6994 *Inorg. Chem.* **2010**, *49*, 6994–7000
DOI: 10.1021/ic1005506

Inorganic Chemistry
Article

Structure and Bonding Energy Analysis of M−Ga Bonds in Dihalogallyl Complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (M = Ni, Pd, Pt; X = Cl, Br, I)

Krishna K. Pandey,*[†] Pankaj Patidar,[†] and Holger Braunschweig*[‡]

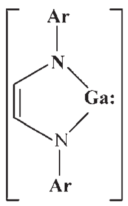
[†] *School of Chemical Sciences, Devi Ahilya University Indore, Indore 452001, India, and*
[‡] *Institute für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

Received March 24, 2010

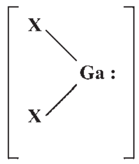
Geometry, electronic structure, and bonding analysis of the terminal neutral dihalogallyl complexes of nickel, palladium, and platinum *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (M = Ni, Pd, Pt; X = Cl, Br, I) were investigated at the BP86 level of theory. The calculated geometries of platinum gallyl complexes *trans*-[X(PMe$_3$)$_2$Pt(GaX$_2$)] (X = Br, I) are in excellent agreement with structurally characterized platinum complexes *trans*-[X(PCy$_3$)$_2$M(GaX$_2$)]. In the gallyl complexes of nickel and palladium, the M−Ga σ bonding orbital is slightly polarized toward the gallium atom, while in the platinum gallyl complexes, the M−Ga σ bonding orbital is slightly polarized toward the platinum atom. It is significant to note that gallium atoms along the M−Ga σ bonds have large p character, which is always >51% of the total AO contributions, while along the Ga−X σ bonds, the p character varies from 72% to 73%. The short M−Ga bond distances, in spite of the significantly small M−Ga π bonding, are due to the large s character of gallium (~45−48%) along the M−Ga bonds. The calculated NPA charge distributions indicate that the metal atom carries negative charge and the Ga atom carries significantly large positive charge. The contributions of the electrostatic interaction terms, $\Delta E_{\mathrm{elstat}}$, are significantly larger in all gallyl complexes than the covalent bonding ΔE_{orb} term. Thus, the [M]−GaX$_2$ bond in the studied gallyl complexes of Ni, Pd, and Pt has a greater degree of ionic character (65.7−72.5%). The π-bonding contribution is, in all complexes, significantly smaller than the σ bonding contribution. In the GaX$_2$ ligands, gallium dominantly behaves as a σ donor. The interaction energy increases in all three sets of complexes via order of Ni < Pd < Pt, and the absolute value of $\Delta E_{\mathrm{Pauli}}$, ΔE_{int}, and $\Delta E_{\mathrm{elstat}}$ contributions to the M−Ga bonds decreases via X = Cl < Br < I in all three sets of complexes.

Introduction

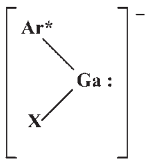
Since the first report of structurally characterized terminal transition metal boryl complexes in 1990,[1,2] the chemistry of transition metal complexes with terminal boryl (BX$_2$) ligands has blossomed in the past 20 years, during which much knowledge of their properties has been obtained.[1−16] In sharp contrast to the transition metal boryl complexes, the coordination chemistry of gallyl ligands (structures A, B, and C) has been much less developed. A number of transition metal complexes with heterocyclic gallyl ligands have been reported. Table 1 gives M−Ga bond distances in structurally characterized gallyl complexes that have been reported in the literature.[17−37]



(A)



(B)



(C)

Only a few structurally characterized terminal transition metal dihalogallyl complexes have been reported. Fischer et al.

---

*To whom correspondence should be addressed. E-mail: kkpandey.schem@dauniv.ac.in (K.K.P.), h.braunschweig@mail.uni-wuerzburg.de (H.B.).

(1) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.

(2) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.

(3) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786.

(4) Irvine, G. I.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

(5) Smith, M. R., III. *Prog. Inorg. Chem.* **1999**, *48*, 505.

(6) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.

(7) Braunschweig, H. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2001; p 213.

(8) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163.

(9) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535.

(10) Braunschweig, H.; Rais, D. *Heteroatom. Chem.* **2005**, *16*, 566.

(11) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254.

(12) Braunschweig, H.; Kollann, C.; Seeler, F. *Struct. Bonding* (*Berlin*) **2008**, *130*, 1.

(13) Anderson, C. E.; Braunschweig, H.; Dewhurst, R. D. *Organometallics* **2008**, *27*, 6381.

