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Reactivity of Pt^0 Complexes toward Gallium(III) Halides: Synthesis of a Platinum Gallane Complex and Oxidative Addition of Gallium Halides to Pt^0

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The reaction of $[Pt(PCy_3)_2]$ and $GaCl_3$ resulted in quantitative formation of the adduct $[(Cy_3P)_2Pt{-}GaCl_3]$, the first known platinum gallane complex. Although similar reactivity with $GaBr_3$ and GaI_3 was expected, NMR spectroscopic data revealed a different reaction course. Crystal structure determination proved that, in the latter case, the product of the oxidative addition was formed. The resulting platinum gallyl complexes represent the first example of an oxidative addition of gallium(III) halides to low-valent transition metals.

Transition-metal gallium complexes have been known for more than 40 years and studied intensely since their first report.[1] Especially because of their numerous applications in metal−organic chemical vapor deposition (MOCVD), gallium complexes have gained additional interest in recent years.[2] The electronic properties of different coordination modes were investigated, with a main research focus being the interaction between the transition-metal center and low-coordinate group 13 diyl ligands $[L_nM(ER)]$ (E = group 13 element).[1d,3] In contrast, fewer examples have been reported of transition-metal-substituted gallanes, wherein the low-valent transition metal acts as a Lewis base $[L_nM \rightarrow GaR_3]$. These complexes display mostly donor-stabilizing substituents at the gallium center,[4] with the exception of a few anionic transition-metal gallane complexes followed by the neutral adducts $[(p\text{-cymene})Ru(GaCp^*)_2(GaCl_3)]$ (**1**) and $[Cp^*Rh(GaCp^*)_2(GaCl_3)]$ reported by Fischer et al. in 2005.[5] Whereas transition-metal gallane adducts are rare, a few transition-metal gallyl complexes $[L_nM{-}GaR_2]$ have been obtained by σ-bond metatheses,[6] in addition to a lone example: an anionic bis(gallyl)zirconium(III) complex, generated by the oxidative addition of a digallane to "$ZrCp_2$" and further treatment with Bu^nLi.[7] The reactivity of trihalogallanes toward low-valent transition-metal complexes has, in contrast to its lighter homologues, received only cursory attention. Especially, the chemistry of BX_3 (X = Cl, Br, I) with Pt^0 is well established and known to form oxidative addition products.[8] Numerous platinum boryl complexes, like the rare dibromoboryl complex **2** (Figure 1), were synthesized by the oxidative addition of the related bromoboranes to Pt^0 in our group. However, AlX_3 species do not react in a similar

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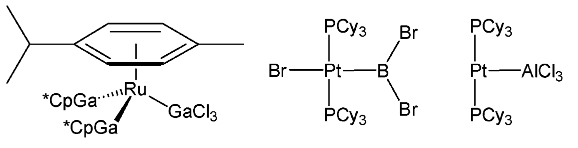
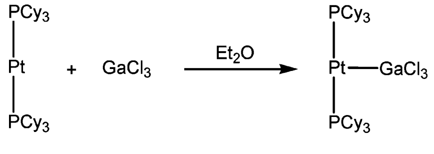


1 **2** **3**

Figure 1. Examples of the different reactivity of transition metals toward group 13 halides.

Scheme 1. Formation of the Neutral Platinum Gallane Adduct **4**



4

way but result in an adduct formation, where the transition-metal center acts as a Lewis base (**3**).[9]

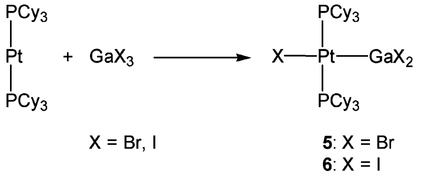
Herein, we report on the synthesis and full characterization of the first platinum gallane adduct *trans*-$[(Cy_3P)_2Pt{-}GaCl_3]$ (**4**) as well as the platinum gallyl complexes *trans*-$[(Cy_3P)_2Pt(Br)(GaBr_2)]$ (**5**) and *trans*-$[(Cy_3P)_2Pt(I)(GaI_2)]$ (**6**). The reaction of a Pt^0 complex with $GaBr_3$ and GaI_3 represents the first oxidative addition of a halogallane to a low-valent transition metal.

