RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

The 13 group metal complexes of sterically-hindered substituted iminophenol. Synthesis and structure.

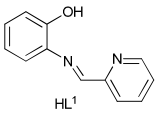
Elena N. Egorova,[*ab] **, Nikolay O. Druzhkov,**[a] **Andrey S. Shavyrin,**[a] **Anton V. Cherkasov,** [a] **Gleb A. Abakumov,**[ab] **and Alexey Yu. Fedorov** [b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The dimethyl derivatives of the 13 group metals I-IV were synthesized by interaction of the N-(1-(5,7-di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[d]oxazol-2-yl)ethylidene)-2,6-diisopropylaniline (**a**) with the Me_3M (M = Al (**I**), Ga (**II**), In (**III**), Tl (**IV**)) with high yield. The obtained complexes were characterized by elemental analysis, ^1H NMR, IR spectroscopy. The structures of **II-IV** were determined by X-ray single crystal analysis. The compounds **II-IV** were found to be monomeric in the solid state due to the bulkiness of the *tert*-butyl and *iso*-propyl groups in contrast to similar derivatives reported previously.

Introduction

Schiff base ligands have been extensively studied mainly due to their preparation accessibilities, structural varieties, easily tunable electronic properties and good solubility in common solvents [1–4]. Additionally, they are widely used as the antibacterial, antiviral, antifungal agents [5] and the anticancer drugs [6-7]. The versatility of the Schiff base ligands may be illustrated by the tridentate specie HL1 (Scheme 1) [8], which is known to form the complexes with Fe(III), Co(III), Ni(II), Zn(II), Cd(II), Ga(III), In(III) and lanthanide(III) ions [9–16]. The complexes of Zn(II), Cd(II), Ga(III) and In(III) show the intense luminescence at room temperature and thus have potential applications as a photoactive materials [9].



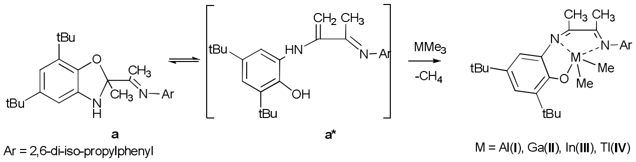
Scheme 1. Tridentate Schiff base ligand

The Schiff bases derived from a large number of carbonyl compounds and amines have already been known. However, the studies of their optical properties like luminescence are rare. Recently we have obtained new ligand N-(1-(5,7-di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[d]-oxazol-2-yl)ethylidene)-2,6-di-*iso*-propylaniline (**a**) based on 3-(2,6-di-*iso*-propylphenylimino)butan-2-one and 2-amino-4,6-di-*tert*-butylphenol. It have been shown that the compound **a** in solution exists in equilibrium with the enamine form containing hydroxy group [17]. In this paper we describe the synthetic details, spectral characteristics, X-ray crystal structures and luminescence properties of new 13 group metal complexes with aforementioned ligand **a**.

Results and discussion

Synthesis and characterization

The N-(1-(5,7-di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[d]oxazol-2-yl)ethylidene)-2,6-di-*iso*-propylaniline (**a**) was obtained by condensation of 2-amino-4,6-di-*tert*-butylphenol with 3-(2,6-di-*iso*-propylphenylimino)butan-2-one [17]. This compound (**a**) smoothly reacts with Me_3M (M = Al, Ga, In, Tl) at room temperature in the ether solution forming dimethylaluminium, dimethylgallium, dimethylindium, dimethylthallium complexes **I-IV** with high yields (see Scheme 2).



Scheme 2. The synthesis of the complexes **I-IV**.

The complexes **I-IV** were isolated as a violet or deep blue solids. The color of the complexes depends from the crystals dispersion of the compounds **II-IV**. Although the 13 group metal alkyl derivatives are extremely moisture and oxygen sensitive, the obtained compounds are fairly stable on the exposure to the air. The complexes could be left at the inert atmosphere for several months without obvious decomposition. The complexes are slightly soluble in the cold saturated hydrocarbons such as pentane or hexane and very soluble in the aromatic hydrocarbons and THF. It is interesting that the compounds **II** and **III** are stable when heated in either coordinating (THF) or non-coordinating (toluene) solvents under vacuum.

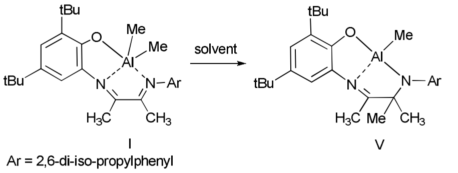
All obtained products gave satisfactory elemental analysis results corresponding to the stoichiometric structure Me_2ML [M=Al (**I**), Ga (**II**), In (**III**), Tl (**IV**), L = 2,4-di-*tert*-butyl-6-(3-(2,6-di-*iso*-propylphenylimino)butan-2-ylidene)amino) phenolato]. All of

RSC Advances Accepted Manuscript

compounds decompose at temperatures above 160 ºC without melting.