Table 1. Selected Structurally Characterized Metal−Gallyl Complexes

complexes[a]	M−Ga bond distance, (Å)	references
$[FeCp^*(GaCp^*)(GaBr_2)(PPh_3)]$		18
$[Cp^*Fe(dppe)(GaI_2)]$	2.3236(14)	19, 20
$[Cp^*Fe(dppe)Ga(Mes)I]$	2.3550(1)	19, 20
$[Cp^*Fe(CO)_2Ga(Mes)I]$	2.3113(12)	19, 20
trans-$[(Cy_3P)_2Pt(Br)(GaBr_2)]$	2.3403(4)	21
trans-$[(Cy_3P)_2Pt(I)(GaI_2)]$	2.3383(4)	21
$[CpFe(CO)_2Ga(Mes^*)Cl]$	2.346(1)	22
$[Cp^*Fe(CO)_2Ga(Mes^*)I]$	2.372(2)	22
$[CpV(CO)_3[Ga\{[N(Ar)C(H)]_2\}]]^-$	2.4618(13)	23
$[Cp'Mn(CO)_2[Ga\{[N(Ar)C(H)]_2\}]]^-$	2.3105(9)	23
$[CpCo(CO)[Ga\{[N(Ar)C(H)]_2\}]]^-$	2.2347(7)	23
$[Cp_2'V[Ga\{[N(Ar)C(H)]_2\}]]$	2.5303(9)	23
$[Cp_2'V[Ga\{[N(Ar)C(H)]_2\}]_2]$	2.5093(12)	23
$[Mn\{CH(SiMe_3)_2\}_2[Ga\{[N(Ar)C(H)]_2\}]]$	2.6658(10)	23
$[Fe(CO)_4[Ga\{[N(Ar)C(H)]_2\}]]$	2.3068(8)	24
$[CpNi[Ga\{[N(Ar)C(H)]_2\}]_2]$	2.2196(11), 2.2154(11)	25
$[Ni\{C[N(Me)C(Me)]_2\}_2[Ga\{[N(Ar)C(H)]_2\}_2]$	2.3242(6)	25
$[Ir(COD)(IMes)[Ga\{[N(Ar)C(H)]_2\}]]$	2.4689(5)	27
$[Rh(COD)(IMes)[Ga\{[N(Ar)C(H)]_2\}]]$	2.4259(6)	27
$[(IMes)Cu[Ga\{[N(Ar)C(H)]_2\}]]$	2.3066(6)	27
$[(IMes)Ag[Ga\{[N(Ar)C(H)]_2\}]]$	2.4161(5)	27
$[(IMes)Au[Ga\{[N(Ar)C(H)]_2\}]]$	2.3782(6)	27
$[(IPr)Cu[Ga\{[N(Ar)C(H)]_2\}]]$	2.2807(5)	27
$[(IPr)Ag[Ga\{[N(Ar)C(H)]_2\}]]$	2.4108(8)	27
trans-$[Pt\{Ga\{[N(Ar)C(H)]_2\}\}_2(PEt_3)_2]$	2.4308(6)	37
cis-$[Pt\{Ga\{[N(Ar)C(H)]2\}\}_2(PEt_3)_2]$	2.4495(6), 2.4313(7)	37
trans-$[Ni\{Ga\{[N(Ar)C(H)]_2\}\}_2(PEt_3)_2]$	2.3614(7)	37
trans-$[Pd\{Ga\{[N(Ar)C(H)]_2\}\}_2(PEt_3)_2]$	2.4514(8)	37
trans-$[PdCl\{Ga\{[N(Ar)C(H)]_2\}\}(PEt_3)_2]$	2.3551(6)	37
trans-$[NiCl\{Ga\{[N(Ar)C(H)]_2\}\}(PEt_3)_2]$	2.2878(5)	37
$[PtCl\{Ga\{[N(Ar)C(H)]_2\}\}(dcpe)]$	2.4151(7)	37
$[PtCl\{Ga\{[N(Ar)C(H)]_2\}\}(dppe)]$	2.3929(7)	37
$[Pt\{Ga\{[N(Ar)C(H)]_2\}\}_2(dppe)]$	2.4157(6), 2.4167(7)	37
$[Ni\{Ga\{[N(Ar)C(H)]_2\}\}_2(tmeda)]$	2.3051(8) 2.3503(8)	37
$[Pd\{Ga\{[N(Ar)C(H)]_2\}\}_2(tmeda)]$	2.3959(9)	37
$[Pd\{Ga\{[N(Ar)C(H)]_2\}\}_2(dppm)]$	2.4032(8)	37
$[Pt\{Ga\{[N(Ar)C(H)]_2\}\}_2(dppm)]$	2.4170(8), 2.4218(7)	37
$[Pt\{Ga\{[N(Ar)C(H)]_2\}\}_2(COD)]$	2.3838(7)	37

[a] Cy = cyclohexyl; Cp = C_5H_5; Cp* = C_5Me_5; Cp′ = C_5H_4Me; Mes = 2,4,6-$Me_3C_6H_2$; Mes* = $C_6H_2Bu^t{}_3$-2,4,6; Ar = $C_6H_3Pr^i{}_2$-2,6; COD = 1,5-cyclooctadiene; Imes = $C\{N(C_6H_2Me_3\text{-}2,4,6)CH\}_2$; Ipr =: $C\{N(Ar)C(H)\}_2$

reported iron dibromogallyl complex $[(\eta^5\text{-}C_5Me_5)\{Ga(\eta^5\text{-}C_5Me_5)\}(PPh_3)Fe(GaBr_2)]$.[18] Aldridge and co-workers reported diiodogallyl complex $[(\eta^5\text{-}C_5Me_5)(dppe)Fe(GaI_2)]$ (dppe = diphenylphosphineethane).[19,20] Recently, Braunschweig et al. isolated the first representative examples of dibromogallyl and diiodogallyl complexes of platinum, *trans*-$[X(PCy_3)_2Pt(GaX_2)]$ (X = Br, I).[21] To the best of our knowledge, the structure and M−GaX_2 bonding energy analysis of the terminal neutral metal dihalogallyl complexes of nickel, palladium, and platinum have never been studied before. Here, we report the geometry and electronic structure, as well as the nature, of M−Ga bonds in the terminal neutral metal dihalogallyl complexes *trans*-$[X(PMe_3)_2M(GaX_2)]$ (M = Ni, Pd, Pt; X = Cl, Br, I). We intend to answer two questions: one of them addresses the degree of ionic and covalent character of the M−Ga bonds, while the second question addresses the extent of the M ← Ga σ bonding and M → Ga π back-bonding contributions to the M−GaX_2 bonds. The alteration of the strength of the M ← Ga σ bonding is discussed when M changes from M = Ni to M = Pt and X changes from X = Cl to X = I.