Gallium(III) halides show surprising reactivity with the relatively mild nucleophile $[Pt(PCy_3)_2]$. The stoichiometric reaction of $GaCl_3$ with $[Pt(PCy_3)_2]$ showed a signal in the $^{31}P\{^1H\}$ NMR spectrum at 49.3 ppm with a Pt−P coupling constant of 2798 Hz and is therefore in the range of known platinum aluminum adducts.[9] By comparison to these complexes, it was supposed that the addition of $GaCl_3$ to $[Pt(PCy_3)_2]$ had yielded the platinum gallane adduct **4** (Scheme 1).

Single-crystal structure analysis allowed us to determine the formulation of **4** unequivocally. Its almost T-shaped geometry with a P−Pt−P angle of 162.21(2)° augments the relationship between **4** and the platinum alane adducts *trans*-$[(Cy_3P)_2Pt{-}AlCl_3]$ and *trans*-$[(Cy_3P)_2Pt{-}AlBr_3]$ [162.07(2)° and 160.09(3)°, respectively].[9]

In comparison to the Pt−Ga distances of trigonal-planar Pt^0 complex $[Pt\{Ga[N(Ar)]_2CNCy_2\}_3]$ (Ar = 2,6-iPr$_2$C$_6$H$_3$)[1f] [the shortest known Pt−Ga distance: 2.3118(6) Å] and the tetrahedral Pt^0 complex $[Pt(GaCp^*)_4]$[10] [2.335(2) Å], the Pt1−Ga1 bond in **4** is significantly elongated [2.4019(2) Å]. The Cl−Ga1−Cl angles are wider than those in the neutral rhodium and ruthenium gallane adducts (106.67° in **4** to 102.37° and 101.47° in **1** on average, respectively).[5d,e] This effect correlates with a slight elongation of the average Ga−Cl bond to 2.265 Å in **1** and 2.244 Å in $[Cp^*Rh(GaCp^*)_2(GaCl_3)]$ in contrast to 2.2072 Å in **4**. The stability of such adducts is related to the Cl−E−Cl (E = group 13 element) angles and E−Cl bond lengths and therefore allows an estimation of the Pt−E bond strength.[11] A comparison of **4** with the neutral platinum alane adduct *trans*-$[(Cy_3P)_2Pt{-}AlCl_3]$[9] led to similar values, considering the different atom sizes, for the Cl−E−Cl angle (106.67° for **4** and 105.91°, respectively) and the Pt1−E bond length [2.4019(2) and 2.3857(7) Å, respectively] and thus suggests a reasonably strong dative bond. While $GaCl_3$ forms an adduct with $[Pt(PCy_3)_2]$, $^{31}P\{^1H\}$ NMR spectroscopic data indicate a different reaction path for the reactions of the latter with $GaBr_3$ and GaI_3 because significantly high-field-shifted peaks (27.6 and 23.1 ppm, respectively) were observed, similar to those known from the oxidative addition of bromoboranes to the Pt^0 complex.[8b,12] Indeed, the orange solids **5** and **6**, which were obtained in almost quantitative yields, constitute products of a corresponding reaction (Scheme 2).

Scheme 2. Formation of the platinum gallyl complexes **5** and **6**.



Suitable crystals for X-ray analysis were obtained of both **5** and **6**. The isostructural compounds feature an almost square-planar geometry at the platinum center and a virtual orthogonal orientation of the gallyl ligand with respect to the PtP_2 axis, thus allowing for a maximum metal−ligand π-back-donation, which is also characteristic for related platinum boryl complexes.[8] The Pt1−Ga1 bond length [**5**, 2.3403(4) Å; **6**, 2.3383(7) Å] is slightly shortened in comparison to the platinum gallane adduct **4** [2.4019(2) Å] and the known platinum gallyl complex $[(dcpe)Pt\{Ga(CH_2tBu)_2\}(CH_2tBu)]$ [2.376(2) Å].[6a] The mutual trans disposition of the halide and gallyl ligands is consistent with a certain trans influence of the latter. A series of related bromoborylplatinum complexes has been investigated and proves, in agreement with theoretical studies, the exceptionally strong trans influence of the boryl group.[8b,13] However, the Pt1−Br1 distance of **5** [2.5087(3) Å] is significantly shorter than those of platinum(II) boryl complexes [2.5617(10)−2.6454(4) Å], accordingly indicating a weaker trans influence of the gallyl moiety.

