Gallium Complexes with Acenaphthene-1-Imino-2-one: Synthesis and Reactivity

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Abstract—The reduction of acenaphthene-1-(2,6-diisopropylphenyl)imino-2-one (Dpp-Mian) by gallium in the presence of iodine primarily results in a bis(ligand) paramagnetic derivative $[(Dpp-Mian)_2GaI]$ and then to a dimeric diamagnetic complex $[(Dpp-Mian)GaI]_2$, the reaction of which with PhC=CH gives a cyc-loaddition product $[\{Dpp-Mian(HC=CPh)\}GaI]_2$. The new compounds are characterized by IR spectros-copy and ¹H NMR spectroscopy. The structures of complexes (Dpp-Mian)_2GaI and $[\{Dpp-Mian(HC=CPh)\}GaI]_2$ are determined by X-ray structure analysis (CIF files CCDC nos. 1571860 and 1571861, respectively). The catalytic activity tests for compounds $[(Dpp-Mian)GaI]_2$ and $[\{Dpp-Mian(HC=CPh)\}GaI]_2$ are conducted in the reactions of 4-chloroaniline with phenylacetylene and carbodiimide and in the reaction of phenylacetylene with 1-naphthol.

Keywords: gallium, N,O-ligands, synthesis, structure, X-ray structure analysis, hydroamination and hydroarylation of unsaturated substrates

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INTRODUCTION

The cycloaddition of unsaturated substrates to transition metal complexes with the neutral 1,4-diaza-1,3-diene or 1,4-dihetero-1,3-diene ligand was described [1]. For example, the iron and ruthenium complexes with ketoimine ligands react with activated alkynes to form stable cycloadducts.



 $E' = CO_2Me; L = CO; PR_3; Dppe$

An interesting feature of these reactions is substrate binding not only with the metal center but also with the ligand due to carbon–carbon bond formation. Similar processes were also observed for the reactions of aromatic ketones with the zirconium [2] and samarium [3] complexes containing dianions of 1,4-diaza-1,3-dienes. Cycloaddition for the nontransition metal complex (Dpp-Bian)Ga– Ga(Dpp-Bian) (I) (Dpp-Bian is 2,6-(diisopropylphenylimino)acenaphthene) has first been discovered in 2010. Compound I reacts with diverse alkynes to form stable cycloadducts [4, 5].



Ar = 2,6-diisopropylphenyl; R = H, R' = H; R = Ph; R' = H; $R = CH_3$, $R' = C(O)OCH_3$

A unique specific feature of the cycloaddition of alkynes to complex I is the complete reversibility of the process, which phenomenologically resembles the π -coordination of unsaturated organic molecules by transition metal compounds. Later these processes were carried out on the aluminum compounds and mononuclear gallium derivatives containing diimine ligands. The reactivity of compounds of this class toward alkynes depends on both the metal nature and the type of the functionally labile ligand bound to the metal. For example, dialane (Dpp-Bian)Al-Al(Dpp-Bian) [6] and its 1,4-diaza-1,3-diene analog [7] are more reactive in the reactions with alkynes than digallane I. Complex (Dpp-Bian)Al-Al(Dpp-Bian) adds methylphenylacetylene toward which digallane I is inert. The mononuclear derivatives (Dpp-Bian)AlEt(Et₂O) and (Dpp-Bian)Ga(S_2CNMe_2) also react with alkynes to form cycloadducts. In addition, the latter can reversibly add methyl vinyl ketone [8, 9].

Unlike digallane I, the magnesium acenaphthene-1,2-diimine complex (Dpp-Bian)Mg(Thf)₃ (II) (Thf is tetrahydrofuran) in the reaction with phenylacetylene behaves as a frustrated Lewis pair [10-12] to give the alkynylmagnesium derivative coordinating the protonated amidoamine Dpp-Bian ligand [13].