Computational Procedure

Calculations of the neutral terminal halogallyl complexes *trans*-$[X(PMe_3)_2M(GaX_2)]$ (**I**, M = Ni, X = Cl; **II**, M = Ni, X = Br; **III**, M = Ni, X = I; **IV**, M = Pd, X = Cl; **V**, M = Pd, X = Br; **VI**, M = Pd, X = I; **VII**, M = Pt, X = Cl; **VIII**, M = Pt, X = Br; **IX**, M = Pt, X = I) have been performed at the nonlocal DFT level of theory using the exchange functional of Becke[38] and the correlation functional of Perdew[39] (BP86). Scalar relativistic effects have been considered using the ZORA formalism.[40] Uncontracted Slater-type orbitals (STOs) using triple-ζ basis sets augmented by two sets of polarization functions were employed for the SCF calculations.[41] The $(1s)^2$ core electrons of the carbon; $(1s2s2p)^{10}$ core electrons of phosphorus, chlorine, and nickel; $(1s2s2p3s3p)^{18}$ core electrons of gallium and bromine; $(1s2s2p3s3p3d4s4p)^{36}$ core electrons of iodine; $(1s2s2p3s3p3d)^{28}$ core electrons of palladium; and $(1s2s2p3s3p3d4s4p4d)^{46}$ core electrons of platinum were treated by the frozen-core approximation.[42]

---

(14) Kays, D. L.; Aldridge, S. *Struct. Bonding* (*Berlin*) **2008**, *130*, 29.

(15) Braunschweig, H.; Dewhurst, R. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1893.

(16) Vidovic, D.; Pierce, G. A.; Aldridge, A. *Chem. Commun.* **2009**, 1157.

(17) Baker, R. J.; Jones, C. *Coord. Chem. Rev.* **2005**, *149*, 1857.

(18) Buchin, B.; Gemel, C.; Kempter, A.; Cadenbach, T.; Fischer, R. A. *Inorg. Chim. Acta* **2006**, *359*, 4833.

(19) Coombs, N. D.; Clegg, W.; Thompson, A. L.; Willock, D. J.; Aldridge, S. *J. Am. Chem. Soc.* **2008**, *130*, 5449.

(20) Coombs, N. D.; Vidovic, D.; Day, J. K.; Thompson, A. L.; Le Pevelen, D. D.; Stasch, A.; Clegg, W.; Russo, L.; Male, L.; Hursthouse, M. B.; Willock, D. J.; Aldridge, S. *J. Am. Chem. Soc.* **2008**, *130*, 16111.

(21) Braunschweig, H.; Gruss, K.; Radacki, K. *Inorg. Chem.* **2008**, *47*, 8595.

(22) Bunn, N. R.; Aldridge, S.; Kays, D. L.; Coombs, N. D.; Day, J. K.; Ooi, L. L.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2005**, *24*, 5879.

(23) Aldridge, S.; Baker, R. J.; Coombs, N. D.; Jones, C.; Rose, R. P.; Rossin, A.; Willock, D. J. *Dalton Trans.* **2006**, 3313.

(24) Baker, R. J.; Jones, C.; Platts, J. A. *Dalton Trans.* **2003**, 3673.

(25) Baker, R. J.; Jones, C.; Platts, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 10534.

(26) Baker, R. J.; Jones, C.; Murphy, D. M. *Chem. Commun.* **2005**, 1339.

(27) Green, S. P.; Jones, C.; Mills, D. P.; Stasch, A. *Organometallics* **2007**, *26*, 3424.

(28) Jones, C.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2007**, 2997.

(29) Arnold, P. L.; Liddle, S. T.; McMaster, J.; Jones, C.; Mills, D. P. *J. Am. Chem. Soc.* **2007**, *129*, 5360.

(30) Green, S. P.; Jones, C.; Lippert, K. A.; Mills, D. P.; Stasch, A. *Inorg. Chem.* **2006**, *45*, 7242.

(31) Jones, C.; Mills, D. P.; Rose, R. P. *J. Organomet. Chem.* **2006**, *691*, 3060.

(32) Jones, C.; Mills, D. P.; Platts, J. A.; Rose, R. P. *Inorg. Chem.* **2006**, *45*, 3146.

(33) Baker, R. J.; Jones, C.; Mills, D. P.; Murphy, D. M.; Hey-Hawkins, E.; Wolf, R. *Dalton Trans.* **2006**, 64.

(34) Baker, R. J.; Jones, C.; Kloth, M. *Dalton Trans.* **2005**, 2106.

(35) Baker, R. J.; Jones, C.; Kloth, M.; Platts, J. A. *Organometallics* **2004**, *23*, 4811.

(36) Baker, R. J.; Jones, C.; Kloth, M.; Platts, J. A. *Angew. Chem., Int. Ed.* **2003**, *43*, 2660.

(37) Jones, C.; Mills, D. P.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2008**, 4395.

(38) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(39) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(40) (a) Chang, C.; Pelissier, M.; Durand, Ph. *Phys. Scr.* **1986**, *34*, 394. (b) Heully, J.-L.; Lindgren, I.; Lindroth, E.; Lundquist, S.; Martensson-Pendrill, A.-M. *J. Phys. B* **1986**, *19*, 2799. (c) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. (d) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1996**, *105*, 6505. (e) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281. (f) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.

(41) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483.