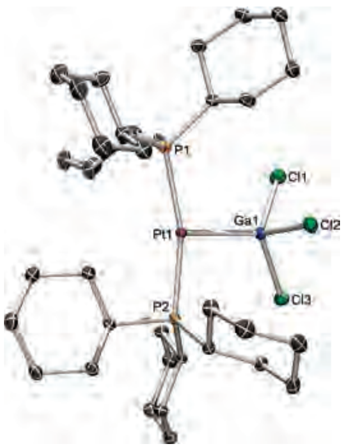


Figure 2. Molecular structure of **4** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Ga1 2.4019(2), Ga1−Cl1 2.2033(5), Ga1−Cl2 2.2091(5), Ga1−Cl3 2.2092(5); P1−Pt1−P2 162.21(2).

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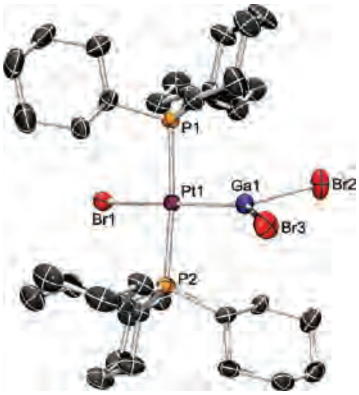

Figure 3. Molecular structure of **5** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Ga1 2.3403(4), Pt1−Br1 2.5087(3), Ga1−Br2 2.3428(5), Ga1−Br3 2.3348(5); P1−Pt1−P2 171.39(3), P1−Pt1−Br1 90.02(2), P2−Pt1−Br1 90.22(2), Br2−Ga1−Br3 101.65(2).

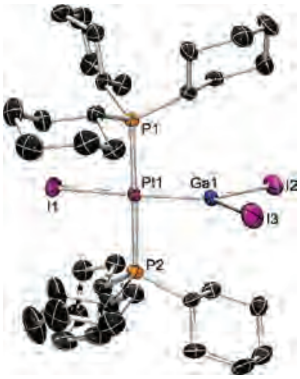

Figure 4. Molecular structure of **6** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Ga1 2.3383(6), Pt1−I1 2.6902(5), Ga1−I2 2.5538(7), Ga1−I3 2.5472(8); P1−Pt1−P2 167.86(4), P1−Pt1−I1 92.40(4), P2−Pt1−I1 91.43(3), I2−Ga1−I3 105.77(3).

In 2006, Fischer et al. reported on the synthesis of [FeCp*(GaCp*)(GaBr$_2$)(PPh$_3$)] (Cp* = η^5-C$_5$Me$_5$), which contains an iron dibromogallyl unit.[14] Herein the Ga−Br bond length is slightly longer than that in **5** (2.4156 and 2.3388 Å, respectively). Aldridge et al. published only recently the iron diiodogallyl complex [Cp*Fe(dppe)(GaI$_2$)].[1d]

A structural comparison of the GaI$_2$ unit showed an extended Ga−I bond length of the latter [2.6287(9) and 2.6314(9) Å of [Cp*Fe(dppe)(GaI$_2$)]; 2.5538(7) and 2.5472(8) Å of **6**] and a smaller I−Ga−I angle [94.32(3)° to 105.77(3)°].

The unusual reactivity of halogallanes toward [Pt(PCy$_3$)$_2$] can be attributed to the differing bond strengths of the Ga−Cl, Ga−Br, and Ga−I linkages. The bond dissociation energies decrease with the atomic number of the halide, and hence, the strong Ga−Cl (354 kJ/mol) bond imposes adduct formation, while the weaker Ga−Br and Ga−I (302 and 237 kJ/mol, respectively) linkages allow for oxidative addition.[15] It should be noted that in the case of EX$_3$ (E = B, Al; X = Cl, Br, I), despite a similar trend in E−X bond dissociation energies, a significantly different reactivity occurs. With the sole exception of the reactions of [Cp*(OC)$_2$Fe−BX$_2$] (X = Cl, Br)[16] with [M(PCy$_3$)$_2$] (M = Pd, Pt),[17] B−X bonds always tend to oxidatively add to platinum, while aluminum trihalides always yielded [(Cy$_3$P)$_2$Pt $\rightarrow$ AlX$_3$] adducts (vide supra).

In conclusion, we obtained the first platinum gallane complex by adduct formation between a Lewis basic Pt^0 complex and GaCl$_3$. Surprisingly, GaBr$_3$ and GaI$_3$ react with [Pt(PCy$_3$)$_2$] via an oxidative addition and therefore represent the first transition-metal dihalogallyl complexes prepared by this method.

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Supporting Information Available: Details of the syntheses, spectroscopic characterization, and experimental details on the X-ray diffraction of compounds **4**−**6** and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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