The obtained complexes have been characterized by IR and ^{1}H NMR spectroscopy. The IR spectra of the complexes **I-IV** feature the medium to strong distinctive C–H stretch vibration bands and the absence of the N–H signals unlike the IR spectra of free ligand **a**. The NMR signals of the metal bonded methyl protons in complexes **I-IV** (Al (-0.33 ppm), Ga (0.11 ppm), In (0.05 ppm), Tl (-0.08 and 0.5 ppm)) are shifted upfield in comparison with the signals of Me_3M (M = Al (-0.36 ppm) , Ga (-0.15 ppm), In (-0.24 ppm) in ^{1}H NMR spectra correspondingly.[18] It is supposed that the coordination of the nitrogen atom to the metal is responsible for the upfield shift of the methyl protons signals.

The confirmation of the molecular structure of the complexes **II-IV** and the determination of their monomeric or dimeric nature were provided by X-ray diffractometry. Unfortunately, we have not obtained the crystals of **I** suitable for X-ray analysis due to its rapid precipitation from the reaction mixture. Followed recrystallization of **I** from various solvents (THF, toluene) is accompanied by changing of the solution color from deep blue to brown and forming of the mixture of several products. The predominant one was found to be amidophenolate derivative **V** as a product of methyl group migration. Other products have not be identified.



Scheme 3. The transformation of the complex **I** in solution.

The formation of the amidophenolate **V** was proved by NMR. After treatment of **I** with THF or toluene during 3 days the two fold decreasing of the metal bonded methyl substituent signal intensity (3:9 methyl:*tert*-butyl ratio vs. 6:9 one for **I**) is observed in the ^{1}H NMR spectrum. Also, the additional ligand bonded methyl signal (2.37ppm) appears.

In the ^{13}C NMR spectrum the signal of the Al-Me group is observed at -7.3 ppm being shifted upfield in comparison with one for **I** (-6.82 ppm). Also, there is only one signal corresponding to C=N group (171.9 ppm) in the ^{13}C NMR spectrum. Finally, there are a lot of carbon signals in the aliphatic and aromatic area of the ^{13}C NMR spectrum which can not be unambiguously attributed.

X-Ray crystallographic study of II-IV

The results of the X-ray structure analysis show that the molecular structures of **II-IV** are similar. The molecular structure of **II** is depicted in Fig. 1. The crystal data and the collection and refinement parameters for **II-IV** are summarized in Table 1 and the selected interatomic distances (Å) and the bond angles (°) are given in Table 2.

X-Ray crystallographic study of II

Single crystals of **II** were obtained by cooling of a saturated ether solution. The complex **II** crystallizes in the monoclinic space group P(2)1/c. Although a few dimethylgallium complexes were found to be dimeric in the solid state [19-21], the compound **II** is

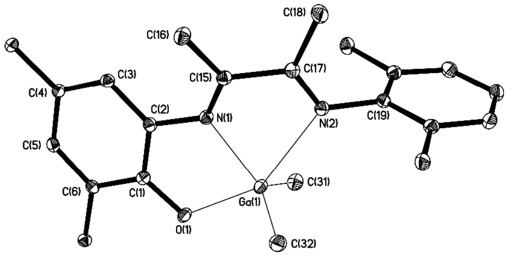


Fig. 1. The molecular structure of **II**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and Me-fragments of *^{i}Pr*-, *^{t}Bu*-groups are omitted.

Table 1. Crystallographic data and structure refinement details for **II-IV**.