Table 2. Selected Optimized Geometrical Parameters for Metal-Gallyl Complexes $[X(PMe_3)_2M(GaX_2)]$ (M = Ni, Pd, Pt; X = Cl, Br; I)[a]

	Ni			Pd			Pt		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
					Bond Distances				
M−X	2.186	2.341	2.523	2.382	2.519	2.687	2.390	2.533 [2.5087(3)][b]	2.702 [2.6902(5)][c]
M−Ga	2.244	2.259	2.265	2.345	2.362	2.371	2.360	2.374 [2.3403(4)]	2.383 [2.3383(6)]
M−P	2.215	2.221	2.233	2.347	2.354	2.364	2.330	2.334	2.341
Ga−X	2.216	2.379	2.593	2.213	2.373	2.585	2.208	2.370 [2.3428(5)] [2.3348(5)]	2.581 [2.5558(7)] [2.5472(8)]
					Bond Angles				
X−M−Ga	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
P−M−P	172.0	172.4	172.0	174.1	173.9	173.0	176.6	176.2 [171.39(3)]	175.0 [167.86(4)]
X−Ga−X	105.8	106.5	106.4	106.5	107.1	107.5	106.1	106.7 [101.65(2)]	107.3 [105.77(3)]
X−M−P	93.9	93.8	94.0	92.9	93.0	93.5	91.7	91.9 [90.22(2)]	92.5 [91.43(3)]
M−Ga−X	127.1	126.9	126.8	126.7	126.4	126.2	126.9	126.6	126.3

[a] Bond distances in angstrom (Å) and angles in degrees. [b] X-ray structural data for $[Br(PCy_3)2Pt(GaBr_2)]$. [c] X-ray structural data for $[I(PCy_3)2Pt(GaI_2)]$

An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to present the coulomb and exchange potentials accurately in each SCF cycle.[43] The calculations were performed utilizing the program package ADF-2008.01.[44]

The binding between the metal $[X(PMe_3)_2M]^+$ and gallyl $[GaX_2]^-$ fragments (singlet state) of complexes **I**−**IX** has been analyzed at C_{2v} symmetry using the energy decomposition scheme of the ADF package which is based on the Morokuma[45] and Ziegler and Rauk[46] methods. On the basis of these studies, the bond energy ΔE between the fragments can be decomposed as

$$\Delta E = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \tag{1}$$

where ΔE_{prep} is the energy required to promote the free fragments from their equilibrium structure in the electronic ground state to that which they take up in the molecule:

$$\begin{aligned}\Delta E_{\text{prep}} &= E_{\text{total}}(\text{distorted fragments})\\ &\quad - E_{\text{total}}(\text{fragments in the equilibrium structure})\end{aligned} \tag{2}$$

In eq 1, ΔE_{int} is the instantaneous interaction energy between the two fragments of the molecule. It can be decomposed into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \tag{3}$$

where ΔE_{elstat} describes the classical Coulomb interaction between the fragments. ΔE_{Pauli}, which is called exchange repulsion or Pauli repulsion, takes into account the destabilizing two-orbital, three- or four-electron interactions between the occupied orbitals of both fragments, and ΔE_{orb} represents orbital interactions between the occupied and virtual orbitals of the two fragments. It has been suggested that the covalent and electrostatic character of the bond can be given by the ratio $\Delta E_{\text{elstat}}/\Delta E_{\text{orb}}$.[47−50]

The electronic structures of the studied complexes were examined by NBO analysis.[51] All MO pictures were made using the MOLDEN program.[52]

Results and Discussion

Geometries. The important bond distances and angles of the dihalogallyl complexes (**I**−**IX**) calculated at the BP86/TZ2P level of theory are presented in Table 2. The structures (only for *trans*-$[Br(PMe_3)_2M(GaBr_2)]$ (M = Ni, Pd, Pt)) for complexes **II**, **V**, and **VIII** are shown in Figure 1. The structures of the X = Cl and X = I complexes are very similar to those presented in this figure and therefore are not included in Figure 1. The optimized Cartesian coordinates of all studied complexes are given in the Supporting Information.

---

(42) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(43) Krijn, J.; Baerends, E. J. Fit Functions in the HFS-Method, Internal Report (in Dutch); Vrije Universiteit Amsterdam: The Netherlands, 1984.

(44) Baerends, E. J.; Autschbach, J. A.; Berces, A.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Groeneveld, J. A.; Gritsenko, O. V.; Grüning, M.; Harris, F. E.; van den Hoek, P.; Jacobsen, H.; van Kessel, G.; Kootstra, F.; van Lenthe, E.; Osinga, V. P.; Patchkovskii, S. Philipsen, P. H. T.; Post, D. Pye, C. C.; Ravenek, W.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Snijders, J. G.; Sola, M.; Swart, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visser, O.; Wezenbeek, E.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Ziegler, T. ADF 2008-01, Scientific Computing & Modelling NV: The Netherlands.

(45) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294.

(46) (a) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (c) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

(47) Diefenbach, A.; Bickelhaupt, M. B.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449.

(48) Frenking, G.; Wichmann, K.; Froehlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Ravon, V. M. *Coord. Chem. Rev.* **2003**, *55*, 238.

(49) Pandey, K. K. *Coord. Chem. Rev.* **2009**, *253*, 37.

(50) Pandey, K. K.; Lledós, A. *Inorg. Chem.* **2009**, *48*, 2748.

(51) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(52) Schaftenaar, G. *MOLDEN3.4*; CAOSCAMM Center: The Netherlands, 1998.

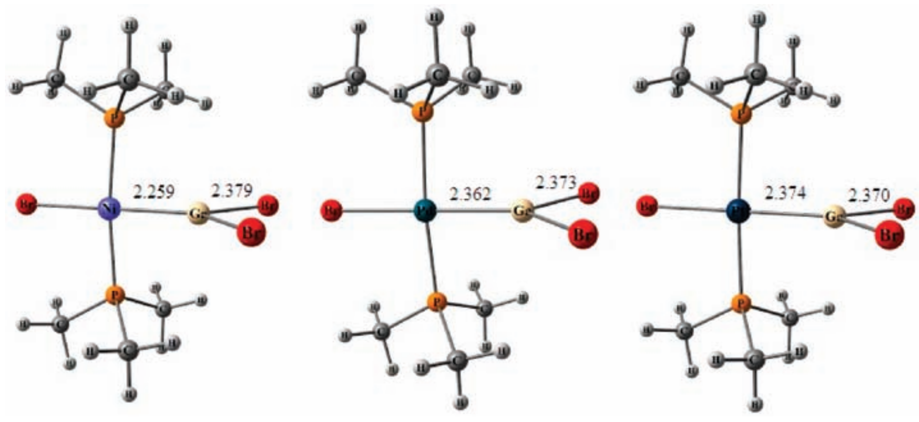


Figure 1. Optimized geometries of dibromogallyl complexes of nickel, palladium, and platinum. The important bond distances and angles are given in Table 2.

