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Chromium and tungsten complexes with a paramagnetic gallaimidazole ligand*

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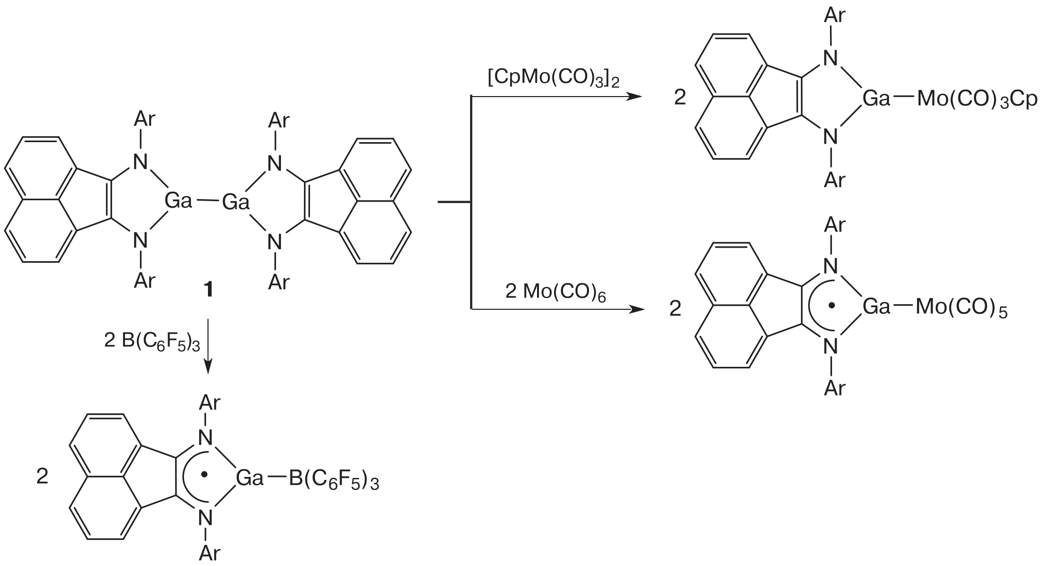
The reaction of digallane [(dpp-bian)Ga—Ga(dpp-bian)] (**1**) (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene dianion) with chromium or tungsten hexacarbonyl affords the complexes [(dpp-bian)Ga—Cr(CO)$_5$] (**2**) and [(dpp-bian)Ga—W(CO)$_5$] (**3**), respectively, containing the neutral radical [(dpp-bian)Ga:]. In both cases, temperature-dependent solvation of the gallium center was observed in a tetrahydrofuran solution. The recrystallization of compound **2** from pyridine gave the new complex [(dpp-bian)(Py)Ga—Cr(CO)$_5$] (**4**). New compounds **2—4** were characterized by EPR and IR spectroscopy and elemental analysis. The molecular structures of complexes **2—4** were established by single-crystal X-ray diffraction.

Key words: gallium, gallaimidazoles, chromium, tungsten, metal—metal bonds, redox-active ligands, molecular structure.

The first compound containing the anionic gallaimidazole ligand [(dab)Ga:]$^-${K[(18)-crown-6](thf)$_2$}$^+$ (dab = (Bu$^t_2$NCH)$_2$) was described in 1999.[1] In subsequent years, the coordination chemistry of the anionic gallaimidazole [(dab)Ga:]$^-$ (dab = (2,6-Pr$^i_2$C$_6$H$_3$NCH)$_2$) was extensively investigated.[2] The complexes of [(dab)Ga:]$^-$ with a diversity of Periodic table metals were synthesized,[3—12] which confirms the versatility of gallaimidazole as a Ga-donor ligand. Anionic gallaimidazoles are isoelectronic with neutral N-heterocyclic germylenes.[13—16] The latter are heavy analogs of Arduengo carbenes, which are currently widely used as ligands in the coordination

Scheme 1



Ar = 2,6-Pr$^i_2$C$_6$H$_3$

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* Dedicated to Academician of the Russian Academy of Sciences A. M. Muzafarov on the occasion of his 70th birthday.