	LGaMe$_2$ (**II**)	LInMe$_2$ (**III**)	LTlMe$_2$ (**IV**)
Formula	$C_{32}H_{49}GaN_2O$	$C_{32}H_{49}InN_2O$	$C_{32}H_{49}TlN_2O$
M_r	547.45	592.55	682.10
Crystal size, mm^3	0.10×0.10×0.05	0.53×0.20×0.07	0.28×0.18×0.05
T, K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/m*
a, Å	9.4025(4)	9.3801(7)	9.4850(6)
b, Å	9.5037(4)	9.5414(7)	9.6118(6)
c, Å	34.1500(1)	34.908(3)	17.0918(1)
α, °	90	90	90
β, °	95.9760(1)	97.4420(1)	98.300(1)
γ, °	90	90	90
Cell volume, Å^3	3035.0(2)	3097.9(4)	1541.90(2)
Z	4	4	2
D_{calc}, g/cm^3	1.198	1.270	1.469
μ, mm^{-1}	0.932	0.788	5.262
F_{000}	1176	1248	688
2θ range, °	52	52	54
Index ranges	-11<=h<=11	-11<=h<=11	-12<=h<=12
	-11<=k<=11	-11<=k<=11	-12<=k<=12
	-42<=l<=42	-43<=l<=43	-21<=l<=21
Reflns collected	25545	25613	14206
Independent reflns	5958	6058	3567
R_{int}	0.0194	0.0403	0.0211
Completness to θ	99.9	99.2	99.9
Data, restraints and parameters	5958 / 0 / 338	6058 / 12 / 352	3567 / 6 / 336
GooF	1.032	1.158	1.084
R_1 (I>2σ(I))	0.0297	0.0434	0.0167
wR_2 (all data)	0.0742	0.1029	0.0399
Largest diff. peak and hole	0.509 / -0.343	2.066 / -1.054	1.501 / -0.619

RSC Advances Accepted Manuscript

Table 2. Selected distances [Å] and angles [°] of complexes **II**-**IV** (M = Ga (**II**), In (**III**), Tl (**IV**)).

	LGaMe$_2$ (**II**)	LInMe$_2$ (**III**)	LTlMe$_2$ (**IV**)
C(1)-O(1)	1.305(2)	1.307(3)	1.321(3)
C(2)- N(1)	1.403(2)	1.397(3)	1.401(3)
C(1)-C(2)	1.424(2)	1.423(4)	1.439(4)
C(15)-N(1)	1.299(2)	1.298(3)	1.295(3)
C(17)-N(2)	1.278(2)	1.277(3)	1.271(3)
C(15)-C(17)	1.496(5)	1.499(4)	1.500(4)
O(1)-M(1)	1.998(1)	2.196(2)	2.328(2)
N(1)-M(1)	2.099(1)	2.320(2)	2.507(2)
N(2)-M(1)	2.402(1)	2.463(2)	2.634(2)
O(1)-M(1)-N(1)	79.20(5)	72.71(7)	68.90(7)
N(1)-M(1)-N(2)	70.83(5)	67.57(8)	62.91(7)
O(1)-M(1)-N(2)	149.84(4)	140.18(7)	131.80(7)
C(31)-M(1)-C(32)	129.27(7)	136.4(1)	160.7(1)

monomeric. The gallium atom is five coordinated with distorted trigonal bipyramidal environment. In compound **II** the nitrogen atoms N(1) and N(2) coordinate to the gallium atom forming intramolecular five-membered rings.Metallacycle Ga(1)N(1)C(15)C(17)N(2) is non planar, the angle between the Ga(1)N(1)N(2) and N(1)C(15)C(17)N(2) planes is 159.5°. Another five-membered ring is formed by Ga(1), O(1), C(1), C(2) and N(1) atoms; this one is planar (maximum deviation of atoms from the plane doesn't exceed 0.1 Å). The Ga(1)-O(1) bond length (1.998(1) Å) is slightly longer than those ones in 4-(N,N-demethylaminophenolato) dimethylgallium (1.911(2) Å) [19], [3,4-dimethoxyphenylmethyleneimino phenolato] dimethyl gallium (1.921(2) Å) [20], (quinolin-8-olate) dimethylgallium (1.868(2) Å) [21], [N-salicylidene-2-aminopyridine] dimethylgallium (1.917(2) Å) [22], bis(3,5-di-*tert*-butyl-2-((pyridin-2-ylmethylimino)methyl)phenolate) gallium (1.899(2) Å) [23], N,N-ethylene(salicylideneiminato) bis[dimethylgallium] (1.886(2) Å) [24] and shorter than those ones in (1-(2-piridyl) methyleneimino-2-naphthonato) dimethylgallium (2.002(4) Å) [25]. It should be noted that the latter compound exists like **II** in a monomeric form in the solid state due to the steric hindrances of the naphthyl moiety. The Ga–N distances (2.099(1) Å for Ga(1)–N(1) and 2.402(1) Å for Ga(1)–N(2)) in **II** are slightly shorter than those ones reported in [20, 22-25 (2.136(2) - 2.316(3) Å)] for Ga(1)-N(1) and are longer than those ones in compound obtained in [23, 24] for Ga(1)-N(2) respectively. These bond distances indicate that the nitrogen atoms are datively bounded to the gallium atom. The difference in Ga–O and Ga–N lengths between the present compound (**II**) and other ones should be caused by the steric bulkiness two *tert*-butyl and two *iso*-propyl groups.

