.63 (12H, terminal-Me_2S). ^{13}C NMR (300 K, $CDCl_3$): δ 30.0 (2C, bridge-Me_2S), 22.7 (4C, terminal-Me_2S). Anal. Found (calcd. for $C_6H_{18}Cl_6Nb_2S_3$): C, 12.33 (12.32); H, 3.00 (3.10).

4.2.2. Preparation of [{$NbCl_2(THT)$}$_2$(μ-Cl)$_2$(μ-THT)] (**1b**)

Diniobium decachloride Nb_2Cl_{10} (1.2 g, 2.2 mmol), Mg (0.16 g, 6.6 mmol) were suspended in CH_2Cl_2 (37 mL), then tetrahydrothiophene (C_4H_8S, THT, thiolane, 0.75 mL, 8.5 mmol) was add to the mixture, and finally Et_2O (6 mL) at room temperature. The mixture was stirred for 4 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (0.9 g, yield 64%). ^{1}H NMR (300 K, $CDCl_3$): δ 4.03 (4H, H_α, bridge-C_4H_8S), 3.41 (8H, H_α, terminal-C_4H_8S), 2.31 (4H, H_β, bridge-C_4H_8S), 2.15 (8H, H_β, terminal-C_4H_8S). ^{13}C NMR (300 K, $CDCl_3$): δ 38.0 (4C, C_α, bridge-C_4H_8S), 35.7 (2C, C_α, terminal-C_4H_8S), 30.4 (4C, C_β, terminal-C_4H_8S), 27.9 (2C, C_β, bridge-C_4H_8S). Anal. Found (calcd. for $C_{12}H_{24}Cl_6Nb_2S_3$): C, 21.75 (21.74); H, 3.55 (3.65).

4.2.3. Synthesis of [{$NbCl_2(Et_2S)$}$_2$(μ-Cl)$_2$(μ-Et_2S)] (**1c**)

Diniobium decachloride Nb_2Cl_{10} (0.5 g, 0.93 mmol), Mg (0.11 g, 4.6 mmol) were suspended in CH_2Cl_2 (75 mL), then diethyl sulfide ($C_4H_{10}S$, Et_2S, 0.5 mL, 4.6 mmol) was add to the mixture, and finally Et_2O (11.5 mL) at room temperature. The mixture was stirred for 4 h at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (0.6 g, yield 88%).

^{1}H NMR (300 K, $CDCl_3$): δ 3.80 (4H, H_α, bridge-Et_2S), 3.10 (8H, H_α, terminal-Et_2S), 1.72 (6H, H_β, bridge-Et_2S), 1.45 (12H, H_β, terminal-Et_2S). ^{13}C NMR (300 K, $CDCl_3$): δ 36.4 (2C, C_α, bridge-Et_2S), 29.9 (4C, C_α, terminal-Et_2S), 13.8 (4C, C_β, terminal-Et_2S), 11.8 (2C, C_β, bridge-Et_2S).

4.2.4. Synthesis of [{$NbCl_2(THTP)$}$_2$(μ-Cl)$_2$(μ-THTP)] (**1d**)

Diniobium decachloride Nb_2Cl_{10} (2.3 g, 4.3 mmol), Mg (0.52 g, 21 mmol) were suspended in CH_2Cl_2 (75 mL), then tetrahydrothiopyran ($C_5H_{10}S$, THTP, thiane, 1.4 mL, 14 mmol) was add to the mixture, and finally Et_2O (12 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (2.5 g, yield 84%). ^{1}H NMR (300 K, $CDCl_3$): δ 3.79 (4H, H_α, bridge-$C_5H_{10}S$), 3.14 (8H, H_α, terminal-$C_5H_{10}S$), 2.48 (4H, H_β, bridge-$C_5H_{10}S$), 2.00 (8H, H_β, terminal-$C_5H_{10}S$), 1.69 (4H, H_γ, terminal-$C_5H_{10}S$), 1.51 (2H, H_γ, bridge-$C_5H_{10}S$). ^{13}C NMR (300 K, $CDCl_3$): δ 44.1 (2C, C_α, bridge-$C_5H_{10}S$), 34.8 (4C, C_α, terminal-$C_5H_{10}S$), 26.9 (4C, C_β, terminal-$C_5H_{10}S$), 26.6 (2C, C_β, bridge-$C_5H_{10}S$), 25.2 (2C, C_γ, terminal-$C_5H_{10}S$), 23.4 (1C, C_γ, bridge-$C_5H_{10}S$). Anal. Found (calcd. for $C_{15}H_{30}Cl_6Nb_2S_3$): C, 25.27 (25.55); H, 4.24 (4.29).

4.2.5. Synthesis of [{$NbCl_2(Me_2Se)$}$_2$(μ-Cl)$_2$(μ-Me_2Se)] (**1e**)

Diniobium decachloride Nb_2Cl_{10} (0.5 g, 0.93 mmol), Mg (0.11 g, 4.6 mmol) were suspended in CH_2Cl_2 (75 mL), then dimethyl selenide (C_2H_6Se, Me_2Se, 0.35 mL, 4.6 mmol) was add to the mixture, and finally Et_2O (11.5 mL) at room temperature. The mixture was stirred for 4 h at room temperature. The suspended solid caused the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (0.6 g, yield 92%). ^{1}H NMR ($CDCl_3$, 300 K): δ 2.76 (6H, bridge-Me_2Se), 1.83 (12H, terminal-Me_2Se). ^{13}C NMR (300 K, $CDCl_3$): δ 31.6 (4C, terminal-Me_2Se), 22.7 (2C, bridge-Me_2Se).