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chemistry. Previously, we synthesized complexes of a number of transition metals with the anionic acenaphthenediimine gallaimidazole ligand [(dpp-bian)Ga:]$^-$ (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene): [(dpp-bian)Ga—FeCp(CO)$_2$], [(dpp-bian)Ga—VCp$_2$], [{(dpp-bian)Ga}$_2$NiCp], [{(dpp-bian)Ga—M(CO)$_5$}-{Na(thf)$_2$}]$_2$ (M = Cr, W), [{(dpp-bian)Ga}$_2$FeCp(CO)]-[Na(dme)$_3$],[17] and [(dpp-bian)Ga—MoCp(CO)$_3$].[18] The first neutral carbenoid [(dpp-bian)Ga:] with transition metal, the complex [(dpp-bian)Ga—Mo(CO)$_5$], was prepared by the reaction of digallane [(dpp-bian)Ga—Ga-(dpp-bian)][19] (**1**) with molybdenum carbonyl Mo(CO)$_6$.[18] It was also shown that digallane **1** reacted with B(C$_6$F$_5$)$_3$ to form the boron complex [(dpp-bian)Ga—B(C$_6$F$_5$)$_3$],[20] in which gallylene is also neutral and bears the unpaired electron (Scheme 1).

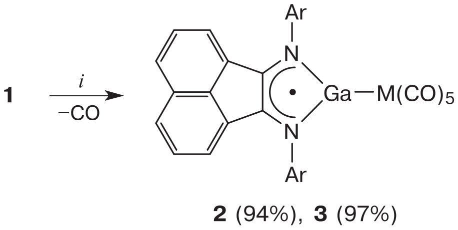
Therefore, we showed that in coordination chemistry, the gallaimidazole [(dpp-bian)Ga:] can exist in both the anionic and neutral forms, acting as a redox-active ligand. Since the neutral carbenoid [(dpp-bian)Ga:] has the unpaired electron on the dpp-bian moiety, it can serve as a spin label in transition metal complexes, allowing the EPR study of the dynamics of the coordination sphere of complexes with this ligand.

Here we report the synthesis, structures, and solution behavior of the new chromium and tungsten complexes with the neutral carbenoid [(dpp-bian)Ga:].

Results and Discussion

Synthesis and characterization of the compounds [(dpp-bian)Ga—Cr(CO)$_5$] (2), [(dpp-bian)Ga—W(CO)$_5$] (3), and [(dpp-bian)(Py)Ga—Cr(CO)$_5$] (4). The reaction of digallane [(dpp-bian)Ga—Ga(dpp-bian)] (**1**) with an excess of chromium or tungsten hexacarbonyl M(CO)$_6$ (M = Cr, W) occurs in tetrahydrofuran at 100 °C in an evacuated glass tube overnight (Scheme 2) and is accompanied by a change in the color of the reaction mixture from dark-blue to green. Green crystals of the compounds [(dpp-bian)Ga—Cr(CO)$_5$] (**2**) and [(dpp-bian)Ga—W(CO)$_5$] (**3**) were isolated from dimethoxyethane and benzene in 94 and 97% yields, respectively.

Scheme 2



2 (94%), **3** (97%)

M = Cr (**2**), W (**3**)

Reagent and conditions: *i*. M(CO)$_6$ (excess), THF, 100 °C, 24 h.

Solutions of compounds **2** and **3** in THF exhibit thermochromism. Thus, they are green at room temperature and red at low temperatures. This phenomenon is apparently associated with the reversible coordination of the solvent molecule to the gallium atom accompanied by the electron pair donation to the vacant *p* orbital of the gallium atom. The use of a solvent with higher donor ability compared to THF can lead to its irreversible coordination to the gallium atom. Actually, the recrystallization of compound **2** from pyridine afforded the new derivative [(dpp-bian)(Py)Ga—Cr(CO)$_5$] (**4**) (91%) containing the pyridine molecule coordinated to the gallium atom. The IR spectra of compounds **2**—**4** show intense absorption bands at 2040, 2055, and 2027 cm^{-1}, respectively, characteristic of C—O stretching vibrations of metal carbonyls. Thus, these vibrations appear in the spectrum of the molybdenum gallaimidazole complex [(dpp-bian)Ga—Mo(CO)$_5$][18] as an intense band at 2056 cm^{-1}.

