DOI: 10.1002/ejic.200800807

Mononuclear η^6-Arene Complexes of Lanthanides: One-Step Syntheses, Crystal Structures, and Arene Exchange

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Keywords: Lanthanides / Gallium halides / Arene ligands

Gallium(III) halides react with cerium(III), ytterbium(III), or dysprosium(III) halides in the presence of alkylated benzenes yielding mononuclear complexes of the general formula [Ln(η^6-arene)(GaX_4)$_3$]. The X-ray structures of [Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**), [Ce(*p*-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(*p*-$C_6H_4Me_2$) (**2**), [Yb(C_6H_5Me)($GaCl_4$)$_3$] (**3**), [Yb(*p*-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(*p*-$C_6H_4Me_2$) (**4**), and [Dy(C_6H_5Me)($GaBr_4$)$_3$] (**5**) were determined. Arene ligands in the cerium–toluene compound **1** can be substituted by polycyclic aromatic hydrocarbons (PAHs); the compounds [Ce(naphthalene)($GaCl_4$)$_3$] (**6**) and [Ce(pyrene)($GaCl_4$)$_3$]·0.5(pyrene) (**7**) have been isolated and structurally characterized.

Introduction

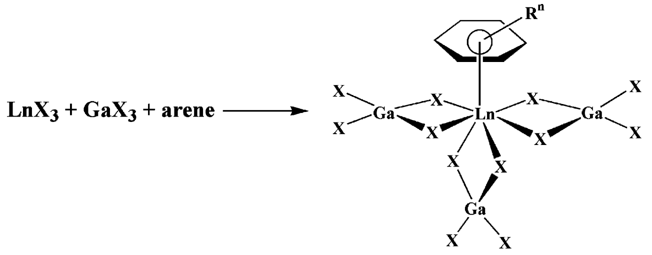
Arene complexes of f-block elements have been of constant interest over the last two decades.[1–17] In general, lanthanide–arene complexes described in the literature can be divided into two groups: mono(arene) and bis(arene) complexes.[2] The oxidation state of the lanthanide atoms varies from +3 to 0;[3–15] coordinated-arene ligands may be present in neutral as well as anionic forms.[6–8]

One of the simple and most effective synthetic routes to mono(arene)–lanthanide complexes, containing arene ligands that are coordinated to the metal in the η^6 mode, is the reaction of a lanthanide halide with aluminium(III) halides in an arene solution. Employing this method, a series of mononuclear complexes of Sm,[3,9–11] La,[6] Nd,[6,10] Gd,[10] Yb,[10] Y,[16] Pr,[16] Eu,[17] and U[3,15] was prepared. Benzene and its alkylated derivatives have been used as the arene ligands.

We have recently found that solutions of gallium(III) halides in arenes are a very effective system for the preparation of arene complexes of d-block elements. Thus, a series of low-valent platinum(0), platinum(I), and palladium(I) complexes supported by direct metal–metal bonds was isolated and crystallographically characterized.[18–20] In these reactions gallium(III) halides not only act as acceptors of the halide atoms, but also facilitate the process of reduction of the transition-metal halides, probably via an oxidation of the arenes. The present study has been performed in order to extend this synthetic approach to the chemistry of the f-block elements. In this article the synthesis and crystallographic characterization of new mononuclear mono(arene) complexes [Ln(η^6-arene)(GaX_4)$_3$] of cerium, ytterbium, and dysprosium are presented; reactions involving arene substitution have also been investigated.

Results and Discussion

The general synthetic route to mononuclear lanthanide–arene complexes is represented in Scheme 1. This includes the reaction between LnX_3 (where Ln = Ce, Yb, Dy; X^- = Cl^-, Br^-) and an excess of the corresponding GaX_3 complex in toluene or *p*-xylene.



Scheme 1. The reaction of gallium(III) halides with f-block-element halides in arenes.