The ability of complex I to "coordinate" phenylacetylene makes it possible to carry out the hydroamination and hydroarylation of this alkyne by anilines and 1-naphthol, respectively, in the presence of catalytic amounts of compound I [5, 14]. In addition, complex I catalyzes the addition of anilines to carbodiimides [15]. In turn, magnesium derivative II is an efficient catalyst of the polymerization of lactides with ring opening [16] and of the hydroamination of some olefins by pyrrolidine [17].

Monoiminoquinones represent a transition structure from *o*-quinones to α -diimines. The properties of monoiminoquinones, primarily, the redox potentials and steric volume, have an intermediate character, which allows one to expect the formation of new types of complexes containing one or two redox-active ligands in the same or in different reduction states and demonstrating new types of reactivity. From the viewpoint of preparing complexes of the new class, the monoiminoacenaphthenone ligands capable of multielectron reducing similarly to acenaphthene-1,2diimines seems promising. We have previously synthesized and characterized a series of the complexes with neutral Dpp-Mian [18]. Magnesium amidoalkoxide $[(Dpp-Mian)Mg(Thf)_2]_2$ (III) was synthesized by reduction with magnesium [19]. Compound III is the first acenaphthenequinoneimine derivative of the nontransition metal and the first metal complex containing the Dpp-Mian ligand in the reduced form. The reaction of compound III with phenylacetylene illustrates brightly the important role of redox-active ligands in imparting these or other chemical properties to the complexes with nontransition metals. Unlike related compound II, complex III reacts with phenylacetylene to give cycloadduct [(Dpp-Mian)(PhC=CH)Mg(Thf)] (IV) similarly to digallane I. The reaction of cycloadduct IV with the second equiv mol PhC≡CH affords the phenylethynyl derivative [(Dpp-Mian)-(PhC=CH₂)- $Mg(C \equiv CPh)(Thf)_2(V).$



We attempted to synthesize new gallium complexes with Dpp-Mian in order to extend concepts on the properties of metal complexes with redox-active ligands. In this work, we report the synthesis of the gallium derivatives containing Dpp-Mian in various redox states [(Dpp-Mian)₂GaI] (VI), [(Dpp-Mian)-GaI]₂ (VII), and [{Dpp-Mian(HC=CPh)}GaI]₂ (VIII) and the results of identification of the synthesized compounds in a solution using ¹H NMR spectroscopy, determination of their molecular structures in the crystalline state by X-ray structure method, and investigation of the catalytic properties of the compounds obtained.

EXPERIMENTAL

All procedures with unstable compounds VI, VII, and VIII were carried out in vacuo or in an inert nitrogen atmosphere using the Schlenk technique. Solvents (involving deuterated solvents) were dried over sodium benzophenone ketyl and were taken by condensation in vacuo prior to use. Compound Dpp-Mian was obtained by a described procedure [19]. IR spectra were recorded on an FSM-1201 spectrometer, and ¹H NMR spectra were measured on a Bruker DPX 200 spectrometer.

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Synthesis of [(Dpp-Mian)₂GaI] (VI). A solution of Dpp-Mian (0.34 g, 1.0 mmol) and iodine (0.06 g, 0.5 mmol) in diethyl ether (15 mL) was poured to a metallic gallium excess (3.0 g). Then the mixture was heated in a water bath for 1 h. The color of the solution gradually changed from red-orange to green. The obtained solution was decanted. Compound VI was crystallized from diethyl ether as green crystals. The yield was 0.38 g (80%), mp = 181° C.

For $C_{52}H_{56}N_2O_3I$	Ga		
Anal. calcd., %	C, 65.49	Н, 5.92	N, 2.94
Found, %	C, 65.56	H, 5.88	N, 2.91

IR (v, cm⁻¹): 1931 w, 1876 w, 1814 w, 1742 w, 1600 m, 1525 m, 1320 m, 1252 w, 1194 w, 1111 w, 1099 w, 1089 w, 1057 w, 1033 m, 972 w, 948 m, 939 m, 911 w, 899 w, 829 m, 818 m, 806 m, 776 m, 766 s, 683 m, 636 m, 590 m, 576 m, 540 w, 520 w, 493 w, 457 w.