Compounds **2**—**4** are paramagnetic. The EPR data provide unequivocal evidence for the presence of the heterocyclic radical [(dpp-bian)Ga:] in these compounds. This radical acts as a neutral two-electron σ-donor to the transition metal and, together with five CO ligands, gives rise to an 18-electron configuration of the metal center. The hyperfine structure of the EPR signals of complexes **2**—**4** in solution is due to hyperfine interactions (HFI) of the unpaired electron with two pairs of protons of the naphthalene system (I = 1/2, 99.99%), two equivalent ^{14}N nuclei of the diimine moiety (I = 1, 99.6%; in the case of compound **4**, there is also HFI interaction between the unpaired electron and the pyridine nitrogen atom), and two magnetic isotopes of gallium, ^{69}Ga (I = 3/2, 60.11%) and ^{71}Ga (I = 3/2, 39.89%).[21] The isotropic g-factors and HFI constants of compounds **2** and **3** at 293 K are given in Table 1.

The EPR spectra of complexes **2** and **3** at different temperatures in a THF solution are very similar. Hence, the spectra only of compound **2** are shown in Fig. 1 and discussed below.

The variation of the temperature of the EPR experiment was accompanied by a significant reversible change in the HFI constants of complex **2** (Figs 2 and 3). As can be seen in Fig. 2, the cooling of a solution of complex **2** in THF leads to an increase in the HFI constants with the magnetic isotope of nitrogen, ^{14}N, and a decrease in the HFI constants with the magnetic isotopes of gallium, ^{69}Ga and ^{71}Ga.

The observed change in the color of a solution of compound **2** in THF apparently is attributed to reversible weak solvation of the gallium center by cyclic ether. The Arduengo carbene-type structures exhibit high aromaticity due to the involvement of the vacant *p* orbital of the low-valent metal center in the interaction with the π sys-

Table 1. Isotropic *g*-factors and HFI constants (a_i/mT) of compounds **2**, **3**, and (dpp-bian)Ga(SBz)$_2$[22] at 293 K

Compound (solvent)	g_i	^{69}Ga	^{71}Ga	2 ^{14}N	^{14}N(Py)	2 ^{1}H*	
						1	*2*
2 (THF)	2.0020	1.485	1.793	0.322	—	0.115	0.102
2 (toluene)	2.0020	1.476	1.782	0.322	—	0.115	0.112
2 (pyridine)	2.0022	0.384	0.483	0.464	0.268	0.127	0.113
3 (THF)	2.0024	1.487	1.795	0.314	—	0.119	0.122
3 (toluene)	2.0021	1.516	1.831	0.320	—	0.220	0.100
(dpp-bian)Ga(SBz)$_2$ (toluene)	2.0026	1.561	1.983	0.495	—	—	—

* The values for two pairs of protons of the naphthalene system are given.

tem of the NCCN moiety.[23,24] The coordination of a THF molecule to the metal center leads to aromaticity suppression[25] and a considerable spin density redistribution in the chelate GaNCCN ring, which is reflected in a change in the HFI constants with magnetic isotopes of nitrogen and gallium. It should be noted that the color of the solution of compound **2** in toluene remained unchanged on cooling (down to the freezing point of the solvent), and no changes in the HFI constants were detected in the EPR spectrum of **2**. The EPR spectrum of complex **2** in pyridine at 293 K (see Fig. 3) is similar to the EPR spectrum of this compound in THF at 200 K. The HFI constant with ^{14}N nuclei in the EPR spectrum of compound **2** in THF at

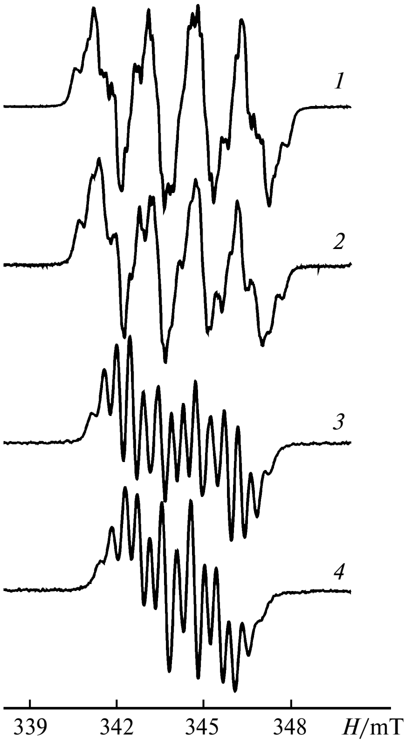


Fig. 1. Temperature dependence of the isotropic EPR spectrum of complex **2** in tetrahydrofuran/K: 280 (*1*), 250 (*2*), 220 (*3*), 200 (*4*).