Since dihalogallyl complexes of nickel and palladium are not known so far, we here report for the first time in the literature the structures of these nickel and palladium dihalogallyl complexes.

As seen in Table 2, the M−Ga bond distances in the studied complexes *trans*-[X$(PMe_3)_2$M(GaX_2)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I; **I**−**IX**) are shorter than those expected for M−Ga single bonds estimated on the basis of covalent radii predictions (Ni−Ga = 2.40 Å, Pd−Ga = 2.56 Å, Pt−Ga = 2.57 Å).[53] Using the relationship between the bond order and bond distance suggested by Pauling,[54] the Pauling bond orders of the optimized M−Ga bond distances in these complexes are 1.7 (**I**), 1.6 (**II**), 1.5 (**III**), 2.0 (**IV**), 1.9 (**V**), 1.8 (**VI**), 2.0 (**VII**), 1.9 (**VIII**), and 1.8 (**IX**). Thus, the M−Ga bonds in the complexes (**I**−**IX**) are stronger than the M-Ga single bonds. It is important to note that the M−Ga π-bonding in the studied metal gallyl complexes (**I**−**IX**) is significantly smaller than the M−Ga σ-bonding, and in the GaX_2 ligands, gallium dominantly behaves as a σ donor (see Table 4 and Figure 4). The reasons for the shortening of M−Ga bond distances will be discussed in subsequent sections.

Upon going from X = Cl to X = I, the calculated M−Ga bond distance increases from 2.244 Å (**I**) < 2.259 Å (**II**) < 2.265 Å (**III**), 2.345 Å (**IV**) < 2.362 Å (**V**) < 2.371 Å (**VI**), and 2.360 Å (**VII**) < 2.374 Å (**VIII**) < 2.383 Å (**IX**). There are two different types of halides in the complexes *trans*-[X$(PMe_3)_2$M(GaX_2)]: one type of halide is bound to the metal in the *trans* position to the GaX_2 groups, while the second type of halide is bound to the gallium atom. Both types of halides have opposite effects on the strength of the M−Ga bonds. The well-known *trans* effect of the halides (bound to M) follows the order $I^- > Br^- > Cl^-$; that is, the strength of the M−Ga bond decreases on going from X = Cl to X = I in the complexes *trans*-[X$(PMe_3)_2$M(GaX_2)]. The gallium bound halides exert various effects on the strength of the M−Ga bonds, which in comparison are not very significant, though: (i) The s character of Ga along the Ga−X bond decreases upon going from Cl to I, and accordingly, the s character of Ga along the M−Ga bonds increases on going from Cl to I. (ii) The nature and properties of the HOMO and LUMO orbitals of the fragments $[X(PMe_3)_2M]^+$ and $[GaX_2]^-$ also play a role in explaining the orbital interaction differences. The energy of the LUMO orbital of the metal fragments varies as $[Cl(PMe_3)_2Ni]^+$ (−8.789 eV) < $[Br(PMe_3)_2Ni]^+$ (−8.689 eV) < $[I(PMe_3)_2Ni]^+$ (−8.489 eV), $[Cl(PMe_3)_2Pd]^+$ (−8.551 eV) < $[Br(PMe_3)_2Pd]^+$ (−8.458 eV) < $[I(PMe_3)_2Pd]^+$ (−8.296 eV), and $[Cl(PMe_3)_2Pt]^+$ (−8.785 eV) < $[Br(PMe_3)_2Pt]^+$ (−8.683 eV) < $[I(PMe_3)_2Pt]^+$ (−8.469 eV), while the energy of the HOMO orbital of the $[GaX_2]^-$ species varies for $[GaCl_2]^-$ in **I**, −0.114 eV; $[GaBr_2]^-$ in **II**, −0.406 eV; $[GaI_2]^-$ in **III**, −0.647 eV; $[GaCl_2]^-$ in **IV**, −0.090 eV; $[GaBr_2]^-$ in **V**, −0.373 eV; $[GaI_2]^-$ in **VI**, −0.606 eV; $[GaCl_2]^-$ in **VII**, −0.078 eV; $[GaBr_2]^-$ in **VIII**, −0.370 eV; and $[GaI_2]^-$ in **IX**, −0.597 eV. As a result, the LUMO of the metal fragment $[I(PMe_3)_2M]^+$ comes closer in energy to the HOMO of the $[GaI_2]^-$ fragment, allowing for better donation and relatively stronger M−Ga σ bond interaction in *trans*-[I$(PMe_3)_2$M(GaI_2)] complexes. The results reveal that, for $[GaX_2]^-$ species, on going from X = Cl to X = I, the M−Ga bond strength should increase. This is opposite of the *trans* effect of the halides. The variation in the M−Ga bond distances (Table 2), WBI of the M−Ga bond (Table 3), and orbital interaction Δ*E*(A1) for the M−Ga bond (Table 4) show that the *trans* effect of halides is relatively greater than the effects of halides bonded to the Ga atom. Hence, the strength of the M−Ga bond decreases on going from X = Cl to X = I in the complexes *trans*-[X$(PMe_3)_2$M(GaX_2)].

The M−X optimized bond distances, 2.186−2.702 Å, in **I**−**IX** are almost equal to that expected for the single M−X bond on the basis of covalent radii predictions (Ni−Cl = 2.19 Å, Ni−Br = 2.34 Å, Ni−I = 2.53 Å; Pd−Cl = 2.35 Å, Pd−Br = 2.50 Å, Pd−I = 2.69 Å; Pt−Cl = 2.36 Å, Pt−Br = 2.51 Å, Pt−I = 2.70 Å). The optimized Ga−X bond distances are slightly longer than that expected for the single Ga−X bond on the basis of covalent radii predictions (Ga−Cl = 2.19 Å, Ga−Br = 2.34 Å, Ga−I = 2.53 Å).