Synthesis of [(Dpp-Mian)GaI]₂ (VII). A solution of Dpp-Mian (0.34 g, 1.0 mmol) and iodine (0.13 g, 1.0 mmol) in diethyl ether (15 mL) was poured to a metallic gallium excess (3.0 g). On heating in a water bath for 1.5 h, the color of the solution changed from red-orange to green and then to violet. The obtained solution was decanted. After the solvent was removed, the residue was washed with hexane. The yield was 0.33 g (61%), mp = 173°C.

For C ₄₈ H ₄₆ N ₂ O ₂ I	$_2Ga_2$		
Anal. calcd., %	C, 53.57	H, 4.31	N, 2.60
Found, %	C, 53.62	H, 4.28	N, 2.56

IR (v, cm⁻¹): 1932 w, 1875 w, 1813 w, 1741 w, 1602 m, 1527 s, 1490 s, 1421 m, 1365 w, 1319 m, 1253 w, 1194 w, 1111 w, 1099 w, 1089 w, 1057 w, 1033 m, 972 w, 948 m, 939 m, 911 w, 899 w, 829 m, 820 m, 807 m, 777 m, 766 s, 683 m, 636 m, 590 m, 577 m, 539 w, 521 w, 494 w, 456 w.

¹H NMR (δ , ppm): 0.24 d (CH(C<u>H</u>₃)₂), 1.04 d (CH(C<u>H</u>₃)₂), 1.30 d (CH(C<u>H</u>₃)₂), 1.62 d (CH(C<u>H</u>₃)₂), 2.11 s (C₆H₅C<u>H</u>₃), 2.86 sept. (C<u>H</u>(CH₃)₂), 4.17 sept. (C<u>H</u>(CH₃)₂), 6.33 s (arom.), 6.58 d (arom.), 6.74 t (arom.), 7.40–6.97 m (arom.).

Synthesis of $[{Dpp-Mian(HC=CPh)}GaI]_2$ (VIII). The heating of a mixture of compound VII (0.3 g, 0.28 mmol) and phenylacetylene (0.31 g, 3.0 mmol) in toluene (35 mL) at 90°C for 2 h resulted in a change in the color of the reaction mixture from blue to violet. After the mixture was cooled down to room temperature, volatile components were removed in vacuo. The remained solid was dissolved in Thf (15 mL) on heating. Complex VIII was crystallized from Thf at room temperature as colorless crystals. The yield was 0.22 g (57%), mp = 152°C (decomp.).

For C₇₀H₇₀N₂O_{3.5}I₂Ga₂

Anal. calcd., %	C, 60.46	Н, 5.22	N, 2.01
Found, %	C, 60.53	H, 5.19	N, 1.97

IR (v, cm⁻¹): 3089 w, 3058 m, 3022 m, 1970 w, 1952 w, 1942 m, 1911 w, 1893 w, 1875 w, 1821 w, 1808 w, 1651 s, 1620 m, 1589 m, 1565 m, 1483 m, 1438 m, 1429 w, 1417 m, 1365 m, 1350 m, 1324 m, 1313 m, 1288 w, 1264 m, 1256 m, 1223 w, 1212 w, 1190 s, 1182 s, 1164 m, 1141 m, 1106 m, 1068 s, 1035 m, 1011 w, 999 w, 977 w, 968 w, 932 s, 911 m, 865 m, 841 m, 830 s, 805 s, 782 s, 769 s, 761 m, 713 s, 702 m, 674 m, 630 m, 604 m, 599 m, 582 m, 576 m, 558 m, 530 m, 504 m, 497 w, 468 m, 459 w.

¹H NMR (δ , ppm): 0.36 d (CH(C<u>H</u>₃)₂), 1.12 d (CH(C<u>H</u>₃)₂), 1.25 dd (CH(C<u>H</u>₃)₂), 1.49–1.36 m (Thf), 2.87 sept. (C<u>H</u>(CH₃)₂), 3.65–3.50 m (Thf), 3.75 sept. (C<u>H</u>(CH₃)₂), 6.06 d (PhC=C<u>H</u>(H)), 6.66–6.40 m (arom.), 7.42–6.90 m (arom.).