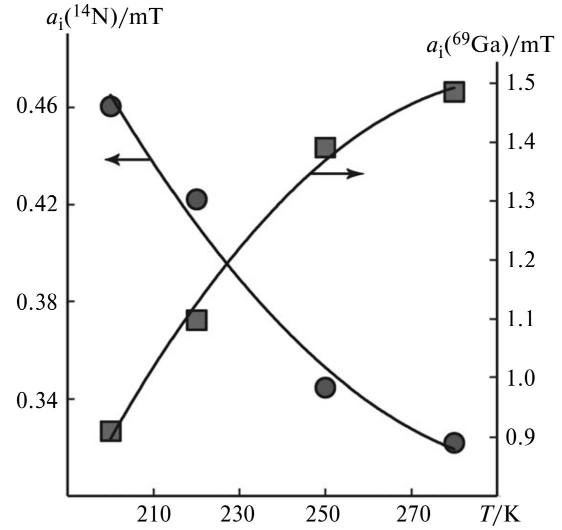


Fig. 2. Temperature dependence of the HFI constants with the magnetic isotopes ^{14}N and ^{69}Ga in the EPR spectrum of compound **2** in THF.

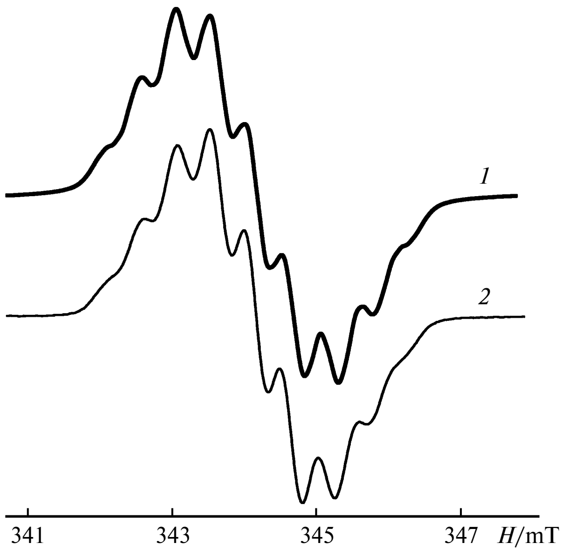


Fig. 3. Experimental (*1*) and simulated (*2*) EPR spectra of complex **2** in pyridine at 293 K.

200 K is equal to that in pyridine at 293 K; both constants are 0.46 mT. This suggests that almost all molecules of compound **2** are coordinated by pyridine in a pyridine solution already at room temperature, *i.e.*, the solution actually contains complex **4**. Since the HFI constants with the ^{14}N, ^{69}Ga, and ^{71}Ga nuclei for compound **2** in a THF solution at room temperature are similar to the constants of complexes **2** at this temperature in toluene (see Table 1), it can be concluded that in a THF solution at 293 K, almost all molecules of compound **2** are not coordinated by the solvent molecules. The ^{14}N HFI constants of compound **2** in THF at 200 K and in pyridine at 293 K are similar to the constants of most other gallium complexes with the radical-anion dpp-bian ligand, *e.g.*, (dpp-bian)Ga(SBz)$_2$, at 293 K (see Table 1). All the above is true for compound **3**, the EPR parameters of which differ only slightly from those of complex **2**.

Molecular structures of compounds 2—4. The structures of compounds **2—4** were established by X-ray diffraction. The molecular structures of compounds **2** and **4** are shown in Figs 4 and 5, respectively. Since molecules **2** and **3** have similar geometric parameters, the structure of compound **3** is not presented. Selected bond lengths and bond angles are given in Table 2.

Compound **2** is an octahedral d$_6$-Cr(0) complex. The Cr—CO bond lengths in compound **2** have similar values (1.858(2)—1.8928(13) Å); however, the CO group, which forms the shortest bond with the chromium atom, is in a *trans* position to the gallium atom. It can be suggested that (dpp-bian)Ga is a weaker σ-donor and π-acceptor compared to CO groups. Besides, the transfer of electron density from the transition metal to gallium through back-bonding is insignificant in compound **2**. This is also evidenced by the ability of the gallium atom to coordinate a pyridine or THF molecule. In complex **2**, the dpp-bian ligand exists as the radical anion. Thus, the bond lengths in the diimine moiety of **2** are similar to those in the molybdenum derivative [(dpp-bian)Ga—Mo(CO)$_5$],[18] which also contains the dpp-bian radical anion: N—C (aver.), 1.3294(13) Å; C—C, 1.426(2) Å in **2**; N—C (aver.), 1.333(2) Å; C—C, 1.426(3) Å in [(dpp-bian)Ga—Mo(CO)$_5$]. The corresponding bond lengths in the molybdenum