The distances C–C and C–N (C(15)–C(17) 1.496(5) Å, N(1)–C(15) 1.299(2) Å, N(2)–C(17) 1.278(2) Å) forming the diazadiene moiety are corresponding to the bond orders of one and two, respectively.

Crystal structure determination of compounds III and IV

The crystals of **III** and **IV** suitable for structural determination were obtained from concentrated hexane solution.

The compound **III** was found to be isomorphic to **II**. The structure of the complex **IV** was resolved and refined in the monoclinic space group *P(2)1/m* with the cell volume (V = 1541.90(2) Å^3, c = 17.0918(1) Å) is a half of the cell volume of **II** and **III** (**II**: V = 3035.0(2) Å^3, c = 34.1500(1) Å, **III**: V = 3097.9(4) Å^3, c = 34.908(3) Å). The asymmetric unit cell in **IV** contains one molecule disordered over two sites. Geometry parameters of the molecules **II**-**IV** are close to each other. The distances In-O (2.196(2) Å), In-N (2.320(2), 2.463(2) Å) in **III** and Tl-O (2.328(2) Å), Tl-N (2.507(2), 2.634(2) Å) in **IV** are slightly longer than those ones in **II** (Ga-O: 1.998(1) Å, Ga-N: 2.099(1), 2.402(1) Å) due to the larger covalent radii of indium (1.42 Å) and thallium (1.45 Å) respectively in comparison with gallium (1.22 Å) [26]. The bond values of the ligand in **III** and **IV** are corresponding with those in **II** (Table 2). As for **II**, the metallacycles MNCCN in **III** and **IV** are non planar. The angles between the MNN and NCCN planes are 159.6° (**III**) and 157.5° (**IV**) respectively. It could be noted that MOCCNCCN fragments in **III** and **IV** are less distorted in comparison **II**. The angles between MOCCN and MNCCN planes are 167.9° (**II**), 169.7° (**III**) and 169.3° (**IV**) respectively.

It should be also noted that the compound **III** is a monomeric in the solid state in contrast to similar indium compound [27, 28] as a result of the presence of sterically hindered *tert*-butyl and *iso*-propyl groups in the structure.

Caution! Thallium and its compounds are toxic and must be handled with care.

Electrochemical study

On the assumption of the crystal structure determination of the compounds **II**-**IV** we have shown that **II**-**IV** contain coordinated diazadiene moiety which is potentially able to the one electron reduction. The electrochemical study of **IV** have been performed to estimate this possibility (compound **IV** was selected due to the absence of any reactivity of the metal bonded methyl groups).

The cyclic voltammetric study of the complex **IV** was performed using CH_2Cl_2 as a solvent and tetrabutylammonium perchlorate as supporting electrolyte at the scan rate of 0.2 V*s^{-1}. One irreversible reductive response at -1.60 V versus Ag/AgCl/KCl electrode was tentatively assigned to the reduction of coordinated diazadiene fragment of the ligand. The reduction is accompanied by the strong adsorption of reaction products on the electrode surface therefore the evaluation of the electron number and the electrochemical reaction reversibility were complicated. At higher reductive response (-2.054 V) the irreversible reduction of the metal ion is observed.

Photoluminescence (PL) determination

The PL emission spectra of the complexes **III** and **IV** were measured as shown on the Fig. 2. The compounds **III** and **IV** possess an intense photoluminescence properties at room temperature, which were not observed for **I** and **II**. The PL emission data shows that the emission bands are located in the violet region. Their emission maxima lies at 402 and 405 nm with the intensities of 458 and 340 a.u. for complexes **IV** and **III** respectively.

RSC Advances Accepted Manuscript

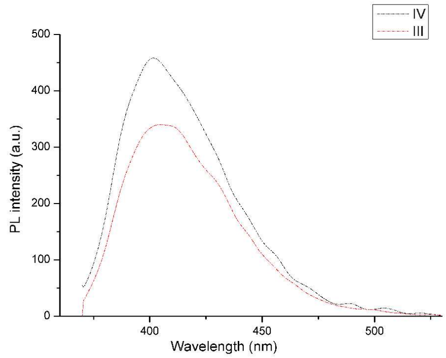


Fig. 2. PL emission spectra of **III** and **IV** (THF, 3.15*10^{-6} mol/l)

Conclusions

In the present work we have described the synthesis of dimethyl derivatives of 13 group metals **I**-**IV**. All of obtained complexes were characterized by elemental analysis, NMR and IR spectroscopy. The structures of gallium, indium and thallium compounds **II**-**IV** were determined by X-ray single crystal analysis. The compounds **II**-**IV** were found to be a monomeric in the solid state due to the bulkiness of the *tert*-butyl and *iso*-propyl groups unlike earlier reported derivatives [19-25]. We have reported that aluminium derivative **I** after recrystallization from various solvents (THF, toluene) undergoes the migration of the methyl group from the metal atom to C=N group of the ligand with the formation of the amidophenolate derivative **V**. We have found that **III** and **IV** possess an intense photoluminescence at room temperature, which was not observed for **I** and **II**. It is suggested that complexes **III** and **IV** may be potentially used as a photoactive materials.