Heating the cerium(III) chloride with an excess of the gallium(III) chloride in a toluene solution leads to the formation of a yellow solution, from which a white crystalline product can be isolated within 2–3 days. An X-ray analysis of the crystals revealed that the complex obtained is the mononuclear Ce(III) compound [Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**), with one arene ligand and three chelating $GaCl_4^-$ anions (Figure 1, left). The toluene ligand is coordinated to cerium in an η^6 manner. In general, the arrangement of the ligands around the cerium atom can be described in terms of a pentagonal bipyramid with the arene ligand and a chlorine atom in the apical positions.

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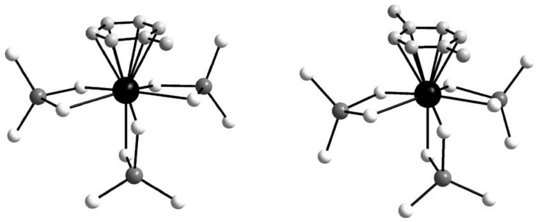


Figure 1. Molecular structures of [Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**) (left) and [Yb(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**4**) (right).

Surprisingly, there are only two crystallographically characterized η^6-arene complexes of cerium: one of them is a diphenylphenolatocerium(III) complex Ce(Odpp)$_3$ (where Odpp$^-$ is the 2,6-diphenylphenolate anion) containing an intra-molecular Ce–phenyl interaction;[13] the second compound is a dinuclear Ce(II) complex with a bridging toluene ligand coordinated in a μ:η^6:η^6 manner to two cerium(II) atoms.[4]

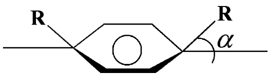
Under similar reaction conditions the complexes [Ce(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**2**), [Yb(C_6H_5Me)($GaCl_4$)$_3$] (**3**), [Yb(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**4**), and [Dy(C_6H_5Me)($GaBr_4$)$_3$] (**5**) have been prepared and characterized by single-crystal X-ray diffraction analyses (Table 3). The molecular structure of the ytterbium–p-xylene complex **4** is shown in Figure 1, right.

Selected inter-atomic distances from complexes **1**–**5** are listed in Table 1. The carbon–lanthanide distances lie between 2.8 and 3.0 Å, and they do not significantly depend on the nature of the lanthanide atom (for cerium compounds the Ln–C distances are slightly longer). Ga–(η-X) distances are longer than those between the gallium and non-bridging halide atoms.

With regard to the prospects of using the $GaCl_3$-arene reaction media for the formation of subvalent lanthanide complexes, some low-valent lanthanide–arene complexes were isolated from $AlCl_3$–arene mixtures, for example, the ytterbium(II) complex [Yb(C_6H_6)Al_2Cl_8]$_n$(C_6H_6)$_n$[21] and europium(II) complex [Eu(C_6Me_6)($AlCl_4$)$_2$]$_4$[17]. In addition, GaX_3-arene solutions display a high reducing ability,[18–20] and one may anticipate the formation of lanthanide complexes with a formal oxidation state that is lower than +3. In practice, even the use of an excess of GaX_3 and heating of the reaction mixture leads to the Ln^{III} complexes in all cases. It is interesting to note that a dark-green solution immediately forms after the addition of toluene to the mixture of $EuCl_3$ and $GaCl_3$, but no crystalline products were isolated. The initial green color may indicate the presence of Eu(II) compounds; the europium(II) complex [Eu(C_6Me_6)($AlCl_4$)$_2$]$_4$ is green[17].

An interesting structural feature that is observed in the complexes **1**–**5** is the distortion of the planarity of the arene ligands. In all cases there is a deviation of the methyl groups out of the aromatic plane. The deviation angle α varies between 2.7 and 11.3° (Table 2). Hubig et al. noted[25] that "there is a trend between bending angle α and the degree of charge transfer from the arene donor to the coordinated acceptor".

Table 2. The deviation of the methyl groups from the aromatic plane in complexes **1**–**5**.