Hydroamination of phenylacetylene and dicyclohexvlcarbodiimide by 4-chloroaniline and hydroarylation of phenylacetylene by 1-naphthol. Catalytic tests were carried out using known procedures [5, 14, 15]. Phenylacetylene was preliminarily purified by distillation, dried over metallic sodium, and sampled by condensation in vacuo. The substrates (0.5 mmol each) and catalyst $(4-8 \mod \%)$ were placed in a preliminarily evacuated ampule for ¹H NMR spectroscopy, and deuterated benzene (0.5 mL) was added to each ampule. After this, the ampule was sealed and the ¹H NMR spectrum of a mixture of the starting reactants was detected at room temperature. Then the reaction mixture was heated in an oil bath in a temperature range of 90-130°C. The process and conversion of the reactants were monitored by ¹H NMR spectroscopy. The ratio between the starting reactants and reaction products was calculated from the integral intensities of the corresponding signals.

X-ray structure analyses of compounds VI and VIII were carried out on a Bruker D8 Quest diffractometer (Mo K_{α} radiation, ω scan mode, $\lambda = 0.71073$ Å). Experimental arrays of intensities were integrated using the SAINT program [20]. Absorption corrections were applied using the SADABS program [21]. The structures were determined by a direct method (SHELXTL program package) [22–24] and refined by full-matrix least squares for F_{hkl}^2 in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and refined by the riding model. The H(1) and H(2) atoms in complex **VIII** were found from the difference electron density synthesis and refined isotropically. Solvate molecules of diethyl ether and Thf

D	Va	Value	
Parameter	VI	VIII	
FW	953.60	1388.52	
Т, К	100	100	
Crystal system	Monoclinic	Triclinic	
Space group	$P2_{1}/n$	PĪ	
a, Å	13.7817(9)	10.068(1)	
b, Å	13.1984(9)	16.111(2)	
<i>c</i> , Å	24.456(2)	20.126(2)	
α , deg	90	103.553(2)	
β, deg	91.390(1)	90.806(2)	
γ, deg	90	93.539(2)	
$V, Å^3$	4447.1(5)	3166.2(6)	
Ζ	4	2	
$\rho_{calc}, g \ cm^{-3}$	1.424	1.456	
μ, mm ⁻¹	1.358	1.874	
<i>F</i> (000)	1960	1400	
Crystal size, mm	$0.70 \times 0.63 \times 0.51$	0.27 imes 0.11 imes 0.07	
Measurement range, θ , deg	2.28-28.00	2.46-25.00	
Range of indices h, k, l	$-18 \le h \le 18,$	$-11 \le h \le 11,$	
	$-17 \le k \le 17,$	$-19 \le k \le 19,$	
	$-32 \le l \le 32$	$-23 \le l \le 23$	
Number of observed reflections	52331	28277	
Number of independent reflections	10726	10986	
R _{int}	0.0295	0.0451	
GOOF (F^2)	1.013	1.041	
$R_1/wR_2 (I > 2\sigma(I))$	0.0264/0.0641	0.0537/0.1462	
R_1/wR_2 (for all parameters)	0.0329/0.0664	0.0658/0.1539	
$ ho_{\rm max}/ ho_{\rm min}$, e Å ⁻³	0.945/-0.469	2.979/-0.984	

Table 1. Crystallographic data and the X-ray structure analysis parameters for compounds VI and VIII

were found in the general positions in crystals of compounds VI and VIII, respectively. The ratios of the solvate molecules to the gallium complex are 1 : 1 (VI) and 1.5 : 1 (VIII). The diethyl ether molecule in compound VI is disordered over two positions. Selected crystallographic characteristics and the parameters of X-ray structure experiments for compounds VI and VIII are presented in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos.

1571860 (**VI**) and 1571861 (**VIII**)) and are available at www.ccdc.cam.ac.uk/structures/.