Experimental

General comments

N-(1-(5,7-Di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[d]-oxazol-2-yl)ethylidene)-2,6-di-*iso*-propylaniline (**a**) [17] and Me$_3$Tl [29] were prepared according to previously described procedures. Solvents were freshly purified by standard methods [30]. The Me$_3$M (M=Al, Ga, In) were used as purchased. All syntheses have been provided in evacuated ampoules.

The NMR spectra were recorded on a “Bruker Avance III” NMR spectrometer (400 MHz) using C$_6$D$_6$ as the solvent with tetramethylsilane as the internal standard. IR-spectra were recorded by “Specord M-80”. Elemental analyses were obtained on “EuroEA-3028-HT”. Metal atom percentage was estimated by the pyrolysis of the investigated samples with the followed weighing of the obtained oxides. The PL spectra were recorded on UV - spectrometer “Perkin Elmer UV/VIS Lambda 25” at room temperature.

Electrochemical studies were carried out using an IPC-pro potentiostate in three electrode mode. The glassy carbon (d = 2 mm) disk was used as working electrode; the auxiliary electrode was a platinum-flag electrode. The reference electrode was an Ag/AgCl/KCl (sat.) with watertight diaphragm. All measurements were carried out under argon. The samples were dissolved in the pre-deaerated solvent. The rate scan was 200 mVs^{-1}. The supporting electrolyte 0.1 M [(*n*-Bu)$_4$N]ClO$_4$ (99%, ‘‘Acros”) was doubly recrystallized from the aqueous ethanol and was dried in vacuum at 50°C for 48 h.

The X-ray data for **II**-**IV** were collected on a Bruker Smart Apex diffractometer (graphite-monochromated, MoKα-radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K). The structures were resolved by direct methods and were refined on F2 using SHELXTL [31] package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS [32] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in Table 1 and corresponding CIF files are available in supporting information. CCDC-1034759 (**II**), 1034760 (**III**), 1034761 (**IV**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge.

Synthesis

Dimethyl aluminium (2,4-di-*tert*-butyl-6-(3-(2,6-diisopropylphenylimino)butan-2-ylidene)aminophenolate) (I)

Me$_3$Al (0.144g, 2 mmol) was added to a solution of a (0.898 g, 2 mmol) in diethyl ether (30 mL). The color immediately changed from colorless to deep blue. The reaction mixture was stirred during 30 min at room temperature, all volatiles were removed and the deep blue crystals were isolated after cooling.

Yields: 0.879 g (87%, based on Me$_3$Al). Found (%): C, 76.21; H, 9.82; Al, 5.36; N, 5.48. Calculated for C$_{32}$H$_{49}$AlN$_2$O (%): C, 76.15; H, 9.79; Al, 5.35; N, 5.55. ^{1}H NMR (C$_6$D$_6$, δ/ppm, J/Hz): -0.33 (s, 6H, CH$_3$Al); 0.91 (d, 6H, (CH$_3$)$_2$CH, J=6.85); 1.29 (d, 6H, (CH$_3$)$_2$CH, J=6.85); 1.36 (s, 9H, tBu); 1.52 (s, 3H, CH$_3$); 1.71 (s, 9H, tBu); 1.80 (s, 3H, CH$_3$); 2.78 (sept, 2H, (CH$_3$)$_2$CH, J=6.85); 7.08-7.13 (m, 3H, H$_{arom}$); 7.20 (d, 1H, H$_{AmPh}$, J=2.22); 7.61 (d, 1H, H$_{AmPh}$, J=2.22). ^{13}C NMR (C$_6$D$_6$, δ /ppm): -6.82 ((CH$_3$)$_2$Al); 18.20; 19.54; 24.00; 24.51; 28.18; 29.04; 31.13; 34.01; 35.35; 115.61; 124.27; 126.90; 130.90; 136.40; 139.87; 141.99; 149.26; 164.32 (C=N); 168.77 (C=N). IR (nujol, ν/cm^{-1}): 465w, 510w, 550m, 589w, 613w, 664s, 683m, 721m, 742m, 770m, 784m, 798s, 847s, 865m, 900w, 919m, 935w, 943w, 982m, 1027w, 1055w, 1134s, 1171s, 1197m, 1209m, 1239m, 1258s, 1307m, 1333m, 1363s, 1443s, 1515s, 1562w, 1627m, 1707w.