Complex	α [°]
[Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**)	2.7
[Ce(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**2**)	8.4; 4.1
[Yb(C_6H_5Me)($GaCl_4$)$_3$] (**3**)	2.5
[Yb(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**4**)	11.3; 5.0
[Dy(C_6H_5Me)($GaBr_4$)$_3$] (**5**)	5.1

In order to investigate the chemical behavior of the mono(arene) complexes **1**–**5** we made attempts to substitute arene ligands by polycyclic aromatic hydrocarbons (PAHs). It should be noted that the direct use of PAHs in the reaction between LnX_3 and GaX_3 is restricted by the high Lewis acidity of the gallium(III) halides. We chose the cerium complex [Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**) as the starting material because of its high yields and easy preparation. 1,2,4-Trichlorobenzene was used as the solvent since the presence of electron-acceptor groups attached to the arene ring decreases the coordination ability of the solvent-arene molecules to the metal center, thus minimizing competition with the PAH ligand.

Heating of [Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**) and an excess of naphthalene (molar ratio 1:9) in 1,2,4-trichlorobenzene leads to the formation of a lemon-yellow crystalline product. X-ray diffraction analysis of the crystals obtained revealed that the product is the mononuclear complex [Ce(naphthalene)($GaCl_4$)$_3$] (**6**). The molecular structure of **6** is shown in Figure 2, left. The neutral naphthalene ligand is coordinated to cerium in an η^6 mode by one benzene ring. The Ce–C distances lie between 2.91 and 3.00 Å (Table 1). Several lanthanide–naphthalene complexes are described in

Table 1. Selected bond lengths (Å) from the lanthanide–arene complexes **1**–**7**.

Complex	Ln–C	Ln–X	Ga–(η-X)	Ga–X
[Ce(C_6H_5Me)($GaCl_4$)$_3$] (**1**)	2.89–3.03	2.81–2.91	2.21–2.24	2.10–2.12
[Ce(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**2**)	2.94–2.96	2.85–2.91	2.22–2.23	2.10–2.12
[Yb(C_6H_5Me)($GaCl_4$)$_3$] (**3**)	2.77–2.94	2.66–2.80	2.22–2.25	2.10–2.12
[Yb(p-$C_6H_4Me_2$)($GaCl_4$)$_3$]·0.5(p-$C_6H_4Me_2$) (**4**)	2.82–2.88	2.70–2.80	2.23–2.24	2.10–2.11
[Dy(C_6H_5Me)($GaBr_4$)$_3$] (**5**)	2.79–2.96	2.85–2.98	2.36–2.39	2.25–2.27
[Ce(naphthalene)($GaCl_4$)$_3$] (**6**)	2.91–3.00	2.83–2.91	2.22–2.24	2.08–2.12
[Ce(pyrene)($GaCl_4$)$_3$]·0.5(pyrene) (**7**)	2.91–3.03	2.83–2.91	2.21–2.24	2.10–2.12

the literature, but in almost all of these compounds naphthalene is present in its anionic form.[14,22–24] Thus, the compound **6** is the first crystallographically characterized cerium complex with a neutral PAH ligand.

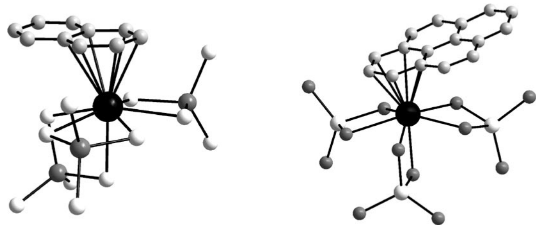


Figure 2. Molecular structures of [Ce(naphthalene)$(GaCl_4)_3$] (**6**) (left) and [Ce(pyrene)$(GaCl_4)_3$]·0.5(pyrene) (**7**) (right).

A similar reaction between [Ce(C_6H_5Me)$(GaCl_4)_3$] (**1**) and pyrene yields yellow crystals. The structure of the product [Ce(pyrene)$(GaCl_4)_3$]·0.5(pyrene) (**7**) was established by X-ray diffraction analysis. The structure of complex **7** is essentially the same as that of complex **6**; inter-atomic distances in these compounds are almost identical.