RESULTS AND DISCUSSION

The reduction with a gallium excess in the presence of an equivalent amount of iodine in Thf or diethyl ether is accompanied by the subsequent change in the color of the solution from red-orange to green and then violet. This reaction gave two metal complexes **VI** and **VII** formed consequently and containing ligands in different reduction states.

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The X-ray structure analysis of the crystals isolated from a green solution shows that complex **VI** (Fig. 1) containing two radical anion ligands is formed in the first step. This is unambiguously indicated by the bond lengths in the ketoimine fragments (Table 2) (average C–N 1.315, C–C 1.428, and C–O 1.288 Å), which are intermediate compared to the bond lengths in the neutral [18] and dianionic Dpp-Mian ligands [19]. The gallium atom in compound **VI** is pentacoordinated. Based on the τ parameter calculated from the maximum angles of the polyhedron O(1)Ga(1)O(2) (158.04(5)°) and N(2)Ga(1)N(1) (135.66(5)°) being equal to ~0.4, this polyhedron can be attributed to a distorted tetragonal pyramid with the iodine atom at the vertex, since $\tau = 0$ for an ideal tetragonal pyramid and $\tau = 1$ for a trigonal bipyramid. Later the synthesis of complex **VI** was conducted purposefully with 0.5 equiv mol of iodine taken for the reaction.

The further reduction of complex Dpp-Mian affords compound **VII** isolated from a violet solution containing the Dpp-Mian dianion. Since product **VII** was not isolated in the crystalline state, its composition and structure were established by spectral methods and from an analysis of the structure of the reaction product with phenylacetylene. The reaction of complex **VII** with phenylacetylene in toluene at 90°C completes within 2 h and affords complex **VIII** isolated in the crystalline state and characterized by X-ray structure analysis.



According to the X-ray structure analysis data (Fig. 2), compound **VIII** is a homochiral dimer: the unit cell contains both R,R- and S,S-enantiomers. The coordination number of both gallium atoms is 5 as in the case of complex VI. The τ parameter calculated for the Ga(1) and Ga(2) atoms is close to 0.5; i.e., the geometry of the considered tetrahedra is intermediate between a trigonal bipyramid and a tetragonal pyramid. The structure of the obtained complex VIII has a number of interesting features. First, the gallium-carbon bond of the vinyl fragment is not subjected to protonolysis with a phenylacetylene excess as it occurs in complex IV [19]. Second, both ethylenediyl fragments are arranged at one side of the dimeric molecule, unlike related digallium complex I. Third, the ethvlenediyl fragment links the gallium atom and N,Oligand that are not bound to each other, which was never observed earlier. Selected bond lengths and bond angles for compounds VI and VIII are presented in Table 2.

An unusual property of digallane I is the ability to catalyze the hydroamination [5] and hydroarylation of phenylacetylene [14], as well as the guanylation of carbodiimides with anilines [15]. The catalytic tests with the earlier used substrates were carried out to compare the catalytic properties of gallium complexes **VII** and **VIII**



Fig. 1. Molecular structure of compound **VI**. Thermal ellipsoids with 30% probability. Hydrogen atoms are omitted.