Dimethyl gallium (2,4-di-*tert*-butyl-6-(3-(2,6-diisopropylphenylimino)butan-2-ylidene)aminophenolate (II)

Prepared as described for **I** from **a** (0.898 g, 2 mmol) and trimethylgallium (0.23 g, 2 mmol). Complex **II** was isolated as violet crystals from Et$_2$O.

Yields: 0.910 g (83%, based on Me$_3$Ga). Found (%): C, 70.25; H, 9.08; Ga, 12.71; N, 5.08. Calculated for C$_{32}$H$_{49}$GaN$_2$O (%): C, 70.20; H, 9.02; Ga, 12.74; N, 5.12. IR (nujol, ν/cm^{-1}): 491w, 515w, 535w, 592m, 612w, 636w, 654w, 677w, 740s, 781s, 790s, 843m, 864m, 911m, 935w, 976s, 1027w, 1050w, 1124s, 1162s, 1192s, 1240s, 1260s, 1308s, 1331m, 1358s, 1376s, 1508m, 1556w, 1598w, 1633m. ^{1}H NMR (C$_6$D$_6$, δ /ppm, J/Hz): 0.11 (s, 6H, (CH$_3$)$_2$Ga); 0.94 (d, 6H, (CH$_3$)$_2$CH, J=6.84); 1.21 (d, 6H, (CH$_3$)$_2$CH, J=6.84); 1.35 (s, 9H, tBu); 1.53 (s, 3H, CH$_3$); 1.76 (s, 9H, tBu); 2.01 (s, 3H, CH$_3$); 2.66 (sept, 2H, (CH$_3$)$_2$CH, J=6.84); 7.06-7.11 (m, 4H, H$_{arom}$); 7.50 (d, 1H, H$_{arom}$, J=2.29). ^{13}C NMR

RSC Advances Accepted Manuscript

(C_6D6, δ /ppm): -4.22 ($(CH_3)_2Ga$); 19.72; 20.45; 23.78; 24.34; 28.02; 29.25; 29.59; 31.50; 31.65; 116.37; 123.98; 126.00; 126.92; 130.39; 134.53; 137.99; 140.10; 142.86; 153.56; 164.85 (C=N); 165.56 (C=N).

Dimethyl indium (2,4-di-*tert*-butyl-6-(3-(2,6-diisopropylphenylimino)butan-2-ylidene)aminophenolate (III)

Prepared as described for **I** from **a** (0.898 g, 2 mmol) and trimethylindium (0.32 g, 2 mmol). After the removal of ether in vacuo, hexane was added to the crude product. Complex **III** was isolated as deep blue crystals from hexane.

Yield: 1.020 g (86%, based on Me_3In). Found (%): C, 64.89; H, 8.37; In, 19.39; N, 4.69. Calculated for $C_{32}H_{49}InN_2O$ (%): C, 64.86; H, 8.33; In, 19.38; N, 4.73. ^{1}H NMR (C_6D_6, δ/ppm, J/Hz): 0.05 (s, 6H, (CH_3)2In); 0.87 (d, 6H, $(CH_3)_2CH$, J=7.8); 1.15 (d, 6H, $(CH_3)_2CH$, J=7.8); 1.37 (s, 9H, tBu); 1.48 (s, 3H, CH_3); 1.80 (s, 9H, tBu); 1.94 (s, 3H, CH_3); 2.63 (sept, 2H, $(CH_3)_2CH$, J=7.8); 7.02-7.60 (m, 5H, H_{arom}). ^{13}C NMR (C_6D_6, δ/ppm): -6.11 (CH3)2In); 20.09; 20.21; 23.88; 24.29; 28.01; 29.37; 31.44; 31.64; 34.03; 35.75; 116.61; 124.03; 126.39; 126.92; 130.53; 133.40; 138.65; 141.17; 142.03; 150.34; 166.67 (C=N); 168.74 (C=N). IR (nujol, ν/cm^{-1}): 487s, 528s, 547w, 587m, 601m, 634w, 649w, 665w, 710s, 760w, 781s, 791s, 840s, 871s, 911s, 935m, 975s, 1004w, 1025w, 1056w, 1125s, 1160s, 1189s, 1200s, 1236m, 1255s, 1283w, 1305m, 1335m, 1366w, 1409w, 1506s, 1534w, 1553m, 1601w, 1629m.