Complex **7** also contains pyrene solvate molecules, which lie between two metal-containing units (Figure 3). The shortest distance between benzene rings of the free and coordinated pyrene ligands is 3.48 Å, which may indicate π–π interactions between the pyrene ligands and solvate molecules.

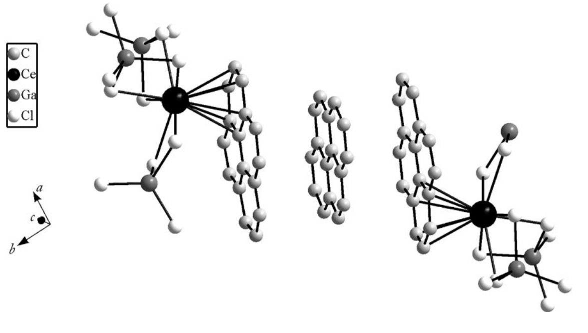


Figure 3. Two [Ce(pyrene)$(GaCl_4)_3$] molecules "sandwiching" a solvate pyrene molecule in the crystal structure of **7**.

It should be noted that the only crystallographically characterized lanthanide–pyrene complex [$(Cp^*La)_3(\mu\text{-}Cl)_3$(thf)(pyrene)] (where Cp* = C_5Me_5) contains the pyrene trianion coordinated to three Cp*La units in a μ:η^2:η^6:η^6 manner.[8] Thus, complex **7** represents the first lanthanide complex with a neutral pyrene ligand.

Conclusions

In the present work the preparation and single-crystal structural analyses of five new mono(arene) complexes [Ln(η^6-arene)$(GaX_4)_3$] [where Ln = Ce^{III}, Yb^{III}, and Dy^{III}] have been reported. A one-step synthesis – the reaction between gallium(III) halide and lanthanide(III) halide in an arene solution – allows the isolation of these complexes in high yields. It was found that the arene ligands may be substituted by polycyclic aromatic hydrocarbons, which indicates that complexes [Ln(η^6-arene)$(GaX_4)_3$] represent useful starting materials for the construction of more complex f-element compounds.

Experimental Section

General: Elemental analyses were performed with a JEOL JSM-6490LV scanning electron microscope (SEM) equipped with a JEOL EX-230 energy dispersive X-ray spectrometer (EDS). Measurements on [Ce(C_6H_5Me)$(GaCl_4)_3$] (**1**) yielded a Ce/Ga ratio of 24:76 in atom-%, while for [Ce(p-$C_6H_4Me_2$)$(GaCl_4)_3$]·0.5(p-$C_6H_4Me_2$) (**2**) the corresponding Ce/Ga ratio was found to be the expected 25:75 (experimental errors are within a tenth of the relative atom-%). Because of solvent evaporation under high vacuum conditions for the Dy and Yb compounds **3**–**5**, no reliable results could be obtained. Using the same conditions of synthesis as applied to the Ce, Dy, and Yb compounds, two Eu compounds could be isolated. Although no crystal structure determination could be completed, the compounds exhibited relative atomic ratios of Eu/Ga = 36:64 for the p-xylene compound and Eu/Ga = 33:67 for the toluene compound, which may indicate the presence of Eu^{II}.

^{13}C NMR and ^1H NMR spectra were recorded with a Bruker DMX 500 MHz spectrometer at 298 K in a $CDCl_3$ solution using TMS as the external reference. NMR spectra of the Dy and Eu compounds are not informative because of paramagnetic effects from non-paired f electrons. In the ^1H-NMR spectra of the Ce and Yb compounds there are numerous peaks around 7.5–8.0 ppm and 2–3 ppm, corresponding to aromatic and aliphatic protons, respectively. However, rotational freedom of the arene ligand prevents a detailed assignment of the NMR signals.

Preparation: All experiments were performed in a glove box under an inert atmosphere of deoxygenated and dried nitrogen (<1 ppm H_2O). In order to achieve the highest yield for all complexes the $LnCl_3/GaCl_3$ molar ratio 1:2 was used. In the case of Dy a ratio of Dy/Ga = 1:3 also resulted in a high yield (27%) in the form of large mm-scale crystals.