Bond	$d, \mathrm{\AA}$	Bond	$d, \mathrm{\AA}$
		VI	
Ga(1)–N(2)	1.984(1)	O(2)–C(25)	1.278(2)
Ga(1)–N(1)	1.995(1)	N(1)–C(2)	1.314(2)
Ga(1)–O(1)	2.002(1)	N(2)–C(26)	1.315(2)
Ga(1)–O(2)	2.010(1)	C(1)–C(2)	1.430(2)
Ga(1)–I(1)	2.5385(2)	C(25)–C(26)	1.425(2)
O(1)–C(1)	1.287(2)		
Į.	V	лп	
Ga(1)–O(1)	1.924(3)	C(1)–O(1)	1.409(6)
Ga(1)–C(57)	1.965(5)	Ga(2)–O(2)	1.921(3)
Ga(1)–O(2)	2.169(3)	Ga(2)–C(25)	1.958(5)
Ga(1)–N(1)	2.200(4)	Ga(2)–O(1)	2.163(3)
Ga(1)–I(1)	2.5226(6)	Ga(2)–N(2)	2.202(4)
C(57)–C(58)	1.347(7)	Ga(2)–I(2)	2.5217(6)
C(1)–C(26)	1.551(7)	C(25)–C(26)	1.317(7)
C(2)–N(1)	1.275(6)		
Angle	ω, deg	Angle	ω, deg
		VI	
N(2)Ga(1)N(1)	135.66(5)	O(1)Ga(1)O(2)	158.04(5)
N(2)Ga(1)O(1)	90.35(5)	N(2)Ga(1)I(1)	113.00(4)
N(1)Ga(1)O(1)	83.19(5)	N(1)Ga(1)I(1)	111.31(4)
N(2)Ga(1)O(2)	83.21(5)	O(1)Ga(1)I(1)	100.44(4)
N(1)Ga(1)O(2)	86.81(5)	O(2)Ga(1)I(1)	101.40(4)
,	V	/III	
O(1)Ga(1)C(57)	122.4(2)	O(1)Ga(1)N(1)	80.1(1)
N(1)Ga(1)C(57)	99.69(18)	N(1)Ga(1)I(1)	104.15(10)
O(2)Ga(2)C(25)	123.02(17)	N(2)Ga(2)C(25)	99.92(17)
C(2)C(1)C(26)	112.6(4)	N(2)Ga(2)I(2)	103.92(11)

Table 2. Selected bond lengths (Å) and bond angles (deg) for compounds VI and VIII

based on Dpp-Mian with the properties of digallane **I**. The ¹H NMR monitoring of the reaction of phenylacetylene with 4-chloroaniline in the presence of 4 mol % complex **VII** showed that the maximum conversion of the starting components to the hydroamination product achieved 77% within 48 h at 90°C.

$$Ph - H + Cl - NH_2 \xrightarrow{(VII) \text{ or } (VIII)} Cl - N$$

These parameters are inferior to those for hydroamination in the presence of digallane I, where the conversion of the starting substances to N-(4-chlorophenyl)-1phenylethane-1-imine was 99% within 6 h [5]. Under similar conditions, the use of 4 mol % compound **VIII** exerts no effect on a mixture of the substrates and no reaction between them occurs. Catalysis is observed only at 130°C, which is likely related to the elimination of a phenylacetylene molecule from complex **VIII** and the formation of more catalytically active derivative **VII**. Since the catalytic activity of compound **VIII** turned out to be low, this compound was not involved in subsequent catalytic tests.

It has previously been shown that the phenylacetylene adduct of compound I catalyzes the reaction of 1-naphthol with phenylacetylene:

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at 45°C within 20 days the hydroarylation product 2-(1-phenylvinyl)naphthalen-1-ol is formed in 70% yield. At 90°C, the reaction proceeds much more rapidly and gives the same product with a significantly higher yield already within several hours. However, the primarily formed product



It is important that the second reaction step (Diels–Alder cycloaddition) does not occur. Thus, in this case, the use of compound **VII** is preferable than, for example, dithiocarbamate complex (Dpp-Bian)-Ga(S₂CNMe₂), in the presence of which (2 mol %) at 85°C the hydroarylation product was obtained in 7 h with a yield that did not exceed 40% [9].

undergoes the Diels-Alder dimerization at elevated temperature [14]. Under the same conditions (90°C) of the reaction of 1-naphthol with phenylacetylene in the presence of 6 mol % complex **VII**, the yield of 2-(1-phenylvinyl)naphthalen-1-ol reaches 95% in 20 h.

The guanylation of carbodiimides is another example for the hydroamination of unsaturated organic compounds catalyzed by the gallium complexes with the redox-active Dpp-Bian ligand [15]. We also showed that compound **VII** actively catalyzed the hydroamination of dicyclohexylcarbodiimide by aniline.