4.2.6. Synthesis of [{$NbCl_2(THSe)$}$_2$(μ-Cl)$_2$(μ-THSe)] (**1f**)

Diniobium decachloride Nb_2Cl_{10} (0.7 g, 1.3 mmol), Mg (0.32 g, 13.3 mmol) were suspended in CH_2Cl_2 (75 mL), then tetrahydroselenophene (C_4H_8Se, THSe, selenolane, 0.72 g, 1.3 mmol) was add to the mixture, and finally Et_2O (11.5 mL) at room temperature. The mixture was stirred for 4 h at room temperature. The suspended solid caused the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving purple powder. The crude product was washed with hexane and dried under reduced pressure (0.7 g, yield 63%). ^{1}H NMR (300 K, $CDCl_3$): δ 3.45 (4H, H_α, bridge-C_4H_8Se), 2.87 (8H, H_α, terminal-C_4H_8Se), 2.03 (4H, H_β, bridge-C_4H_8Se), 1.25 (8H, H_β, terminal-C_4H_8Se). ^{13}C NMR (300 K, $CDCl_3$): δ 44.6 (2C, C_α, bridge-C_4H_8Se), 32.8 (4C, C_α, terminal-C_4H_8Se), 31.9 (2C, C_β, bridge-C_4H_8Se), 31.3 (4C, C_β, terminal-C_4H_8Se).

4.2.7. Synthesis of [{$NbBr_2(Me_2S)$}$_2$(μ-Br)$_2$(μ-Me_2S)] (**1g**)

Diniobium decabromide Nb_2Br_{10} (2.4 g, 2.4 mmol), Mg (0.18 g, 7.40 mmol) were suspended in CH_2Cl_2 (72 mL), then Me_2S (0.75 mL, 10 mmol) was add to the mixture, and finally Et_2O (12 mL) at room temperature. The mixture was stirred for 3 days at room temperature. The suspended solid caused the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving violet powder. The crude product was washed with hexane and dried under reduced pressure (1.0 g, yield 51%). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.60 (6H, bridge-Me_2S), 2.77 (12H, terminal-Me_2S). ^{13}C NMR (300 K, $CDCl_3$): δ 35.9 (2C, bridge-Me_2S), 24.8 (4C, terminal-Me_2S). Anal. Found (calcd. for $C_6H_{18}Br_6Nb_2S_3$): C, 8.07 (8.46); H, 2.16 (2.13).

4.2.8. Preparation of [{$NbBr_2(THT)$}$_2$(μ-Br)$_2$(μ-THT)] (**1h**)

Diniobium decabromide Nb_2Br_{10} (2.4 g, 2.4 mmol), Mg (0.18 g, 7.3 mmol) were suspended in CH_2Cl_2 (72 mL), then THT (0.7 mL, 7.9 mmol) was add to the mixture, and finally Et_2O (12 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving violet powder. The crude product was washed with hexane and dried under reduced pressure (1.6 g, yield 69%). ^{1}H NMR (300 K, $CDCl_3$): δ 4.29 (4H, H_α, bridge-C_4H_8S), 3.47 (8H, H_α, terminal-C_4H_8S), 2.34 (4H, H_β, bridge-C_4H_8S), 2.13 (8H, H_β, terminal-C_4H_8S). ^{13}C NMR (300 K, $CDCl_3$): δ 39.5 (2C, C_α, bridge-C_4H_8S), 39.1 (4C, C_α, terminal-C_4H_8S), 29.5 (4C, C_β, terminal-C_4H_8S), 26.8 (2C, C_β, bridge-C_4H_8S). Anal. Found (calcd. for $C_{12}H_{24}Br_6Nb_2S_3$): C, 15.90 (15.50); H, 2.83 (2.60).

*4.2.9. Preparation of [{$TaCl_2(Me_2S)$}$_2$(μ-Cl)$_2$(μ-Me_2S)] (**2a**)*

Ditantalum decachloride Ta_2Cl_{10} (2.4 g, 3.4 mmol), Mg (0.28 g, 12 mmol) were suspended in toluene (75 mL), then Me_2S (1.0 mL, 14 mmol) was add to the mixture, and finally Et_2O (10 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving yellow brown powder. The crude product was washed with hexane and dried under reduced pressure. (1.6 g, yield 60%). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.40 (6H, bridge-Me_2S), 2.66 (12H, terminal-Me_2S). ^{13}C NMR (300 K, $CDCl_3$): δ 41.0 (2C, bridge-Me_2S), 23.1 (4C, terminal-Me_2S). Anal. Found (calcd. for $C_6H_{18}Cl_6Ta_2S_3$): C, 9.47 (9.47); H, 2.38 (2.28).