[Ce(C_6H_5Me)$(GaCl_4)_3$] (1): Toluene (3 mL) was added to the solid mixture of $CeCl_3$ (200 mg) and $GaCl_3$ (285 mg). The mixture was heated for 2 h (80–90 °C) whilst stirring with repeated additions of toluene. The reaction flask was wrapped in aluminium foil and set aside for 2 d. White crystals formed. Yield 43%.

[Ce(p-$C_6H_4Me_2$)$(GaCl_4)_3$]·0.5(p-$C_6H_4Me_2$) (2): Compound **2** was prepared in a manner similar to that of compound **1** (200 mg of $CeCl_3$ and 285 mg of $GaCl_3$), but using p-xylene (3 mL) instead of toluene. Time of heating was 1–2 h. White crystals were grown within 2 d with a yield of 37%.

[Yb(C_6H_5Me)$(GaCl_4)_3$] (3): Compound **3** was prepared in a manner similar to that of compound **1**, but using $GaCl_3$ (252 mg) and $YbCl_3$ (200 mg) instead of $CeCl_3$. Orange crystals were grown within 1 week. Yield 46%.

[Yb(p-$C_6H_4Me_2$)$(GaCl_4)_3$]·0.5(p-$C_6H_4Me_2$) (4): Compound **4** was prepared in a manner similar to that of compound **1**, but using $GaCl_3$ (252 mg), $YbCl_3$ (200 mg) and p-xylene (3 mL) instead of $CeCl_3$ and toluene. Orange crystals were grown within 1 week. Yield 31%.

[Dy(C_6H_5Me)$(GaBr_4)_3$] (5): Compound **5** was prepared in a manner similar to that of compound **1**, but using $GaBr_3$ (308 mg) and $DyBr_3$ (200 mg) instead of $CeCl_3$. White crystals were grown within 24 h. The yield is at least 20%.

[Ce(naphthalene)(GaCl$_4$)$_3$] (6): Complex **1** (90 mg, 0.104 mmol) was dissolved in 1,2,4-trichlorobenzene (3 mL), and naphthalene (120 mg, 0.94 mmol) was added to the solution. The mixture was heated for 3 h (80–90 °C) whilst stirring. The reaction flask was wrapped in aluminium foil and set aside for 2 d. Lemon-yellow crystals formed. Yield is approximately 10%.

[Ce(pyrene)(GaCl$_4$)$_3$]·0.5(pyrene) (7): Compound **7** was prepared in a manner similar to that of compound **6**, but using complex **1** (90 mg, 0.104 mmol) and pyrene (120 mg, 0.59 mmol) instead of naphthalene. Yellow needles were grown within 2 weeks. Yield is approximately 10%.

Table 3. Crystallographic data and experimental details of the X-ray studies of compounds **1**–**7**.

	1	**2**	**3**	**4**
Empirical formula	$C_7H_8CeCl_{12}Ga_3$	$C_{20}H_{25}Ce_2Cl_{24}Ga_6$	$C_7H_8Cl_{12}Ga_3Yb$	$C_{20}H_{25}Cl_{24}Ga_6Yb_2$
Lattice constants				
a [Å]	9.6967(10)	18.360(3)	9.6343(7)	18.152(2)
b [Å]	19.8942(14)	16.430(2)	19.6281(12)	16.2889(14)
c [Å]	12.8760(10)	20.127(5)	12.8404(12)	19.894(2)
β [°]	103.930(9)	113.737(11)	104.424(7)	113.438(7)
Cell volume [Å^3]	2410.8(4)	5557.8(18)	2351.6(3)	5396.9(10)
ρ(calcd.) [g cm^{-3}]	2.388	2.169	2.541	2.313
M_r [g mol^{-1}]	866.86	3629.52	899.78	1880.60
Z	4	4	4	4
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
T [K]	298	298	298	298
Diffractometer	Bruker-Nonius KappaCCD			
Radiation, λ [pm]	71.073			
Abs. coeff. [cm^{-1}]	64.9	56.4	87.0	75.8
Crystal size	0.81 × 0.77 × 0.65	0.71 × 0.62 × 0.28	0.40 × 0.30 × 0.20	0.52 × 0.43 × 0.36
Abs. corr.	numerical	numerical	numerical	multi-scan
Reflections	9291	61079	24388	31090
Unique refl., R_{int}	4212, 0.040	12074, 0.047	5362, 0.028	11083, 0.060
Parameters	208	469	208	469
R values	R_1 = 0.041 (3498 obsd. refl.) wR_2 = 0.099	R_1 = 0.044 (7761 obsd. refl.) wR_2 = 0.097	R_1 = 0.021 (4570 obsd. refl.) wR_2 = 0.039	R_1 = 0.054 wR_2 = 0.141
Goodness of fit	1.30	1.24	1.15	1.16
Flack parameter				
Largest electron density difference peak/hole [e Å^{-3}]	0.80/–0.63	0.97/–0.72	0.54/–0.43	2.17/–1.87