The X−M−Ga bond angles in these complexes are linear, and the X−Ga−X bond angles are in the range

---

(53) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(54) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 239. The relationship of bond order to length is given by $d_n = d_1 - 0.71 \log(n)$, where n is the bond order and d_1 and d_n are the lengths of bonds with bond orders of 1 and n, respectively.

Table 3. Wiberg Bond Indices and Results of the NBO Analysis in Metal-gallyl Complexes [X$(PMe_3)_2$M-GaX_2] (M = Ni, Pd, Pt; X = Cl, Br, I)

Wiberg Bond Indices

	Ni			Pd			Pt		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
M−Ga	0.76	0.74	0.72	0.70	0.68	0.66	0.77	0.74	0.71
M−X	0.73	0.80	0.87	0.62	0.69	0.74	0.67	0.73	0.78
M−P	0.68	0.68	0.68	0.62	0.61	0.60	0.71	0.70	0.69
Ga−X	0.72	0.81	0.88	0.73	0.81	0.89	0.74	0.83	0.90

NBO Analysis

	Ni			Pd			Pt		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
					M−Ga σ Bond				
occupancy	1.666	1.672	1.668	1.618	1.621	1.612	1.673	1.671	1.660
M									
%	49.97	49.57	49.55	49.45	48.34	47.27	52.88	51.78	50.69
%s	21.02	22.19	23.00	24.18	24.88	25.11	25.18	26.06	26.53
%p	54.78	53.73	53.43	52.93	52.32	52.48	52.68	51.93	51.91
%d	24.19	24.08	23.57	22.88	22.78	22.40	22.11	21.98	21.53
%f	0.00	0.00	0.00	0.01	0.01	0.01	0.04	0.03	0.03
Ga									
%	50.03	50.43	50.45	50.55	51.66	52.73	47.12	48.22	49.31
%s	47.63	48.16	48.24	45.18	45.60	45.58	45.17	45.60	45.68
%p	52.06	51.58	51.52	54.57	54.19	54.23	54.54	54.12	54.15
%d	0.32	0.26	0.23	0.25	0.21	0.19	0.29	0.27	0.16
					Ga−X σ Bond				
occupancy	1.966	1.959	1.948	1.966	1.959	1.948	1.969	1.962	1.952
Ga									
%	17.02	20.18	23.63	17.21	20.34	23.77	17.46	20.67	24.21
%s	26.40	26.04	25.90	27.58	27.32	27.23	27.44	27.20	27.13
%p	73.04	73.35	73.39	71.84	72.08	72.07	71.97	72.18	72.18
%d	0.56	0.60	0.71	0.58	0.60	0.69	0.60	0.62	0.69
X									
%	82.98	79.82	76.37	82.79	79.66	76.23	82.54	79.33	75.79
%s	27.27	23.85	20.65	26.18	23.05	20.18	26.76	23.47	20.58
%p	72.53	75.92	79.12	73.62	76.72	79.58	73.04	76.30	79.19
%d	0.20	0.23	0.23	0.20	0.23	0.23	0.20	0.23	0.23

106−107°, i.e., less than 120°. It can be inferred from these observations that the hybridization of Ga along Ga−X bonds is not sp^2. As seen in Table 2, the optimized bond distances for Pt−Ga and Ga−X (X = Br, I) are in close agreement with the experimental values for *trans*-[X$(PCy_3)_2$Pt(GaX_2)].[21]

Bonding Analysis of the M−GaX_2 Bonds of the Complexes I−IX. We begin the analysis of the M−Ga bonding in the metal gallyl complexes [X$(PMe_3)_2$M(GaX_2)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I; **I**−**IX**) with a discussion of bond orders and atomic charges. In Table 3, we presented the calculated Wiberg bond indices (WBI)[55] and the results of the natural bond orbital (NBO) analysis.

A seen from Table 3, the WBI values of the M−Ga bonds of **I**−**IX** are in the range of 0.66−0.77. Unlike the M−Ga bond distances, upon going from X = Cl to X = I, the WBI value of the M−Ga bonds decreases (Table 3). The WBI values for the Ga−X bonds are within 0.72−0.90 in complexes (**I**−**IX**). The WBI value for the M−X bonds increases on going from X = Cl to X = I in all three sets of complexes.

A more definitive picture of M−Ga bonding is obtained through NBO analysis of the delocalized Kohn−Sham orbitals. The characteristics of the M−Ga σ bonding orbitals are listed in Table 3. In the gallyl complexes of nickel and palladium, **I**−**VI**, the M−Ga σ bonding orbitals are slightly polarized toward the gallium atom, while in the platinum gallyl complexes **VII**−**IX**, the M−Ga σ bonding orbitals are slightly polarized toward the platinum atom. The occupations for M−Ga σ bonding orbitals are in the range 1.612−1.673.

It is significant to note that gallium atoms along the M−Ga σ bonds have large p character which is always > 51% of the total AO contributions, while along the Ga−X σ bonds the p character varies 72−73%. It is important to note that the hybridization at the gallium atoms in gallyl complexes **I**−**IX** is not sp^2 hybridized. The shorter M−Ga bond distances, in spite of the significantly smaller M−Ga π-bonding (Table 4), may be explained on the basis of the greater s character of gallium (~45−48%)

---

(55) Wiberg, K. A. *Tetrahedron* **1968**, *24*, 1083.