The conversion of the substrates to the product reaches 83% at 90° C within 20 h when complex **VII** (8 mol %) is added to an equimolar mixture of 4-chloroaniline and dicyclohexylcarbodiimide. These parameters are comparable to those for the system including digallane I as a catalyst, although they take place under more rigid conditions with a larger amount of the catalyst and within a longer time.



Fig. 2. Molecular structure of compound VIII. Thermal ellipsoids with 30% probability. Hydrogen atoms, except for H(1) and H(2), are omitted.

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REFERENCES

- 1. Siebenlist, R., Frühauf, H.-W., Vrieze, K., et al., *Organometallics*, 2002, vol. 21, p. 5628.
- Scholz, J. and Görls, H., *Inorg. Chem.*, 1996, vol. 35, p. 4378.
- Scholz, J., Görls, H., Schumann, H., and Weimann, R., Organometallics, 2001, vol. 20, p. 4394.
- Fedushkin, I.L., Nikipelov, A.S., and Lyssenko, K.A., J. Am. Chem. Soc., 2010, vol. 132, p. 7874.
- 5. Fedushkin, I.L., Nikipelov, A.S., Morozov, A.G., et al., *Chem.-Eur. J.*, 2012, vol. 18, p. 255.
- Fedushkin, I.L., Moskalev, M.V., Lukoyanov, A.N., et al., *Chem.-Eur. J.*, 2012, vol. 18, p. 11264.
- Zhao, Y., Liu, Y., Lei, Y., et al., *Chem. Commun.*, 2013, vol. 49, p. 4546.
- Fedushkin, I.L., Moskalev, M.V., Baranov, E.V., and Abakumov, G.A., *J. Organomet. Chem.*, 2013, vol. 747, p. 235.
- 9. Fedushkin, I.L., Kazarina, O.V., Lukoyanov, A.N., et al., *Organometallics*, 2015, vol. 34, p. 1498.
- 10. Stephan, D.W. and Erker, G., *Angew. Chem., Int. Ed. Engl.*, 2010, vol. 49, p. 46.
- 11. Stephan, D.W., Acc. Chem. Res., 2015, vol. 48, p. 306.
- 12. Frustrated Lewis Pairs: Themed Collection, *Dalton Trans.*, 2012, vol. 41, p. 8999.

- 13. Fedushkin, I.L., Khvoinova, N.M., Skatova, A.A., and Fukin, G.K., *Angew. Chem., Int. Ed. Engl.*, 2003, vol. 42, p. 5223.
- 14. Moskalev, M.V., Yakub, A.M., Morozov, A.G., et al., *Eur. J. Org. Chem.*, 2015, p. 5781.
- 15. Kazarina, O.V., Moskalev, M.V., and Fedushkin, I.L., *Russ. Chem. Bull. Int. Ed.*, 2015, vol. 1, p. 32.
- 16. Fedushkin, I.L., Morozov, A.G., Chudakova, V.A., et al., *Eur. J. Inorg. Chem.*, 2009, p. 4995.
- 17. Yakub, A.M., Moskalev, M.V., Bazyakina, N.L., et al., *Russ. Chem. Bull. Int. Ed.*, 2016, vol. 12, p. 2887.
- 18. Razborov, D.A., Lukoyanov, A.N., Makarov, V.M., et al., *Russ. Chem. Bull. Int. Ed.*, 2015, vol. 10, p. 2377.

- 19. Razborov, D.A., Lukoyanov, A.N., Baranov, E.V., and Fedushkin, I.L., *Dalton Trans.*, 2015, vol. 44, p. 20532.
- 20. SAINT. Data Reduction and Correction Program. Version 8.27B, Madison: Bruker AXS, 2012.
- 21. Sheldrick G.M., SADABS. Version 2014/2. Bruker/Siemens Area Detector Absorption Correction Program, Madison: Bruker AXS, 2014.
- 22. Sheldrick G.M., SHELXTL. Version. 6.14. Structure Determination Software Suite, Madison: Bruker AXS, 2003.
- 23. Sheldrick, G.M., Acta Crystfllogr., Sect. A: Found. Adv., 2015, vol. 71, p. 3.

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