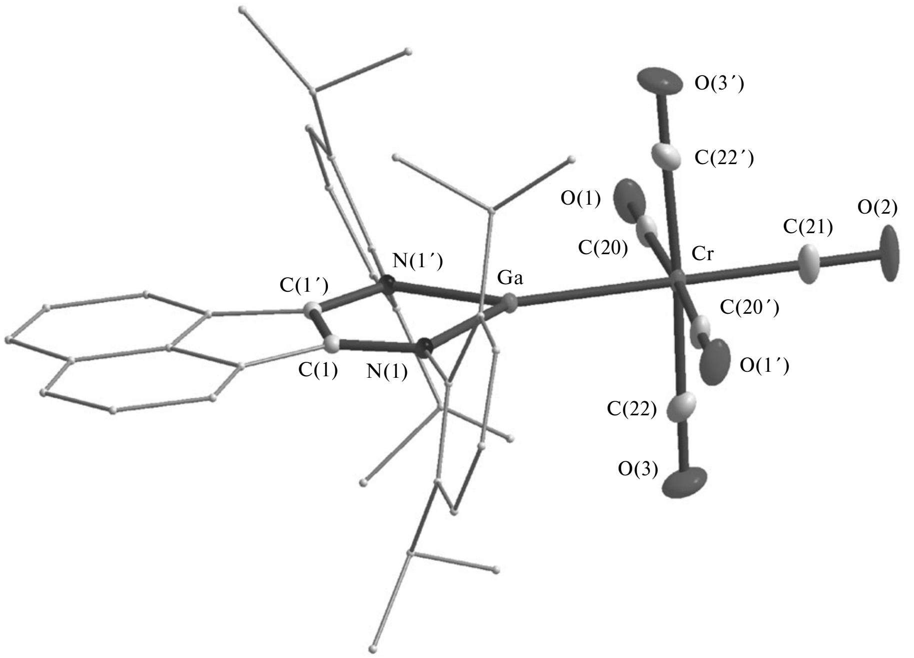


Fig. 4. Molecular structure of compound **2** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (*d*) and bond angles (ω) of compound **2**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Ga—N(1)	1.9725(8)	Cr—C(22)	1.8865(15)	N(1´)—Ga—N(1)	83.84(5)
Ga—N(1´)	1.9726(8)	Cr—C(22´)	1.8864(15)	Ga—Cr—C(20)	88.11(4)
Ga—Cr	2.3836(3)	N(1)—C(1)	1.3294(13)		
Cr—C(20)	1.8928(13)	C(1)—C(1´)	1.4615(13)		
Cr—C(21)	1.858(2)				