*4.2.10. Preparation of [{$TaCl_2$(THT)}$_2$(μ-Cl)$_2$(μ-THT)] (**2b**)*

Ditantalum decachloride Ta_2Cl_{10} (2.4 g, 3.4 mmol), Mg (0.28 g, 12 mmol) were suspended in toluene (75 mL), then THT (1.2 mL, 14 mmol) was add to the mixture, and finally Et_2O (10 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving reddish brown powder. The crude product was washed with hexane and dried under reduced pressure (1.6 g, yield 56%). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.77 (4H, H_α, bridge-C_4H_8S), 3.44 (8H, H_α, terminal-C_4H_8S), 2.51 (4H, H_β, bridge-C_4H_8S), 2.09 (8H, H_β, terminal-C_4H_8S). ^{13}C NMR (300 K, $CDCl_3$): δ 42.0 (2C, C_α, bridge-C_4H_8S), 38.4 (4C, C_α, terminal-C_4H_8S), 30.5 (4C, C_β, terminal-C_4H_8S), 27.8 (2C, C_β, bridge-C_4H_8S). Anal. Found (calcd. for $C_{12}H_{24}Cl_6Ta_2S_3$): C, 16.74 (17.18); H, 2.73 (2.88).

*4.2.11. Synthesis of [{$TaCl_2$(THTP)}$_2$(μ-Cl)$_2$(μ-THTP)] (**2d**)*

Ditantalum decachloride Ta_2Cl_{10} (2.4 g, 3.4 mmol), Mg (0.28 g, 12 mmol) were suspended in toluene (75 mL), then THTP (1.4 mL, 14 mmol) was add to the mixture, and finally Et_2O (10 mL) at room temperature. The mixture was stirred for 4 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving reddish brown powder. The crude product was washed with hexane and dried under reduced pressure (1.6 g, yield 53%). ^{1}H NMR (300 K, $CDCl_3$): δ 3.74 (4H, H_α, bridge-C_5H_{10}S), 3.12 (8H, H_α, terminal-C_5H_{10}S), 2.76 (4H, H_β, bridge-C_5H_{10}S), 1.91 (8H, H_β, terminal-C_5H_{10}S), 1.62 (6H, H_γ, bridge- and terminal-C_5H_{10}S). ^{13}C NMR (300 K, $CDCl_3$): δ 55.3 (2C, C_α, bridge-C_5H_{10}S), 33.8 (4C, C_α, terminal-C_5H_{10}S), 27.1 (4C, C_β, terminal-C_5H_{10}S), 25.7 (2C, C_β, bridge-C_5H_{10}S), 24.2 (2C, C_γ, terminal-C_5H_{10}S), 23.2 (1C, C_γ, bridge-C_5H_{10}S). Anal. Found (calcd. for $C_{15}H_{30}Cl_6Ta_2S_3$): C, 20.50 (20.45); H, 3.32 (3.43).

*4.2.12. Synthesis of [{$TaBr_2(Me_2S)$}$_2$(μ-Br)$_2$(μ-Me_2S)] (**2g**)*

Ditantalum decabromide Ta_2Br_{10} (2.0 g, 1.7 mmol), Mg (0.12 g, 5.2 mmol) were suspended in toluene (75 mL), then Me_2S (0.5 mL, 6.9 mmol) was add to the mixture, and finally Et_2O (5 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The suspended solid formed the precipitation, which was removed by filtration, and the resultant filtrate was concentrated to dryness leaving red powder. The crude product was washed with hexane and dried under reduced pressure (1.3 g, yield 75%). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.75 (6H, bridge-Me_2S), 2.88 (12H, terminal-Me_2S). ^{13}C NMR (300 K, $CDCl_3$): δ 46.9 (2C, bridge-Me_2S), 25.1 (4C, terminal-Me_2S). Anal. Found (calcd. for $C_6H_{18}Br_6Ta_2S_3$): C, 6.99 (7.01); H, 1.77 (1.77).

4.3. Catalytic cyclotrimerization of phenylacetylene with complexes

Phenylacetylene in 200-fold equivalent was added to each complexes **1a**–**2g** (50 mg) in any solvent (20 mL), and the mixture was stirred at any temperature. The solution caused the formation of a precipitate. We calculate the completion of the reaction determined by the comparison of literature data [15]. The solution was removed by filtration and the resultant filtrate was concentrated to dryness. The crude product was washed with hexane and dried under reduced pressure. The results are collected in Tables 2–4, respectively.

Triphenylbenzene, **3** and **4**: Identification and regioisomeric ratio of 1,3,5- and 1,2,4-triphenylbezene were carefully determined by comparison of literature data [15] as well as by checking the ^{1}H NMR using the signal at δ = 7.93.

*4.4. Analysis data. Compounds **3** and **4***

Compound **3**: ^{1}H NMR (Acetone-d_6) δ 7.93 (s, 3H), 7.88 (d, 6H), 7.52 (t, 6H), 7.42 (tt, 3H).

Compound **4**: ^{1}H NMR (Acetone-d_6) δ 7.18–7.78 (m, 18H).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.035.

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