	5	**6**	**7**
Empirical formula	$C_7H_8Br_{12}DyGa_3$	$C_{10}H_8CeCl_{12}Ga_3$	$C_{24}H_{15}CeCl_{12}Ga_2$
Lattice constants			
a [Å]	10.0648(10)	9.8001(7)	13.7428(12)
b [Å]	20.5339(14)	13.5547(11)	12.0404(8)
c [Å]	13.4953(12)	19.9297(8)	21.4050(13)
β [°]	105.380(9)		96.893(6)
Cell volume [Å^3]	2689.2(4)	2647.4(3)	3516.3(4)
ρ(calcd.) [g cm^{-3}]	3.514	2.265	2.036
M_r [g mol^{-1}]	1422.71	902.89	1078.04
Z	4	4	4
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
T [K]	298	298	298
Diffractometer	Bruker-Nonius KappaCCD		
Radiation, λ [pm]	71.073		
Abs. coeff. [cm^{-1}]	235.4	59.2	44.7
Crystal size	0.36 × 0.24 × 0.19	0.98 × 0.54 × 0.50	0.38 × 0.25 × 0.22
Abs. corr.	numerical	numerical	numerical
Reflections	26491	8565	46322
Unique refl., R_{int}	6138, 0.067	3923, 0.044	8022, 0.065
Parameters	208	235	361
R values	R_1 = 0.049 (4479 obsd. refl.) wR_2 = 0.097	R_1 = 0.042 (2882 obsd. refl.) wR_2 = 0.098	R_1 = 0.042 (5324 obsd. refl.) wR_2 = 0.071
Goodness of fit	1.12	1.14	1.11
Flack parameter		–0.01(3)	
Largest electron density difference peak/hole [e Å^{-3}]	1.48/–1.36	0.73/–0.68	0.84/–0.61

Starting Materials: $GaCl_3$ (Aldrich Chemical Company, 99.99%, $H_2O < 100$ ppm), $GaBr_3$, (Alfa Aesar Company, 99.999%), $CeCl_3$ (Alfa Aesar Company, 99.9%), $YbCl_3$ (Aldrich Chemical Company, 99.9%), and $DyBr_3$ (Aldrich Chemical Company, 99.99%) were used as received.

Structure Determination: Because of the extreme sensitivity towards humidity, crystals of all compounds were sealed inside glass capillaries in a dry nitrogen atmosphere. Diffraction data were collected with a Bruker-Nonius KappaCCD diffractometer. Numerical absorption corrections were applied.[26] The structures were solved by direct methods[27] and refined on F^2 with anisotropic thermal parameters for all non-H atoms.[28] H atoms were refined on calculated positions using a riding model. Table 3 summarizes the results of the structure determinations.

CCDC-642443 (for **1**), -642444 (for **2**), -642447 (for **3**), -642448 (for **4**), -642445 (for **5**), -642449 (for **6**), and -642446 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The Swedish Science Council as well as Göran Gustafsson's Foundation are acknowledged for financial support.

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Received: August 13, 2008