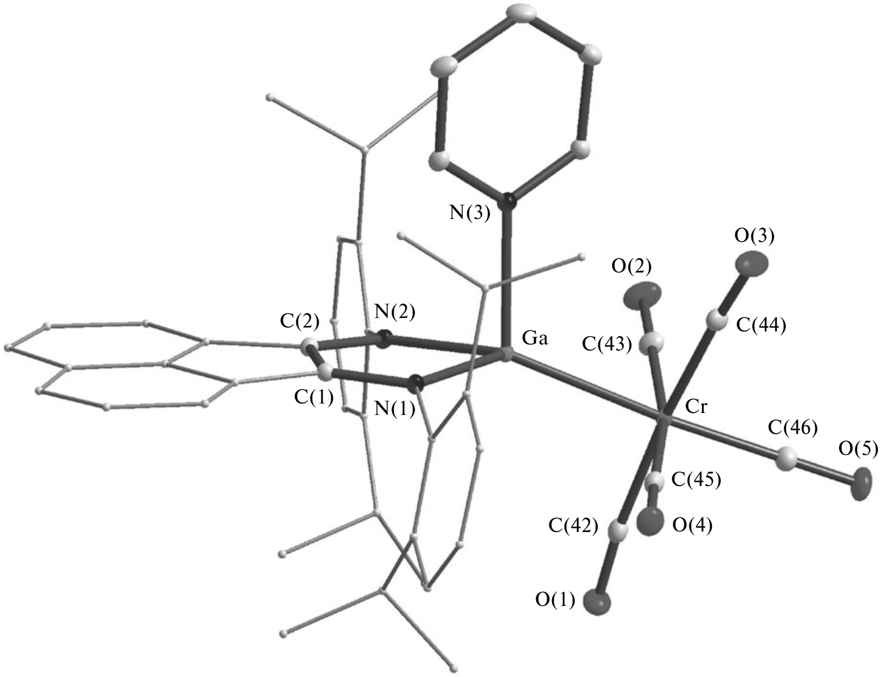


Fig. 5. Molecular structure of compound **4** with thermal ellipsoids of key atoms drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (*d*) and bond angles (ω) of compound **4**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Ga—N(1)	2.0176(8)	Cr—C(44)	1.8778(12)	N(2)—Ga—N(1)	83.36(3)
Ga—N(2)	2.0542(8)	Cr—C(45)	1.8807(11)	N(2)—Ga—N(3)	90.46(3)
Ga—N(3)	2.1727(9)	Cr—C(46)	1.8584(11)	N(2)—Ga—Cr	135.48(2)
Ga—Cr	2.4580(2)	N(1)—C(1)	1.3402(12)	N(3)—Ga—Cr	113.10(2)
Cr—C(42)	1.9030(12)	N(2)—C(2)	1.3333(12)		
Cr—C(43)	1.8942(12)	C(1)—C(2)	1.4404(13)		

complex [(dpp-bian)Ga—MoCp(CO)$_3$]^{18} (N—C (aver.), 1.386 Å; C—C, 1.385(4) Å) or the chromium complex [{(dpp-bian)Ga—Cr(CO)$_5$}{Na(thf)$_2$}]$_2$^{17} (N—C (aver.), 1.390 Å; C—C, 1.356(2) Å) with the dpp-bian dianion are essentially different.

The molecular structure of complex **4** (Fig. 5, Table 3) differs from that of compound **2**. The pyridine nitrogen atom donates the lone pair to the vacant p_z orbital of the gallium atom (N(2)—Ga—N(3), 90.46(3)°). The chromium atom deviates from the plane through the Ga—N(1)—C(1)—C(2)—N(2) atoms by 0.936 Å in the direction opposite to that of the coordinated pyridine molecule. The Ga—N bond lengths in complex **4** are also noticeably longer (on the average, by 0.06 Å) compared to complex **2**, while the bond lengths in the diimine moiety change only slightly, but the Ga—Cr bond is significantly elongated (by 0.07 Å).

Therefore, the complexes with the paramagnetic gallaimidazole ligand [(dpp-bian)Ga:] were synthesized by the reactions of digallane containing the redox-active acenaphthene-1,2-diimine ligand with chromium and tungsten hexacarbonyls. Temperature-dependent solvation of the gallium center is observed in a tetrahydrofuran solution of the synthesized compounds, which affects the spin density redistribution in the chelate GaNCCN ring.

Experimental

Since all the newly synthesized compounds are sensitive to atmospheric oxygen and moisture, all manipulations for the synthesis, isolation, and identification of these compounds were carried out *in vacuo* using the Schlenk technique or under a nitrogen atmosphere (Glovebox M. Braun). 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) was synthesized by the condensation of acenaphthenequinone and 2,6-diisopropylaniline (Aldrich) in acetonitrile. Tetrahydrofuran, 1,2-dimethoxyethane, benzene, and toluene were dried and stored over sodium benzophenone, pyridine was stored over sodium metal, and all the solvents were withdrawn by vacuum condensation

Table 4. Crystallographic data and the X-ray diffraction data collection and refinement statistics for compounds **2**—**4**