Dimethyl tallium (2,4-di-*tert*-butyl-6-(3-(2,6-diisopropylphenylimino)butan-2-ylidene)aminophenolate (IV)

Prepared as described for **III** from **a** (0.898 g, 2 mmol) and trimethylthallium (0.498 g, 2 mmol). Complex **IV** was isolated as deep blue crystals from hexane.

Yield: 1.118 g (82%, based on Me_3Tl).). Found (%): C, 56.38; H, 7.27; N, 4.06; Tl, 29.95. Calculated for $C_{32}H_{49}N_2OTl$ (%): C, 56.34; H, 7.24; N, 4.11; Tl, 29.96. IR (nujol, ν/cm^{-1}): 1631m (C=N), 1593m, 1547m, 1502s, 1364m, 1326m, 1303s, 1277s, 1255s, 1232s, 1190s, 1160s, 1119s, 1051w, 1025w, 976s, 939m, 908m, 871s, 841m, 777s, 732m, 641w, 585m, 532m, 510w, 476m. ^{1}H NMR (C_6D_6, 400 MHz, δ/ppm, J/Hz): 0.41 (br s, 3H, $Tl(CH_3)_2$); 1.03 (d, 6H, $(CH_3)_2CH$, J=6.83); 1.20 (d, 6H, $(CH_3)_2CH$, J=6.83); 1.39 (br s, 3H, $Tl(CH_3)_2$); 1.51 (s, 9H, tBu); 1.61 (s, 3H, CH_3); 1.99 (s, 9H, tBu); 2.18 (s, 3H, CH_3); 2.70 (sept, 2H, $(CH_3)_2CH$, J=6.83); 6.99 (d, 1H, H_{AmPh}, J=2.52); 7.26 (m, 3H, H_{arom}); 7.70 (d, 1H, H_{arom}, J=2.52). ^{13}C NMR (C_6D_6, δ/ppm): 14.35 $(CH_3)_2Tl$); 19.96 (CH_3); 21.22 (CH_3); 24.04 ($(CH_3)_2CH$); 27.79 ($(CH_3)_2CH$); 29.74 ($(CH_3)_3CH$); 31.83 ($(CH_3)_2CH$); 33.95 ($(CH_3)_2CH$); 35.83 ($(CH_3)_2CH$); 107.38; 114.53; 117.35; 123.83; 125.12; 125.35; 131.66; 133.88; 137.33; 141.45; 143.81; 155.31 (C=N); 168.24 (C=N).

Methyl aluminium (2,4-di-*tert*-butyl-6-(3-(2,6-diisopropylphenylimido)butan-2-ylidene)aminophenolate (V)

The complex **I** was dissolved in THF/toluene. The blue color disappears during several hours. Solvent was removed in vacuum and residue was dissolved in C_6D_6.

^{1}H NMR (C_6D_6, δ/ppm, J/Hz): -0.27 (s, 3H, $(CH_3)Al$); 1.01 (d, 6H, $(CH_3)_2CH$, J=6.45); 1.05 (d, 6H, $(CH_3)_2CH$, J=6.45); 1.1 (s, 9H, tBu); 1.27 (s, 9H, tBu); 1.67 (s, 6H, $(CH_3)_{amide}$); 2.37 (s, 3H, CH_3); 2.54 (sept, 2H, $(CH_3)_2CH$, J=6.45); 7.00-7.12 (m, 5H, H_{arom}).

Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research (projects no. 13-03-97103r_povoljie_a, 14-03-31071_mol_a), the Council for Grants of the President of Russian Federation for Support of Leading Scientific Schools (grant no. NSh 271.2014.3) and Fund competitive support to students, graduate students and young researchers and teachers UNN.

Notes and references

[a] *G.A. Razuvaev Institute of Organometallic Chemistry RAS, Tropinina str. 49, 603950, Nizhny Novgorod, Russia. E-mail: ee@iomc.ras.ru; Fax: +7 8312 4627497; Tel: +7 8312 4627682*

[b] *Lobachevsky State University of Nizhny Novgorod, Gagarin Ave. 23/5, 603950, Nizhny Novgorod, Russia*

† CCDC-1034759 (**II**), 1034760 (**III**), 1034761 (**IV**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