Table 4. Energy Decomposition Analysis[a] of Metal−Gallyl Complexes [X(PMe$_3$)$_2$M−GaX$_2$] (M = Ni, Pd, Pt; X = Cl, Br, I) at BP86/TZ2P Level

	Ni			Pd			Pt		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
ΔE_{int}	−147.8	−141.2	−133.8	−149.7	−142.4	−134.4	−160.9	−153.4	−144.4
$\Delta E_{\mathrm{pauli}}$	161.2	150.8	146.7	168.8	158.5	154.5	202.8	191.8	188.2
$\Delta E_{\mathrm{elstat}}$	−211.5	−196.4	−184.3	−230.8	−214.2	−201.0	−260.3	−242.4	−228.8
ΔE_{orb}	−97.5	−95.7	−96.2	−87.7	−86.7	−87.9	−103.5	−102.8	−103.8
ΔE(A1)[b]	−82.7	−80.7	−79.8	−75.0	−73.8	−73.7	−89.8	−88.8	−88.7
ΔE(A2)	−1.6	−1.6	−1.9	−1.2	−1.2	−1.5	−1.1	−1.1	−1.4
ΔE(B1)	−5.1	−5.3	−5.9	−4.6	−4.8	−5.3	−5.2	−5.5	−5.9
ΔE(B2)	−8.1	−8.1	−8.6	−7.0	−6.9	−7.4	−7.3	−7.4	−7.8
ΔE_{prep}	11.5	10.9	11.2	12.6	11.7	11.9	12.4	11.4	11.6
ΔE(-De)	−136.3	−130.4	−122.6	−137.1	−130.7	−122.5	−148.6	−142.0	−132.8
%IC[c]	(68.5%)	(67.2%)	(65.7%)	(72.5%)	(71.2%)	(69.6%)	(71.6%)	(70.2%)	(68.8%)

[a] Energy contributions in kcal/mol. [b] The values in parentheses are the percentage contribution to the total orbital interactions reflecting the σ character of the bond. [c] Percentage ionic character.

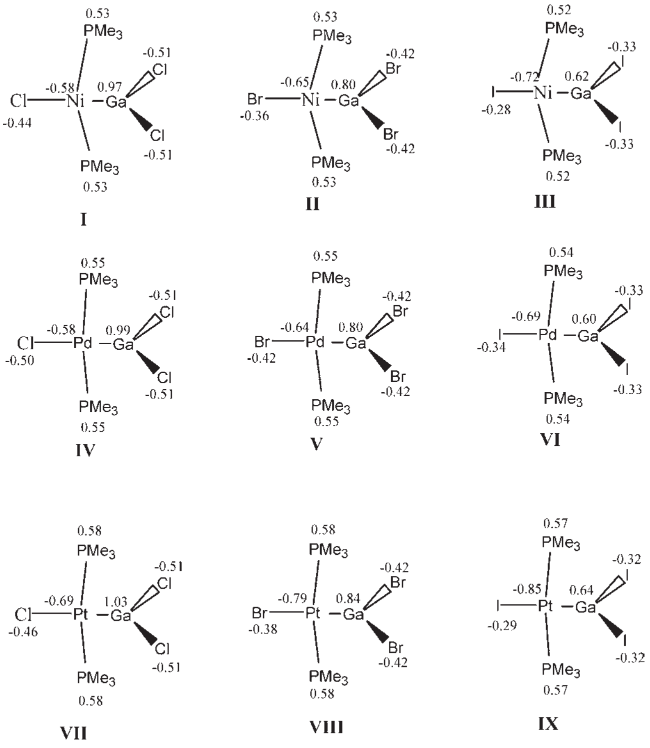


Figure 2. Natural population analysis (NPA) charge distributions in dihalogallyl complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I; **I−IX**).

along the M−Ga bonds. The metal atoms in the M−Ga σ bonds are ~dsp^2 hybridized with an increase in s character and a decrease in p character on going from M = Ni to M = Pt.

We will now discuss the charge decomposition analysis. The natural population analysis (NPA) charges of complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I; **I−IX**) are presented in Figure 2. The calculated NPA charge distributions indicate that the metal atom carries negative charge and the Ga atom carries significantly large positive charge. As a result, a large electrostatic interaction may be predicted between metal and gallium atoms (see Table 4). PMe$_3$ ligands carry positive charge, while X atoms are negatively charged in the complexes **I−IX**.

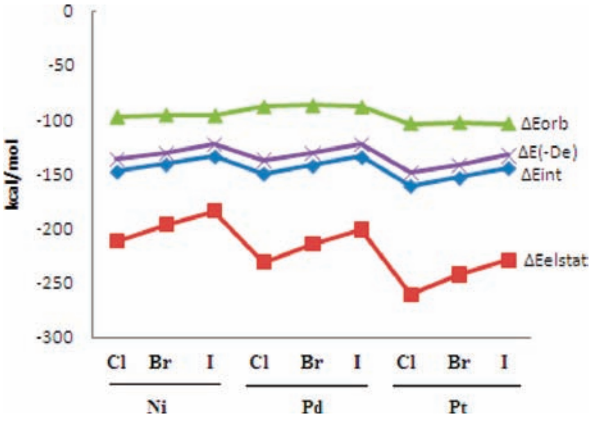


Figure 3. Trends of the interaction energy contribution, orbital interaction (covalent contribution), electrostatic interaction (ionic contribution), and bond dissociation energy (-De) to the M−Ga bond in the dihalogallyl complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I; **I−IX**).

Energy Decomposition Analysis of the M−Ga Bonding of the Complexes I−IX. Besides the charge decomposition analysis at the NBO level, we also carried out an energy decomposition analysis of the M−Ga bonds in the calculated metal−gallyl complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (**I−IX**). The results are given in Table 4 and Figure 3.