Parameter	**2**	**3**	**4**
Molecular formula	$C_{41}H_{40}GaCrN_2O_5$	$C_{41}H_{40}GaWN_2O_5$	$C_{49}H_{48}CrGaN_3O_5$
Molecular weight	762.47	894.32	880.62
T/K	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbcn*	*Pbcn*	$P2_1/c$
a/Å	16.9388(8)	17.1533(3)	11.17658(16)
b/Å	15.5887(8)	15.7972(4)	22.9564(3)
c/Å	14.5329(7)	14.4720(5)	17.9016(3)
α/deg	90	90	90
β/deg	90	90	106.5264(15)
γ/deg	90	90	90
V/Å^3	3837.5(3)	3921.55(18)	4403.33(11)
Z	4	4	4
d_{calc}/g cm^{-3}	1.320	1.515	1.328
μ/mm^{-1}	1.030	3.662	0.908
$F(000)$	1580	1780	1832
Crystal size/mm	0.25×0.23×0.20	0.30×0.10×0.10	0.40×0.40×0.20
Scan range, θ/deg	2.26—28.00	2.94—27.99	3.08—30.00
Index ranges h, k, l	$-22 \leqslant h \leqslant 22$ $-20 \leqslant k \leqslant 20$ $-19 \leqslant l \leqslant 19$	$-22 \leqslant h \leqslant 22$ $-20 \leqslant k \leqslant 20$ $-19 \leqslant l \leqslant 19$	$-15 \leqslant h \leqslant 15$ $-32 \leqslant k \leqslant 32$ $-25 \leqslant l \leqslant 25$
Number of observed reflections	47983	63662	89180
Number of unique reflections (R_{int})	4617 (0.0245)	4728 (0.0416)	12798 (0.0318)
Goodness of fit (F^2)	1.049	1.046	1.052
R_1	0.0258	0.0231	0.0318
wR_2 ($I > 2\sigma(I)$)	0.0691	0.0522	0.0709
R_1	0.0309	0.0366	0.0371
wR_2 (based on all data)	0.0718	0.0560	0.0729
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.590/−0.236	1.182/−0.855	0.531/−0.334