1. G. van Koten and K. Vrieze, *Advances in Organometallic Chemistry*, ed. F. G. A. Stone and R. West, Acad. Press, New York, London, 1982, **21**, 152.
2. L.F. Lindoy and S.E. Livingstone, *Coord. Chem. Rev.*, 1967, **2**, 173.
3. P. Preishuber-Pflugl and M. Brookhart, *Macromolecules*, 2002, **35**, 6074.
4. D.J. Tempel, L.K. Johnson, R.L. Huff, P.S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2000, **122**, 6686.
5. S. Chandra and X. Sangeetika, *Spectrochim. Acta,* 2004, **60**, 147.
6. D. Kessel, A.F.A. Sayyab, E.M.H. Jaffar and A.H.H.A. Lanil, *Iraqi J. Sci.,* 1981, **22**, 312.
7. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, 1970, **13**, 768.
8. A.R. Stefankiewicz, M. Wałęsa-Chorab, H.B. Szcześniak, V. Patroniak, M. Kubicki, Z. Hnatejko and J. Harrowfield, *Polyhedron,* 2010, **29**, 178.
9. A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay and S. Mitra, *Polyhedron,* 2006, **25**, 1753.
10. G. Juhasz, S. Hayami, O. Sato and Y. Maeda, *Chem. Phys. Lett.*, 2002, **364**, 164.
11. S. Hayami and Y. Maeda, *Inorg. Chim. Acta,* 1997, **255**, 181.
12. J.R. Dilworth, S.D. Howe, A.J. Hutson, J.R. Miller, J. Silver, R.M. Thompson, M. Harman and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1994, 3553.
13. S. P. Mukhopadhyay, *J. Chem., Crystallogr.*, 2005, **35**, 737.
14. N. Reddig, M.U. Triller, D. Pursche, A. Rompel and B. Krebs, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2458.
15. D.M. Epstein, S. Choudhary, M.R. Churchill, K.M. Keil, A.V. Eliseev and J.R. Morrow, *Inorg. Chem.*, 2001, **40**, 1591.
16. V. Patroniak, A.R. Stefankiewicz, J.-M. Lehn, M. Kubicki and M. Hoffmann, *Eur. J. Inorg. Chem.,* 2006, 144.
17. G.A. Abakumov, N.O. Druzhkov, E.N. Egorova, T.N. Kocherova, A.S. Shavyrin and A.V. Cherkasov, *RSC Adv.*, 2014, **4**, 14495.
18. S.J. Schauer, C.L. Watkins and L.K. Krannich

RSC Advances Accepted Manuscript

Polyhedron, 1995, 14, 3505.
19. Y. Shen, Y. Wang, Y. Zhang, Y. Li, X. Tao and H. Xu, *J. Organomet. Chem.,* 2007, **692**, 5345.
20. Y. Zhang, Y. Shen, Y. Li, Y. Wang, Y. Li, X. Tao and H. Xu, *Inorg. Chim. Acta,* 2008, **361**, 2279.
21. D.G. Hendershot, M. Barber, R. Kumar and J.P. Oliver, *Organometallics,* 1991, **10**, 3302.
22. Y.-Z. Shen, H. Gu, Y. Pan, G. Dong, T. Wu, X.-P. Jin, X.-Y. Huang and H. Hu, *J. Organomet. Chem.,* 2000, **605**, 234.
23. C. Imbert, H.P. Hratchian, M. Lanznaster, M.J. Heeg, L.M. Hryhorczuk, B.R. McGarvey, H.B. Schlegel and C.N. Verani, *Inorg. Chem.,* 2005, **44**, 7414.
24. K.S. Chongs, T.J. Rettig, A. Storr and J. Trotter, *CAN. J. CHEM.,* 1977, **55**, 2540.
25. Y. Shen, H. Gu, Y. Zhu and Y. Pan, *J. Organomet. Chem.,* 2006, **691**, 1817.
26. B. Cordero, V. Gómez, A.E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832.
27. A. Acosta-Ramirez, A.F. Douglas, I. Yu, B.O. Patrick, P.L. Diaconescu and P. Mehrkhodavandi, *Inorg. Chem.*, 2010, **49**, 5444.
28. T.-Y. Chou, Y. Chi, S.-F. Huang and C.-S. Liu, *Inorg. Chem.*, 2003, **42**, 6041.
29. H. Gilman and R.G. Jones, *J. Am. Chem. Soc.*, 1946, **68**, 517.
30. D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1980.
31. G. M. Sheldrick, Structure Determination Software Suite, SHELXTL v.6.12, Bruker AXS, Madison, Wisconsin, USA, 2000.
32. G.M. Sheldrick, Bruker/Siemens Area Detector Absorption Correction Program, SADABS v.2.01, Bruker AXS, Madison, Wisconsin, USA, 1998.

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry [year]