The tabulated bond dissociation energies in Table 4 reveal the expected periodic trend in bond strengths due to d-orbital extent: the Pt−Ga bonds are stronger than corresponding nickel and palladium complexes. Figure 3 shows a diagram of the bond dissociation energies ΔE (-De), interaction energies ΔE_{int}, orbital interaction energies ΔE_{orb}, and electrostatic interactions $\Delta E_{\mathrm{elstat}}$. The breakdown of the interaction energy ΔE_{int} into the repulsive term $\Delta E_{\mathrm{Pauli}}$ and the attractive terms ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ shows that $\Delta E_{\mathrm{Pauli}}$ repulsive interactions have the larger absolute value for X = Cl in the studied complexes (**I−IX**; Table 4).

The contributions of the electrostatic interaction terms $\Delta E_{\mathrm{elstat}}$ are significantly larger in all gallyl complexes (**I−IX**) than the covalent bonding ΔE_{orb} term. Thus, the [M]−GaX$_2$ bond in the studied gallyl complexes of Ni, Pd, and Pt has a greater degree of ionic character (65.7−72.5%). Table 4 also gives a breakdown of the orbital interactions ΔE_{orb} into the M ← Ga σ donation

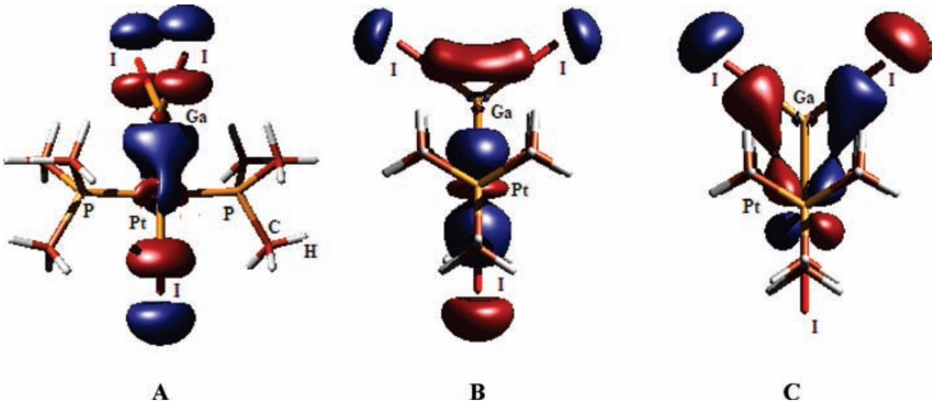


Figure 4. Plot of Pt−Ga σ (A and B) and π (C) molecular orbitals of *trans*-[I(PMe$_3$)$_2$Pt(GaI$_2$)].

and M → Ga π back-donation components. It is significant to note that the π-bonding contribution is, in all complexes, significantly smaller than the σ bonding contribution. From the data presented in Table 4, it could be concluded that (1) in the GaX$_2$ ligands, gallium dominantly behaves as a σ donor; (2) the interaction energy increases in all three sets of complexes via the order Ni/Pd/Pt; and (3) the absolute value ΔE_{Pauli}, ΔE_{int}, and ΔE_{elstat} contribution to the M−Ga bonds decreases via X = Cl < Br < I in all three sets of complexes.

To visualize the M−Ga bonding in terminal neutral dihalogallyl complexes, envelope plots of some relevant orbitals of the platinum complex [I(PMe$_3$)$_2$Pt(GaI$_2$)] (**IX**) are given in Figure 4. Figure 4A and B give a pictorial description of the Pt−Ga σ bonding, while Figure 4C is a Pt−Ga π orbital, showing very weak Pt(d$_\pi$)−Ga(p$_\pi$) bonding.

Conclusions

A theoretical study has been presented where the structure and bonding situation in nine neutral gallyl complexes of nickel, palladium, and platinum are investigated. From the above-presented calculated data, one can draw the following conclusions:

1. Here, for the first time (except the Pt complexes **VIII** and **IX**), we reported the geometry and electronic structure of, as well as analyzed the nature of, M−GaX$_2$ bonds in the terminal neutral metal gallyl complexes of nickel, palladium, and platinum complexes *trans*-[X(PMe$_3$)$_2$M(GaX$_2$)] (where M = Ni, Pd, and Pt and X = Cl, Br, and I). The calculated geometry parameters of platinum gallyl complexes [X(PMe$_3$)$_2$Pt(GaX$_2$)] (X = Br and I) are in excellent agreement with their available experimental values.[21]
2. In all studied complexes, the π-bonding contribution to the total M−GaX$_2$ bond is significantly smaller than that of the σ-bonding one. Thus, in the GaX$_2$ ligands, gallium dominantly behaves as a σ donor.
3. The M−Ga bond distance in complexes **I**−**IX** only slightly increases, while the WBI values for M−Ga bonds slightly decrease upon going from Cl to I.
4. The contributions of the electrostatic interaction terms ΔE_{elstat} are significantly larger in all gallyl complexes (**I**−**IX**) than the covalent bonding ΔE_{orb} term. Thus, the [M]−GaX$_2$ bond in the studied gallyl complexes of Ni, Pd, and Pt has a greater degree of ionic character (65.7−72.5%).
5. It is significant to note that the π-bonding contribution is, in all complexes, significantly smaller than the σ bonding contribution. The interaction energy increases in all three sets of complexes via the order Ni/Pd/Pt, and the absolute values of ΔE_{Pauli}, ΔE_{int}, and ΔE_{elstat} contributions to the M−Ga bonds decrease via X = Cl < Br < I in all three sets of complexes.

We believe that a more detailed understanding of the bonding in metal−gallyl complexes is a requisite, particularly for the synthesis of terminal transition metal−gallyl complexes. In this aspect, the above-presented findings are important contributions to the fast developing metal−gallyl chemistry.

Supporting Information Available: Cartesian coordinates of the optimized geometries of metal dihalogallyl complexes (**I**−**IX**) and their fragments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.