immediately before use. The IR spectra were recorded on a FSM-1201 spectrometer. The EPR spectra were measured on a Bruker EMX spectrometer (9.75 GHz). The computer simulation of the EPR spectra was performed and exact values of the HFI constants were determined with the EasySpin software package.[26] The melting points were measured in sealed evacuated tubes. Elemental analysis was carried out by combustion of samples in oxygen using the Pregl technique. Digallane **1** was prepared by the heating of a solution of dpp-bian in toluene (50 mL) under reflux with an excess of gallium metal in an evacuated tube at 120 °C for 12 h (see Ref. 19) and was used *in situ*. The yields of products **2** and **3** were calculated with respect to the amount of dpp-bian used in the synthesis of starting digallane **1**.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene gallium chromium pentacarbonyl, (dpp-bian)Ga—Cr(CO)$_5$ (2). Chromium hexacarbonyl (0.33 g, 1.5 mmol) was added to a solution of digallane **1** [(dpp-bian)Ga—Ga(dpp-bian)], which was prepared *in situ* from dpp-bian (0.5 g, 1.0 mmol), in THF (30 mL). The reaction mixture was stirred on heating (100 °C) for 24 h. An excess of chromium carbonyl and THF were removed *in vacuo*, and the residue was dissolved in dimethoxyethane. The resulting green solution was concentrated to 10 mL and kept for 24 h at 10 °C. Dark-green (almost black) crystals of compound **2** that precipitated were separated from the solution by decantation, washed with cold dimethoxyethane, and dried *in vacuo*. The yield was 0.72 g (94%). M.p. > 230 °C (decomp.). Found (%): C, 64.15; H, 6.02. $C_{41}H_{40}GaCrN_2O_5$. Calculated (%): C, 64.58; H, 5.89. The EPR spectrum was recorded in toluene, $T = 293$ K, $g_i = 2.0020$; HFI constants: $a_i(2\ ^{14}N) = 0.322$, $a_i(2\ ^1H) = 0.115$, $a_i(2\ ^1H) = 0.112$, $a_i(^{69}Ga) = 1.476$, $a_i(^{71}Ga) = 1.782$ mT. IR (Nujol mulls), ν/cm^{-1}: 2040 v.s, 1986 w, 1918 v.s, 1747 w, 1687 w, 1671 w, 1591 m, 1538 s, 1431 s, 1420 s, 1385 m, 1362 w, 1342 w, 1326 m, 1297 w, 1257 m, 1217 w, 1189 m, 1148 m, 1118 w, 1081 w, 1061 w, 1043 w, 977 w, 957 w, 933 m, 890 m, 876 m, 826 m, 805 m, 787 w, 769 s, 700 w, 675 v.s, 657 v.s, 586 w, 549 m, 515 w, 478 s, 453 w.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene gallium tungsten pentacarbonyl, (dpp-bian)Ga—W(CO)$_5$ (3). Compound **3** was synthesized as described for compound **2** using tungsten hexacarbonyl (0.53 g, 1.5 mmol) as the starting reagent. Dark-green (almost black) crystals of compound **3** were isolated from benzene in 97% yield (0.87 g). M.p. > 200 °C (decomp.). Found (%): C, 56.02; H, 4.98. $C_{41}H_{40}GaWN_2O_5$. Calculated (%): C, 55.56; H, 4.51. The EPR spectrum was recorded in toluene, $T = 293$ K, $g_i = 2.0021$; HFI constants: $a_i(2\ ^{14}N) = 0.320$, $a_i(2\ ^1H) = 0.220$, $a_i(2\ ^1H) = 0.100$, $a_i(^{69}Ga) = 1.516$, $a_i(^{71}Ga) = 1.831$ mT. IR (Nujol mulls), ν/cm^{-1}: 2055 v.s, 1932 v.s, 1910 v.s, 1627 w, 1590 w, 1539 s, 1364 w, 1326 w, 1300 w, 1255 w, 1217 w, 1185 w, 1149 m, 1116 w, 1081 w, 1060 w, 1043 w, 1008 w, 976 w, 953 w, 933 m, 891 m, 875 m, 825 m, 804 m, 785 w, 774 s, 767 s, 701 w, 672 w, 648 w, 591 s, 575 s, 549 w, 515 w, 454 w.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene gallium chromium pentacarbonyl pyridinate, (dpp-bian)(C_5H_5N)Ga—Cr(CO)$_5$ (4). A solution of compound **2** in THF (30 mL), which was prepared from dpp-bian (0.5 g, 1.0 mmol), was concentrated *in vacuo* to dryness. The residue was dissolved in pyridine (30 mL). The resulting brown solution was concentrated to 10 mL and kept for 24 h at 10 °C. The dark-brown crystals of compound **4** that precipitated were separated from the solution by decantation, washed with cold pyridine, and dried *in vacuo*. The yield was 0.80 g (91%). M.p. > 200 °C (decomp.). Found (%): C, 65.95; H, 5.87. $C_{49}H_{48}CrGaN_3O_5$. Calculated (%): C, 65.83; H, 5.69. The EPR spectrum was recorded in pyridine, $T = 293$ K, $g_i = 2.0022$; HFI constants: $a_i(2\,^{14}N) = 0.464$, $a_i(^{14}N\ Py) = 0.268$, $a_i(2\,^{1}H) = 0.127$, $a_i(2\,^{1}H) = 0.113$, $a_i(^{69}Ga) = 0.384$, $a_i(^{71}Ga) = 0.483$ mT. IR (Nujol mulls), ν/cm^{-1}: 2067 w, 2027 v.s, 1947 v.s, 1906 v.s, 1889 v.s, 1671 w, 1641 w, 1604 m, 1594 w, 1575 w, 1530 s, 1481 m, 1451 v.s, 1361 w, 1315 s, 1256 m, 1248 m, 1216 m, 1186 m, 1146 w, 1114 w, 1081 w, 1067 w, 1056 w, 1041 s, 1008 m, 946 w, 932 m, 884 w, 864 m, 835 w, 804 s, 776 m, 767 m, 757 m, 706 m, 683 s, 665 s, 638 w, 630 m, 592 w, 549 w, 513 w, 488 m, 457 w.

X-ray diffraction study of **compounds 2—4.** The X-ray diffraction data sets for compounds **2**—**4** were collected on Bruker D8 Quest (**2**) and Agilent Xcalibur E (**3** and **4**) diffractometers (ω-scanning technique, Mo-K_α radiation, $\lambda = 0.71073$ Å, $T = 100$ K). The experimental intensity data were integrated using the SAINT[27] (for **2**) and CrysAlisPro programs[28] (for **3** and **4**). All structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms. All hydrogen atoms were positioned geometrically and refined isotropically. Calculations were performed using the SHELXTL program package.[29] Absorption corrections were applied with the SADABS[30] (for **2**) and SCALE3 ABSPACK programs[31] (for **3** and **4**). In the crystal structure of complex **4**, there is one independent benzene solvent molecule lying on a special position. One of Pr^i substituents of the bian ligand in complex **4** is disordered over two positions. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics are given in Tables 2—4. The structures were deposited with the Cambridge Crystallographic Data Centre (CCDC 2007904 (**2**), 2007905 (**3**), and 2007906 (**4**)) and are available, free of charge, at ccdc.cam.ac.uk/getstructures.

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